Composites Science and Technology

Chandrasekar Muthukumar
Senthilkumar Krishnasamy
Senthil Muthu Kumar Thiagamani
Suchart Siengchin *Editors*

Aging Effects on Natural Fiber-Reinforced Polymer Composites

Durability and Life Prediction

Springer

Composites Science and Technology

Series Editor

Mohammad Jawaid, Laboratory of Biocomposite Technology, Universiti Putra Malaysia, INTROP, Serdang, Malaysia

Composites Science and Technology (CST) book series publishes cutting edge research monographs (both edited and authored volumes) comprehensively covering topics shown below:

- Composites from agricultural biomass/natural fibres include conventional composites-Plywood/MDF/Fiberboard
- Fabrication of Composites/conventional composites from biomass and natural fibers
- Wood, and Wood based materials
- Chemistry and biology of Composites and Biocomposites
- Modelling of damage of Composites and Biocomposites
- Failure Analysis of Composites and Biocomposites
- Structural Health Monitoring of Composites and Biocomposites
- Durability of Composites and Biocomposites
- Thermal properties of Composites and Biocomposites
- Flammability of Composites and Biocomposites
- Tribology of Composites and Biocomposites
- Bionanocomposites and Nanocomposites
- Applications of Composites, and Biocomposites

To submit a proposal for a research monograph or have further inquries, please contact springer editor, Ramesh Premnath (ramesh.premnath@springer.com).

More information about this series at https://link.springer.com/bookseries/16333

Chandrasekar Muthukumar ·
Senthilkumar Krishnasamy ·
Senthil Muthu Kumar Thiagamani ·
Suchart Siengchin
Editors

Aging Effects on Natural Fiber-Reinforced Polymer Composites

Durability and Life Prediction

Springer

Editors
Chandrasekar Muthukumar
School of Aeronautical Sciences
Hindustan Institute of Technology and Science
Chennai, India

Senthil Muthu Kumar Thiagamani
Department of Mechanical Engineering
Kalasalingam Academy of Research and Education
Krishnankoil, India

Senthilkumar Krishnasamy
Department of Mechanical Engineering
Francis Xavier Engineering College
Tirunelveli, India

Suchart Siengchin
Materials and Production Engineering, The Sirindhorn International Thai German Graduate School of Engineering (TGGS)
King Mongkut's University of Technology North Bangkok
Bangkok, Thailand

ISSN 2662-1819 ISSN 2662-1827 (electronic)
Composites Science and Technology
ISBN 978-981-16-8359-6 ISBN 978-981-16-8360-2 (eBook)
https://doi.org/10.1007/978-981-16-8360-2

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

We dedicate this book to our beloved parents

Preface

Natural fibers have gained significant attention in the recent years due to their attractive features such as bio-degradability, low density, abundant availability and lower cost compared to the synthetic fibers. However, biocomposites reinforced with the natural fibers in polymer matrix are susceptible to degradation during their service life in the outdoor conditions due to the humidity and temperature prevailing in the environment and the indoor conditions.

Factors such as water uptake and thickness swelling due to the hydrophilic characteristic of the natural fiber and matrix plasticization effect affect the performance of biocomposites and limit their scope in the outdoor applications. This book covers the degradation effects and the performance of biocomposites under various aging conditions. The mechanism behind improved environmental resistance of biocomposites reinforced with the surface modified fibers, nanofiller and compatibilizer has been discussed.

All the chapters in this book were written by the authors with expertise in the field of polymer-based Biocomposites subjected to environmental aging conditions. We appreciate and extend our sincere gratitude to the contributing authors for their time and efforts. This book is suitable for researchers, academicians, professionals, technicians and senior undergraduate students looking to undertake research or gain insight into the aging studies on the polymer-based Biocomposites.

Chennai, India — Chandrasekar Muthukumar
Tirunelveli, India — Senthilkumar Krishnasamy
Krishnankoil, India — Senthil Muthu Kumar Thiagamani
Bangkok, Thailand — Suchart Siengchin

Acknowledgments We appreciate the cooperation and support from the acquisition editor of Springer, Singapore, staff members of the publisher and typesetter associated with this project.

Contents

Introduction to Aging in Bio Composites 1
G. Anand, N. Santhosh, and S. Vishvanathperumal

Influence of Moisture Absorption on Mechanical properties of Biocomposites reinforced Surface Modified Natural Fibers 17
M. Ramesh, L. Rajeshkumar, D. Balaji, and V. Bhuvaneswari

Effect of Water Absorption on the Tensile, Flexural, Fracture Toughness and Impact Properties of Biocomposites 35
Jyotishkumar Parameswaranpillai, Jenny Jacob, Midhun Dominic C.D., Chandrasekar Muthukumar, Senthil Muthu Kumar Thiagamani, Aswathy Jayakumar, Suchart Siengchin, and Sabarish Radoor

Effect of Compatibilizer on the Aging and Degradation Mechanism of the Natural Fiber-Reinforced Thermoplastic Composites 51
C. Ganesan, M. Chandrasekar, M. S. Nisha, and S. Subha

Effects of Hygrothermal Aging on the Mechanical Properties of the Biocomposites 63
Athul Joseph, Vinyas Mahesh, Vishwas Mahesh, Dineshkumar Harursampath, and M. A. R. Loja

Degradation Effects of Completely Biodegradable Composites to Moisture Absorption and Water Aging 85
Emel Kuram

Hygrothermal Aging and Their Influence on Mechanical Properties of the Bio-composites 115
Hossein Ebrahimnezhad-Khaljiri

Effects of Natural Weathering on Aesthetics, Thermal and Mechanical Properties of the Bio-composites 137
Tarkan Akderya, Cemal Bilir, and Buket Okutan Baba

Degradation Effects on the Mechanical and Thermal Properties of the Bio-Composites Due to Accelerated Weathering 159
Juliana Botelho Moreira, Suelen Goettems Kuntzler, Cleber Klasener da Silva, Jorge Alberto Vieira Costa, and Michele Greque de Morais

Effects of Natural Weathering on Aesthetics, Thermal and Mechanical Properties of Completely Biodegradable Composites 173
Clement Matthew Chan, Steven Pratt, and Bronwyn Laycock

Effect of Aging and UV Exposure on Mechanical Properties of Natural Fiber Composites 189
Ajitanshu Vedrtnam, Dheeraj Gunwant, Harsha Verma, and Kishor Kalauni

Fatigue Life Prediction of Bio-composites Subjected to Environmental Aging 219
G. Jeevi, R. Karthikeyan, Nalini Ranganathan, M. Abdul Kader, and Sanjay K. Nayak

Effect of Moisture Absorption on Interfacial Shear Properties of the Bio-Composites 237
Dheeraj Kumar, Ranjan Kumar Mitra, Trilok Chouhan, Md Farrukh, and Nadeem Faisal

Hygrothermal Aging, Kinetics of Moisture Absorption, Degradation Mechanism and Their Influence on Performance of the Natural Fibre Reinforced Composites 257
M. Ramesh, M. Tamil Selvan, and K. Niranjana

Performance of Natural Fiber Based Nanocomposites Under Environmental Aging Conditions 279
Atanu Kumar Das, Md Nazrul Islam, Afroza Akter Liza, and Ahsan Rajib Promie

Influence of Moisture Absorption on Physico-Chemical Properties of Natural Fiber-Based Hybrid Composites 297
Md Sarif Sakaeyt Hosen, Md Jaynal Abedin, Md Enamul Hoque, and Md Zillur Rahman

Aging Effects on Mechanical Properties of Biocomposites with Recycled Polymers 317
Md. Sarif Sakaeyt Hosen, Md Enamul Hoque, Md. Zillur Rahman, and Suresh Sagadevan

Influence of Seawater Ageing on the Physical and Mechanical Properties of the Natural Fiber-Reinforced Composites 335
J. Jefferson Andrew and H. N. Dhakal

Editors and Contributors

About the Editors

Chandrasekar Muthukumar, Ph.D. is an Assistant Professor in the School of Aeronautical Sciences, Hindustan Institute of Technology and Science, Chennai, India. He earned a bachelor's degree in Aeronautical engineering from the Kumaraguru College of Technology, Coimbatore, India. His master's degree is in aerospace engineering from the Nanyang Technological University – TUM Asia, Singapore and his Ph.D. in aerospace engineering is from the Universiti Putra Malaysia (UPM), Malaysia. His Ph.D. was funded through a research grant from the Ministry of Education, Malaysia. During his association with the UPM, he obtained internal research funding from the university worth 16,000 and 20,000 MYR, respectively. He has 5 years of teaching and academic research experience. His interests include fiber metal laminates (FMLs), natural fibers, biocomposites, additive manufacturing and non-destructive testing. His publications are based on the fabrication and characterization techniques of biocomposites. He has authored and co-authored research publications in SCIE journals, book chapters, and articles in the conference proceedings. He is a peer reviewer for the Journal of Industrial Textiles, Polymer Composites, Materials Research Express, Journal of Natural Fibres, etc.

Senthilkumar Krishnasamy, Ph.D. is an Associate Professor in the Department of Mechanical Engineering at Francis Xavier Engineering College, Tirunelveli, Tamilnadu, India. He earned a bachelor's degree in mechanical engineering at Anna University, Chennai, India, in 2005. He earned a master's degree in CAD/CAM at Anna University, Tirunelveli, India, in 2009. He earned a Ph.D. in mechanical engineering at Kalasalingam University, Krishnankoil, Tamilnadu, India in 2016. From 2010 to 2018, Dr. Krishnasamy worked in the Department of Mechanical Engineering at Kalasalingam Academy of Research and Education (KARE), India. He completed a postdoctoral fellowship at Universiti Putra Malaysia, Serdang, Selangor, Malaysia and King Mongkut's University of Technology North Bangkok (KMUTNB) under the research topics of experimental investigations on mechanical, morphological,

thermal, and structural properties of kenaf fiber/mat epoxy composites and sisal composites and fabrication of eco-friendly hybrid green composites on tribological properties in a medium-scale application. Then, he worked as a Research Scientist at the Center of Innovation in Design and Engineering for Manufacturing (CoI-DEM), King Mongkut's University of Technology, Bangkok, Thailand. His area of research includes the modification and treatment of natural fibers, nanocomposites, 3D printing, and hybrid reinforced polymer composites. He has published research papers in international journals, book chapters, and at conferences in the field of natural fiber composites. He also edits books with different publishers.

Senthil Muthu Kumar Thiagamani, Ph.D. is an Associate Professor in the Department of Mechanical Engineering at Kalasalingam Academy of Research and Education (KARE), Tamil Nadu, India. In 2004, he earned a Diploma in Mechanical Engineering at the State Board of Technical Education and Training, Tamil Nadu. In 2007, he graduated from Anna University, Chennai with a Bachelor's degree in Mechanical Engineering. In 2009, he obtained his Master's degree in Automotive Engineering at Vellore Institute of Technology, Vellore. In 2018, he earned a Ph.D. in Mechanical Engineering, specializing in Biocomposites, at KARE. He completed postdoctoral research in the Materials and Production Engineering Department at the Sirindhorn International Thai-German Graduate School of Engineering (TGGS), KMUTNB, Thailand in the year 2019. He started his academic career in 2010 as Lecturer in Mechanical Engineering at KARE. He has around 12 years of teaching and research experience. He is a visiting researcher at KMUTNB, Thailand. He is a member of the Society of Automotive Engineers and the International Association of Advanced Materials. His research interests include biodegradable polymer composites and their characterization. He has authored several articles in peer-reviewed international journals and book chapters and in conference proceedings. He has edited books on the different themes of Biocomposites published by CRC Press, John Wiley and Springer. He is an Editorial Board Member of the ARAI Journal of Mobility Technology. He also serves as a reviewer for various journals to name few are Journal of Industrial Textiles, Journal of Cleaner Production, Materials Today Communications, Journal of Polymers and the Environment, SN Applied Sciences, Mechanics of Composite Materials, and International Journal of Polymer Science.

Prof. Dr.-Ing. habil. Suchart Siengchin is President of King Mongkut's University of Technology North Bangkok (KMUTNB), Thailand. He received his Dipl.-Ing. in Mechanical Engineering from University of Applied Sciences Giessen/Friedberg, Hessen, Germany, M.Sc. in Polymer Technology from University of Applied Sciences Aalen, Baden-Wuerttemberg, Germany, M.Sc. in Material Science at the Erlangen-Nürnberg University, Bayern, Germany, Doctor of Philosophy in Engineering (Dr.-Ing.) from Institute for Composite Materials,University of Kaiserslautern, Rheinland-Pfalz, Germany and Postdoctoral Research from School of Materials Engineering,Purdue University, USA. In 2016 he completed the Habilitation (Dr.-Ing. habil.) in Mechanical Engineering from Chemnitz University of Technology, Saxony, Germany and worked as a Lecturer for Mechanical and Process

Engineering Department at The Sirindhorn International Thai-German Graduate School of Engineering (TGGS), KMUTNB. He has been full Professor at KMUTNB and became the Vice President for Research and Academic Enhancement in 2012 and elected President of KMUTNB in November 2016. He won the Outstanding Researcher Award in 2010, 2012 and 2013 at KMUTNB. Science and Engineering topics.

Contributors

Md Jaynal Abedin Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

Tarkan Akderya Department of Biomedical Engineering, Faculty of Engineering and Architecture, University of Bakırçay, Menemen, Izmir, Turkey

G. Anand Department of Mechanical Engineering, Achariya College of Engineering Technology, Puducherry, India

J. Jefferson Andrew Department of Mechanical Engineering, Khalifa University, Abu Dhabi, UAE

Buket Okutan Baba Department of Mechanical Engineering, Faculty of Engineering and Architecture, Izmir Katip Çelebi University, Çiğli, Izmir, Turkey

D. Balaji Department of Mechanical Engineering, KPR Institute of Engineering and Technology, Coimbatore, Tamil Nadu, India

V. Bhuvaneswari Department of Mechanical Engineering, KPR Institute of Engineering and Technology, Coimbatore, Tamil Nadu, India

Cemal Bilir Department of Pediatric Surgery, Faculty of Medicine, University of Bakırçay, Menemen, Izmir, Turkey

Clement Matthew Chan School of Chemical Engineering, The University of Queensland, St Lucia, QLD, Australia

M. Chandrasekar School of Aeronautical Sciences, Hindustan Institute of Technology and Science, Chennai, India

Trilok Chouhan ITM University, Gwalior, India

Jorge Alberto Vieira Costa College of Chemistry and Food Engineering, Federal University of Rio Grande (FURG), Rio Grande, RS, Brazil

Atanu Kumar Das Department of Forest Biomaterials and Technology, Swedish University of Agricultural Sciences, Umeå, Sweden

Cleber Klasener da Silva College of Chemistry and Food Engineering, Federal University of Rio Grande (FURG), Rio Grande, RS, Brazil

Michele Greque de Morais College of Chemistry and Food Engineering, Federal University of Rio Grande (FURG), Rio Grande, RS, Brazil

H. N. Dhakal Advanced Polymer and Composites (APC) Research Group, School of Mechanical and Design Engineering, University of Portsmouth, Portsmouth, UK

Midhun Dominic C.D. Department of Chemistry, Sacred Heart College, Kochi, Kerala, India

Hossein Ebrahimnezhad-Khaljiri Faculty of Materials Science and Engineering, K. N. Toosi University of Technology, Tehran, Iran

Nadeem Faisal Central Institute of Petrochemicals Engineering and Technology, Balasore, India

Md Farrukh Netaji Subhas Institute of Technology, Patna, India

C. Ganesan Amity Institute of Aerospace Engineering, Amity University, Noida, Uttar Pradesh, India

Dheeraj Gunwant Department of Mechanical Engineering, Invertis University, Bareilly, UP, India;
GET Group of Institutions, Bazpur, Uttarakhand, India

Dineshkumar Harursampath Department of Aerospace Engineering, Indian Institute of Science (IISc), Bangalore, India

Md Enamul Hoque Department of Biomedical Engineering, Military Institute of Science and Technology (MIST), Dhaka, Bangladesh

Md. Sarif Sakaeyt Hosen Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

Md Nazrul Islam Forestry and Wood Technology Discipline, Khulna University, Khulna, Bangladesh

Jenny Jacob Department of Bioscience, Mar Athanasios College for Advanced Studies Tiruvalla, Pathanamthitta, (MACFAST)Kerala, India

Aswathy Jayakumar Natural Composites Research Group Lab, King Mongkut's University of Technology, North Bangkok (KMUTNB), Bangkok, Thailand

G. Jeevi Central Institute of Plastics Engineering & Technology (CIPET), TVK Industrial Estate, Chennai, India

Athul Joseph Department of Aerospace Engineering, Indian Institute of Science (IISc), Bangalore, India

M. Abdul Kader Advanced Research School for Technology and Product Simulation, TVK Industrial Estate, Chennai, India

Kishor Kalauni Department of Mechanical Engineering, Invertis University, Bareilly, UP, India

R. Karthikeyan Advanced Research School for Technology and Product Simulation, TVK Industrial Estate, Chennai, India

Dheeraj Kumar National Institute of Technology, Durgapur, India

Suelen Goettems Kuntzler College of Chemistry and Food Engineering, Federal University of Rio Grande (FURG), Rio Grande, RS, Brazil

Emel Kuram Department of Mechanical Engineering, Gebze Technical University, Gebze, Kocaeli, Turkey

Bronwyn Laycock School of Chemical Engineering, The University of Queensland, St Lucia, QLD, Australia

Afroza Akter Liza Forestry and Wood Technology Discipline, Khulna University, Khulna, Bangladesh

M. A. R. Loja CIMOSM – Centro de Investigação em Modelação e Optimização de Sistemas Multifuncionais; ISEL, IPL – Instituto Politécnico de Lisboa, Lisboa, Portugal;
Institute of Earth Sciences, University of Évora, Colégio Luís António Verney, Évora, Portugal;
IDMEC, Instituto Superior Técnico – Universidade de Lisboa, Lisboa, Portugal

Vinyas Mahesh Department of Mechanical Engineering, National Institute of Technology, Silchar, Assam, India

Vishwas Mahesh Department of Aerospace Engineering, Indian Institute of Science (IISc), Bangalore, India;
Department of Industrial Engineering and Production, Siddaganga Institute of Technology, Tumkur, India

Ranjan Kumar Mitra National Institute of Technology, Durgapur, India

Juliana Botelho Moreira College of Chemistry and Food Engineering, Federal University of Rio Grande (FURG), Rio Grande, RS, Brazil

Chandrasekar Muthukumar School of Aeronautical Sciences, Hindustan Institute of Technology & Science, Kelambakkam, Chennai, India

Sanjay K. Nayak Central Institute of Plastics Engineering & Technology (CIPET), TVK Industrial Estate, Chennai, India

K. Niranjana Department of Aeronautical Engineering, KIT-Kalaignarkarunanidhi Institute of Technology, Coimbatore, Tamil Nadu, India

M. S. Nisha Department of Aeronautical Engineering, Hindustan Institute of Technology and Science, Chennai, India

Jyotishkumar Parameswaranpillai Department of Bioscience, Mar Athanasios College for Advanced Studies Tiruvalla, Pathanamthitta, (MACFAST)Kerala, India

Steven Pratt School of Chemical Engineering, The University of Queensland, St Lucia, QLD, Australia

Ahsan Rajib Promie Forestry and Wood Technology Discipline, Khulna University, Khulna, Bangladesh

Sabarish Radoor Natural Composites Research Group Lab, King Mongkut's University of Technology, North Bangkok (KMUTNB), Bangkok, Thailand

Md. Zillur Rahman Department of Mechanical Engineering, Bangabandhu Sheikh Mujibur Rahman Aviation and Aerospace University (BSMRAAU), Dhaka, Bangladesh

L. Rajeshkumar Department of Mechanical Engineering, KPR Institute of Engineering and Technology, Coimbatore, Tamil Nadu, India

M. Ramesh Department of Mechanical Engineering, KIT-Kalaignarkarunanidhi Institute of Technology, Coimbatore, Tamil Nadu, India

Nalini Ranganathan Advanced Research School for Technology and Product Simulation, TVK Industrial Estate, Chennai, India

Suresh Sagadevan Nanotechnology and Catalysis Research Centre, University of Malaya, Kuala Lumpur, Malaysia

N. Santhosh Department of Mechanical Engineering, MVJ College of Engineering, Near ITPB, Whitefield, Bangalore, India

Suchart Siengchin Natural Composites Research Group Lab, King Mongkut's University of Technology, North Bangkok (KMUTNB), Bangkok, Thailand

S. Subha Department of Aeronautical Engineering, Hindustan Institute of Technology and Science, Chennai, India

M. Tamil Selvan Department of Mechanical Engineering, KIT-Kalaignarkarunanidhi Institute of Technology, Coimbatore, Tamil Nadu, India

Senthil Muthu Kumar Thiagamani Department of Mechanical Engineering, Kalasalingam Academy of Research and Education, Krishnankoil, Tamil Nadu, India

Ajitanshu Vedrtnam Departamento de Arquitectura, Universidad de Alcalá, Madrid, Spain;
Department of Mechanical Engineering, Invertis University, Bareilly, UP, India

Harsha Verma Department of Polymer and Process Engineering, SRE Campus, IIT Roorkee, Roorkee, India

S. Vishvanathperumal Department of Mechanical Engineering, S.A. Engineering CollegeThiruverkadu, Tamilnadu, Chennai, India

Abbreviations

3DN CMC	3-dimensional needled textile reinforcement on ceramic matrix composite
AA-g-PLA	Acrylic acid grafted polylactic acid
AAL	Alkali-treated aligned long
ACC	All-cellulose-composites
AEPO	Acrylate epoxidized palm oil
AFM	Atomic force microscopy
AHP	Ammonium dihydrogen phosphate
AUL	Aligned untreated long
BC	Bacterial cellulose
BFRP	Basalt fiber-reinforced polymer
BS	Bending strength
CB	Cuttlebone
CF	Cotton fabric
CFRP	China reed fiber-reinforced biopolymer
CFRPs	Carbon fiber-reinforced plastics
CI	Crystallinity index
CMC	Carboxymethyl cellulose
CNC	Cellulose nanocrystal
CNCs	Cellulose nanocrystals
CNF	Carbon nanofiber
CNFs	Cellulose nanofibers
CNW	Cellulose nanowhiskers
CS	Crush corn stalk
DAP	Diammonium Phosphate
DCP	Dicumyl peroxide
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
EB	Electron Beam
EFB	Empty food bunch
EFB	Empty fruit bunches

EPC	Ex-situ Polymerization
EPMC	Ex-situ moisture content
ESC	Environmental stress cracking
EVA	Ethylene vinyl acetate
F/T	Freezing
FA	Fly ash
FA	Furfural alcohol
FBRHC	Fully bio-reinforced hybrid composites
FBVEs	Flax-basalt fiber vinyl ester stitched
FBVEu	Flax-basalt fiber vinyl ester unstitched
FE	Finite element
FEM	Finite element method
FRPCs	Fiber-reinforced polymer composites
FS	Flexural strength
FSC	Fatigue strength coefficient
FSE	Fatigue strength exponent
FT	Fourier Transformation
FT	Fracture toughness
FTIR	Fourier-transform infrared spectroscopy
FVE	Flax vinyl ester
G_{1C}	Fracture energy
GFRP	Glass fiber-reinforced polymer
G_{IC}	Inter-laminar fracture toughness
GNPs	Graphene nanoplatelets
GO	Graphene oxide
HA	Hydroxyapatite
HDPE	High-density polyethylene
HH	Hemp composites
HNC	Halloysite nanoclay
HP	Hemp direction
HS	Moisture saturation
IFSS	Interfacial shear strength
ILSS	Inter-laminar shear strength
IPC	In-situ Polymerization
IPMC	In-situ moisture content
IR	Infrared
IS	Impact strength
ITA	Wood flour composites
JF	Jute fiber
K_{1C}	Mode I plane strain fracture toughness
KBF	Kenaf bast fiber
KC	Kaolinite clay
KCF	Kenaf core fibers
KH	Kenaf-hemp
KJ	Kenaf-jute

LCA	Life cycle assessment
LCA	Light Combat Aircraft
LDPE	Low-density polyethylene
LDPEW	Low-density polyethylene waste
MA	Maleic anhydride
MAH	Maleic anhydrides
MAPP	Malleated polypropylene
MC	Methylcellulose
MC	Moisture content
MCC	Microcrystalline
MCC	Microcrystalline cellulose
MFC	Microfibrallated cellulose
MgO	Dead burned magnesia
MMA	Methyl methacrylate
MMT	MONTMORILLONITE
MOE	Modulus of Elasticity
MPC	magnesium phosphate cement
Nf	Number of cycle
NFCs	Natural fiber-reinforced composites
NR	Natural rubber
OM	Optical microscopy
OMMT	Montmorillonite
OPC	Ordinary Portland cement
PALF	Pineapple leaf fibers
PBAT	Poly (butylene adipate-co-terephthalate)
PBRHC	Partially bio-reinforced hybrid composites
PBS	Polybutylene succinate
PCL	Poly(ε-caprolactone)
PCL	Polycaprolactone
PDLLA	Poly(d,l-lactide)
PE	Polyethylene
PEG	Polyethylene glycol
PFRP	Plantain fiber-reinforced polyester
PHA	Polyhydroxyalkanoate
PHB	Polyhydroxybutyrate
PHBV	Poly (3-hydroxybutyrate-co3-hydroxyvalerate)
PKFs	Palm kernel fibers
PLA	Poly Lactic Acid
PLA-g-MA	Maleic-anhydride-grafted PLA
PLLA	Poly (l-lactic acid)
PMC	Polymer matrix composites
PMMA	Polymethyl methacrylate
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane

PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PWW	Pinewood waste
RC	Red coral
RH	Relative humidity
RSPE	Roselle-sisal polyester
RT	Room temperature
SDLRPCs	Sugarcane dry leaves composites
SEM	Scanned electron microscopy
SEM	Scanning electron microscopy
SF	Sisal fiber
TEM	Transmission electron microscopy
TFA	Trifluoroacetic acid
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TM	Tensile modulus
TPNR	Thermoplastic elastomer
TPS	Thermoplastic starch
TPU	Thermoplastic polyurethane
TS	Tensile strength
TS	Thickness swelling
UCS	Ultimate compressive stress
UHMWPE	Ultra-high molecular weight polyethylene
UP	Unsaturated polyester
UV	Ultra Violet
WBPE	Waterborne polyester
WF	Wood flour
WPCs	Wood-plastic composites
WPU	Waterborne polyurethane
WS	Water saturation
WSD	Water saturated
WSF/T	Freeze-thaw
XRD	X-ray diffraction

Introduction to Aging in Bio Composites

G. Anand, N. Santhosh, and S. Vishvanathperumal

Abstract Environmental concerns have impacted the global scenario, particularly with respect to the use of plastics and their byproducts for real time applications. In this lieu, there is a need for development of bioplastics and bio composites. Thus, the bio composites can be an effective alternative to the traditional plastics to reduce the carbon footprint and to facilitate a sustainable product for enhanced performance and better service conditions. In this regard, this chapter aims at expanding the scientific knowledge on the bio composites and their response under different aging environments. In this chapter, detailed information on the aging mechanism, modes of aging and the methodologies to improve the durability and performance of the bio composites are discussed thoroughly. Specific impetus has been put on the future perspectives and the need for new techniques in aging studies of biopolymers. Further, the pros and cons with respect to the aging of these biopolymers and bio composites can be helpful for researchers.

Keywords Biodegradable · Polymers · Bio composites · Aging · Durability · Sustainable · Performance

1 Introduction

The growing concern of ecological impact has resulted in an exceedingly renewed interest in biodegradable polymers and bio composites. Newer materials are being

G. Anand (✉)
Department of Mechanical Engineering, Achariya College of Engineering Technology, Puducherry 605110, India
e-mail: anand.12ng@gmail.com

N. Santhosh
Department of Mechanical Engineering, MVJ College of Engineering, Near ITPB, Whitefield, Bangalore 560 067, India

S. Vishvanathperumal
Department of Mechanical Engineering, S.A. Engineering CollegeThiruverkadu, Tamilnadu 600 077 Chennai, India

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_1

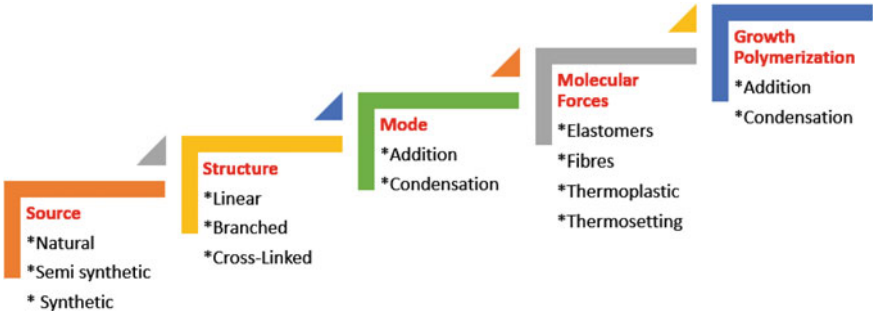


Fig. 1 Schematic block diagram representing the types of polymers

evolved with impact on greener and sustainable practices. The recyclability and the eco sustainability have become progressive important.

In this regard, more impetus is being given on the biodegradability of the polymers and the composites. Natural polymers are being used extensively for synthesis of the bio composites, and the chance of obtaining enzymatically changed derivatives for specific applications has led to the research and development activities in biopolymers.

Polymers are long chain of monomers that are made up of repeating blocks. Polymers are essentially classified based on the source, structure, mode and molecular forces. The classification of polymers is depicted by a schematic block diagram as in Fig. 1.

Among, the categories of all the polymers, natural polymers are of major significance, being categorized as polypeptides and polysaccharides, and further, the major types of natural polymers are chiton, rubber, nucleic acids, proteins, cellulose and carbohydrates. The Fig. 2 gives the schematic block diagram of the major types of natural polymers.

Fig. 2 Types of natural polymers

These natural polymers are of major constituents of bio-composites for addressing the issues related to non-degradable nature of the petrochemical based polymers for the fabrication of the composites. They are therefore very important to provide better options for synthesis of the biodegradable composites. Henceforth, the biodegradable composites have gained research momentum and have evolved as a major material of interest among the research community for replacing synthetic polymers in the biosynthesis of the composites. Majority of these natural polymers have oxygen as the major element, which is responsible for its biodegradability. Among the natural polymers, cellulose from the plant source is a polysaccharide that is finding its use for manufacturing bio composites. Also, starch which is also a polysaccharide is found among the plant sources like rice, wheat, corn, sorghum, and peas; which is also an important constituent of the bio composites. Chitin is that the third most copious sugar found in the skeleton of shellfish, lobsters, crab and shrimps. Chitosan is also a variety of polysaccharide that are extensively used in the fabrication of bio composites.

Further, the proteins of collagen, caesin, albuminoid are also forming the constituents of bio composites and are effectively used in the fabrication of these bio composites for real time applications.

In this regard, there is a scope for research in the synthesis of bio composites, by identifying the gap in the literature reported on the bio composites.

Nicollier et al. (2001) have carried out extensive work on the glass fiber reinforced polymer (GFRP) and have compared the properties of GFRP with the China reed fiber reinforced bio polymer (CFRP) for the application in Light Combat Aircraft (LCA) and have found that the cumulative energy consumption for LCA component with GFRP was 1400 MJ, whereas the energy requirement for LCA component fabricated from CFRP was 717 MJ, which results in conservation of 49% of the energy needs per flight of the aircraft.

Hassan and Peppas (2000) have reported the use of polyvinyl alcohol based cellulose composites for biomedical applications, especially for tissue replacement for wounds and burns. Thus, the biopolymers can be effectively used for biomedical applications as well.

Srubar et al. (2012) have reported their work carried out on the use of cellulose fillers in the bio composites and have showed that the flexural properties improved with the increase in cellulose filler content up to 6 wt.%, beyond which it started decreasing due to agglomeration and micro coring.

Cao et al. (2007) have worked on the bagasse fiber reinforced bio-composites and have reported that the flexural strength, tensile characteristics of these composites were relatively higher as compared to the synthetic polymer based composites and have better biodegradability.

Reddy and Yang (2011) have worked on the jute fiber reinforced bio composites and the effect of absorption of moisture by these composites, however the absorption of moisture by these composites can be reduced by suitable post treatment, owing to which, the studies have revealed that the post treated bio composites show excellent flexural and tensile properties as compared to un treated composites.

Wu and Liao (2012) have worked on the green composites reinforced with rice straws, their studies have revealed that the biodegradability of the composites developed was greater than the epoxy composites reinforced with synthetic fibers, and also the tensile strength exhibited an improvement of 29% as compared to the synthetic epoxy composites.

Behera et al. (2012) synthesized jute reinforced composites with intermittent cross linking and impregnation of the additives. The major advantage of these composites is the biodegradability that is an added advantage as compared to synthetic composites, apart from the tensile strength and flexural characteristics.

Sharmin et al. (2012) synthesized methylcellulose (MC)-based bio composites and found that the insoluble monomers grafting using gamma rays enhances the biodegradability and thereby enhances its mechanical properties owing to the intermittent use of reinforcing agents.

Yu and Qiu (2011) have investigated isothermal and non-isothermal behavior of bio composites and reported that the crystallization behaviors of polyhedral bio composites enhances with polylactide loading in the matrix of the natural composite, and they have further noted that the aging of bio composites enhances the mechanical properties. For the poly lactic loading, the cold crystallization rate increases with the aging, thereby enhancing the crystallization temperature.

Wang and Sain (2007) have reported about the synthesis of soya bean stock nanofibers reinforced poly lactic films and have determined that the dispersed micro cellulose has three times higher Young's modulus as compared to the base polymer.

Brown and Laborie (2007) have tailored the composition and morphology of polyethylene bio composites and have hypothesized that the physico-thermal characteristics of the bio composites can be fine-tuned with the reinforcement of the fibrils in the polyethylene matrix phase, and further, the aging of the bio composites has led to better flexural properties of the bio composites.

Zimmermann et al. (2004) reinforced micro fibrillae in polyvinyl alcohol and carried out the mechanical characterization of the bio polymers with the fibril content varying up to 20 wt.%, and have reported that the mechanical properties of the bio composites will be high for hydrophilic reinforcements as compared to the synthetic reinforcements and the aging conditions along with plasticizes have shown better morphology and micro hardness.

Further, the aging studies are a major aspect of research, which eventually helps in assessing the durability of the bio composites. Taylor et al. (2016) have investigated the effect of aging on the flax fibers reinforced thermosetting resins and have reported that the aged bio composites have displayed better mechanical properties and resistance to weathering.

Joshi et al. (2004) reviewed the energy needs of manufacturing conventional glass fibers and the natural fibers by comparing results of different researchers (refer Table 1). From the table compiled by Joshi et al., it is evident that the fabrication of glass fiber requires nearly 4 to 5 times more energy than the flax and china reed fiber production. The glass fiber mat requires 54.7 MJ/kg of energy, while the flax fiber mat requires 9.55 MJ/kg of energy; china reed fiber requires 3.64 MJ/kg of energy for synthesis of every unit kg of fibers.

Table 1 Energy requirements in MJ per unit kg of fiber production [Joshi et al. (2004)]

Glass fiber [Diener et al. (1999)]		Flax fiber [Diener et al. (1999)]		China reed fiber [Patel et al. (2002)]	
Raw materials	1.7	Seed production	0.05	Cultivation	2.5
Mixture	1.0	Fertilizers	1.0	Transport Plant	0.40
Transport	1.6	Transport	0.9	Fiber extraction	0.08
Melting	18.5	Cultivation	2.0	Fiber grinding	0.40
Spinning	5.9	Fiber separation	2.7	Transport fiber	0.26
Mat production	23.0	Mat production	2.9		
Total	54.7	Total	9.55	Total	3.64

From, the review of the literature and the subsequent inferences drawn from the review, it can be understood that the bio composites can be synthesized by reinforcing both bio and petro polymers with an array of natural fiber and filler reinforcements viz., the jute fibers, coir, banana fiber, rice husk, bagasse etc., to obtain the final bio composite.

The Fig. 3 gives the schematic of the process of evolving bio-composites from the bio based polymers and the natural fibers, while the Fig. 4 gives the schematic of the types of bio reinforcements and the bio polymers used as constituents in the bio composites.

There are several methods to synthesize the bio composites, however the impetus is majorly on the durability of the bio composites. In this regard, Liu et al. (2008) have worked on the thermal and mechanical aging of the soya polymer based bio composites with the organo-clay as the reinforcement. They have reported from the critical analysis of the results that the flexural modulus increased with the mechanical aging by subjecting the polymers to alternating static and dynamic loads. Further, there are several types of aging that enhance the durability of the bio composites, thus it is very important to understand the effect of aging on the properties of the bio composites.

Fig. 3 Schematic of the process of evolving bio composites

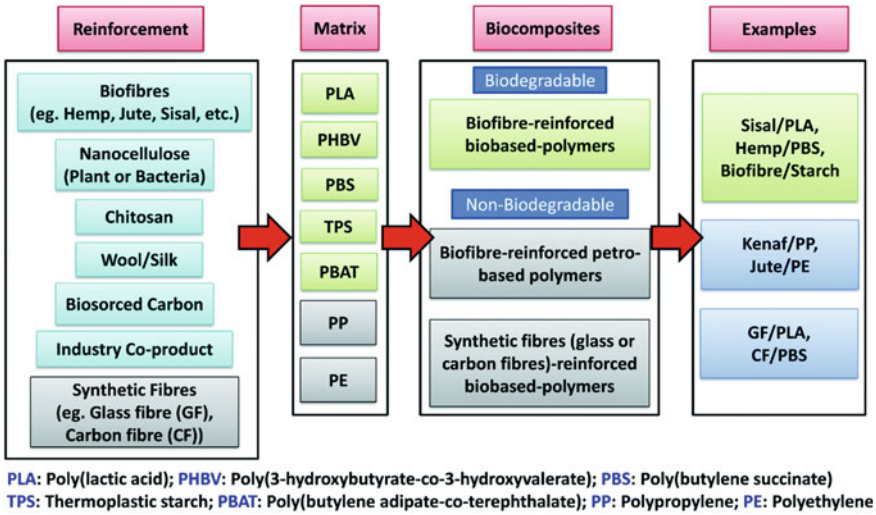


Fig. 4 Schematic of the types of bio reinforcements and bio polymers [Chang et al. (2020)]

2 Aging of Bio Composites

The aging refers to the changes in the physicochemical characteristics of the polymers in the bio composites after prolonged exposure of the composites to varying mechanical, thermal, and environmental conditions.

The chemical changes including the oxidation results in degradation of the composites especially due to prolonged exposure. Also, the physical changes like ablation, abrasion, and physical wear and tear of the composites may result in irreversible changes. Additionally the mechanical variations including the enthalpy changes, thermal variations, could result in dynamic changes in the composites.

Aging of the composites is a profound aspect given the expanding utilization of composites in primary applications in numerous domains. Aging of composites tends to imbibe a considerable lot of the vulnerabilities regarding the characterization of composites and also the process tends to explain how they age under different conditions. This chapter audits the cycles of uncertainties in aging and demonstrates the physical and chemical maturing of polymeric composites, maturing of glass-bio polymer matrix composites, stress corrosion, thermo-oxidative maturing, physical and chemical maturing. The aging process also affects the aircraft components and is a major factor to be controlled for better performance. Aging additionally serves as a major source of information for design engineers and materials engineers for designing the biopolymer structures for naval, aerospace and automobile applications.

All the major composites are subjected to gaining when exposed to prolonged conditions of environmental variations. The change in materials characteristics can

be physical, chemical, thermal, mechanical or biological, photo-oxidative in nature based on the agents responsible for aging of the composites.

The aging process are majorly classified as natural aging and synthetic aging based on the agents of aging process.

Natural aging refers to the aging of polymers under the natural circumstances subject to varying weather conditions viz., rain, wind, erosion, and surface degradations.

The thermo-oxidative aging refers to the aging of polymers subject to oxidative conditions under the exceedingly high temperatures and thermal variations. The aging will be catalyzed by the severe thermal conditions and oxidation will increase with the increase in temperature due to the affinity of the biopolymers to readily adsorb oxygen at high temperatures, however, once the bio composites are exposed to high temperatures, they become saturated with the adsorption of the oxygen on the surface of the composites.

The biological aging refers to the aging of the bio composites under the microbial actions, especially the influence of bacteria and fungus. The biological aging also involves leaching of the bio composites.

Biological aging is a typical type of aging process affecting the performance of bio composites, as most commonly utilized thermoplastics are impervious to microbiological assault. The solitary cases for biological aging has affected the surfaces of polyurethane based biopolymers, particularly with respect to natural debasement. However, no prescient procedures for the testing of regular polymers subject to biological aging are evolved in spite of the fact that, there are guidelines for testing the opposition of composites to biological degradation.

Mechanical aging of the polymers is the next major type of aging attributed to the varying dynamic and static loads under the influence of number of cycles of intermittent loading. This is particularly important to test the durability of the bio composites that are susceptible to fatigue.

Chemical aging is another important process of the aging of the bio composites due to the effect of aggressive reactants that eventually result in the chemical degradation of the bio composites up to a certain extent, beyond which the surface of the composite becomes oxidized and form a passive film which will resist any further chemical attack.

All the bio composites are under the action of aging, when exposed to varying environmental conditions, especially due to physical and chemical attacks in the oxidative environments or normal ambient environmental conditions.

The materials structure can be affected by oxidation which is for the most part known as a maturing interaction. In severe environmental conditions, the oxidation cycle occurs quickly at a high temperature and brings about quicker maturing of the parts owing to material degradation. There are various kinds of aging processes that needs due consideration for assessing the aging pattern of the composites. The kind of aging for polymer materials are reported in this chapter. Rapid aging contemplates are impersonations of explicit ecological conditions which can anticipate the oxidation components of the bio composites. Consequently, aging process is vital to comprehend the material maturing conduct for the suitable applications.

3 Aging Tests

Arrays of aging tests are available to characterize the bio composites subjected to aging process. The aging tests are majorly focused to evaluate the aging behavior of materials under different conditions. There are several types of aging tests viz., accelerated aging tests, artificial aging tests, and environmental aging tests.

3.1 Artificial Aging Tests

The artificial aging test simulates the natural conditions on a laboratory scale. This eventually creates the required conditions artificially under the influence of physical conditions on a sub scale of laboratory conditions. For example, if the composite is to be exposed for wet humid conditions of the coastal belt, then the same conditions with 60% relative humidity will be simulated in the laboratory by conditioning the ambient conditions.

3.2 Accelerated Aging Tests

Accelerated aging involves a set of additional environmental parameters to accelerate the time period of aging. The chemical reactions as well as the physical conditions are multiplied to enhance the diffusion of reactants, as a result, the varied reactions will accelerate the aging process and evoke a accelerated degeneration and subsequent maturing as compared to natural aging conditions, this will in turn give a passive resistance to the natural degeneration which occurs slowly under gradual environmental conditions, thereby facilitating the durability of the bio composites. In accelerated aging tests, the bio composites are tested for de-lamination, weathering and erosion of the surface and subsurface layers of the bio composites, by aging in the autoclave under accelerated conditions. Accelerated aging tests, thus results in a completely accelerated failure mechanism as compared to natural environmental conditions.

3.3 Environmental Aging Test

In environmental aging, bio composite specimens are exposed to natural environmental conditions of sunlight, humidity, and temperature. After the exposure of the bio composites to the several months of environmental aging, the samples are characterized by visual observation for the crack initiation, crack growth, and subsequent failure, along with the color change and further the samples are characterized

by analytical methods of Ultra Violet (UV)—Spectroscopy, Fourier Transformation (FT) Infrared Spectroscopy, and subsequently by static and dynamic mechanical tests. This will eventually give a measure of the aging of the bio composites in different conditions, since the materials will age in a different way in a tropical region as compared to Mediterranean and sub temperate regions.

3.4 Durability Tests

The durability tests that are carried out to evaluate the bio composites include the thermo oxidative aging, photo oxidative aging, hygro-thermal aging tests, creep and fatigue tests and microbial resistant tests. The Fig. 5 gives the overview of various tests that are carried out to evaluate the durability of the bio-composites synthesized.

Several researchers have carried out research on the aging characterization of bio composites and some of the research findings reported are presented in this section.

Lourdin et al. (2002) carried out the bending tests to contemplate the bending characteristics of maltose-starch based composites subjected to aging. From, the findings of the bending tests, it was reported that the flexural rigidity of the aged composites subjected to mechanical aging showed 18.6% improvement as compared

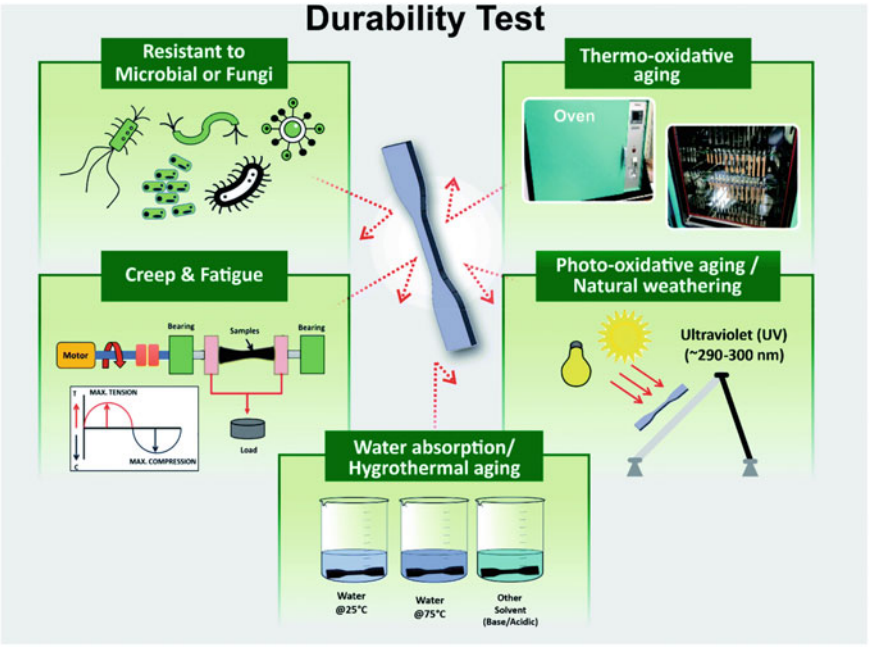


Fig. 5 Schematic of various durability tests carried out on the composite specimens [Chang et al. (2020)]

to un-aged composites. This was attributed to the micro coring and segregation of the fibers in the starch matrix due to the alternate cycles of loading and unloading.

Lawton et al. (2006) reported the impact of aging on the tractable properties of starch–based bio composites. Elasticity and tensile characteristics diminished with the aging time. Further, it was reported that the moisture content had greatest impact on the elastic properties. Composites aged at 60% humidity were subjected to greatest reduction in the tensile characteristics of the composites. This was undoubtedly attributed to stress relief in the interior surfaces of the composites. However, Bio Composites containing starch and equivalent measures of poly lactic acid were not influenced by moisture after initial aging of the composite laminates. Composites containing cross-linked starch had essentially more noteworthy characteristics than composites containing oxidized starch. The starch types and aging had quite an influence on the tensile characteristics of the composites.

Shogren and Jasberg (1994) estimated the elasticity of starch extricates during aging and related the increase in tensile properties to the pace of enthalpy unwinding utilizing differential scanning calorimetry curves. They further contemplated on the subjective relationships between the enthalpy unwinding and mechanical relaxation.

Duigou et al. (2009) contemplated the durability of flax/poly lactic acid composites in the saline medium. A few strategies have been utilized to analyze how the composites exhibit changes with aging, further bringing out sub atomic changes in the weight and morphological structures of the composites.

4 Effect of Aging on the Characteristics of Bio Composites

Bio composites at present are still in development stage due to the incipient information available on the effect of aging on biodegradation of these materials. To assess the capability of bio composites for various applications, it is fundamental to study as to how they behave under different environmental conditions.

The outcomes are very vital to know how these bio composites behave under different conditions. In this regard, several researchers have carried out research on the domain of bio composites.

Orliac et al. (2003) considered the impacts of different plasticizers on the mechanical properties, moisture absorption, and maturing of thermo-formed composites produced using sunflower proteins. The thermoplastic capability of a sunflower protein was carried out with the major objective of obtaining thin films of biodegradable polymers. The measure of plasticizer in these films was evaluated, so that the deficiency of plasticizers because of environmental aging could be understood. Further, the results of Chromatography showed that the measure of the plasticizers diminished significantly with time. This, most likely, was because of the moderately low boiling point and the interactions of these alcoholic groups to protein chains. Further, they demonstrated that the cross links of the protein chains are exceptionally fragile and it requires a coherent bonding to overcome the ill effects of environmental aging.

Dai and Liu (2006) contemplated the impact of crystallinity and aging on the mechanical properties of gelatin films for varying percentage of gelatin and maturing enthalpy. The mechanical properties of a gelatin film were estimated from static and dynamic tests. DSC was utilized to quantify crystallinity, and aging enthalpy was measured. It was reported that renatured collagen, which comprises of triple-helical superstructure of broadened polypeptide chains. Further, the mechanical characteristics of gelatin based bio composites are in this way considered for varying material arrangement and handling conditions. The impact of actual aging can be best identified by DSC estimations, using which they have reported about the transition temperature of crystallization of polymeric chains in the bio-composites.

Takagi and Ochi (2004) detailed the biodegradability of starch-based green composites reinforced with 50 wt. % of Manila hemp filaments. It was reported from their findings that there was no critical decline in the rigidity following mechanical aging. Notwithstanding, the elasticity also did not change much after subjecting the composites to mechanical aging for 5 days. Following 5 days, the strength diminished to about 20% and following 20 days the strength was decreased to 25% of the underlying strength of the composite. PLA has better resistance to degradation under environmental conditions. However, degradation still occurs gradually with increased humidity and thermo-oxidative conditions on account of the increased rate of hydrolysis at high temperatures.

Li et al. (1990) reported that hydrolysis occurs rapidly in the interiors of a thick sample as compared to the exterior surface majorly owing to the leaching of PLA subsurface layers by rapid flow of water on the bio-composite surface. Further, the carboxylic corrosion was higher outside because of draining of the acidic PLA oligomers into the encompassing fluid medium. Further, the investigations have shown that specific proteases, including proteinase K, pronase, and bromelain, have been found to expand the pace of debasement of PLA, while rate of esterase process is decreased. Pranamuda et al. (1997) found that PLA debasing are appropriated in soil conditions and assume a vital part in its bio degradation. Further, Amycolatopsis is corroding PLA subsurface in microbial culture at 30 °C. Jarerat and Tokiwa (2001) showed that PLA subsurface was corroded by the Tritirachium organisms at 30 °C in the gelatin medium. Hakkarainen (2002) found that PLA films were degenerated to powder following 5 weeks in a blended culture of microorganisms at 30 °C, though the film in the abiotic medium looked flawless. They likewise found that PLA atomic loads, were decreased positively in the biotic medium, most likely because of cleavage close to the cross linking chains. It was discovered that underlying corrosion is expected to be subjected to abiotic hydrolysis as it were followed by biotic absorption and subsequent breakdown. PLA is totally mineralized to CO_2, water, and a limited quantity of biomass following by the severe environmental degradation. Torres et al. (1999) discovered development of contagious mycelia on PLA composites after two months in soil; however the same composite specimen after biological aging under the action of fungal treatment took 182 days for degradation. Urayama et al. (2002) discovered just a 20% reduction in atomic weight of 100% L-PLA plates subjected to alcoholic treatment, following 20 months in soil while a 70% reduction was noted for 75% L-PLA, which clearly is an indication of the ability

of poly lactic acid based bio composites to resist degradation after initial chemical aging in alcoholic environment. Ho and Pometto (1999) found that about 15% of a PLA film was mineralized to CO_2 following 152 days in a research lab respirometer with ambient soil conditions at 28 °C. Calmon et al. (1999) found that PLA films had weight reductions of up to 35% after subjecting to moist conditions in soil for a very long time, contingent upon PLA type and area. Osawa et al. (2000) found that the atomic load of PLA in PLA/starch 70/30 composites diminished by about 60% after internment in soil for 45 days.

Buffum et al. (2015) explored the mechanical characteristics of seven distinctive service products produced using biodegradable waste fiber and plastics for example bagasse, a bagasse bamboo mix, PLA, wheat straw, potato starch, and bamboo straws, wheat straw mix after they were exposed to UV light. They found that the greater part of the mechanical strength of the bio-polymers diminished essentially, with PLA composition in any event decreasing the rigidity and modulus. The impact of UV radiation on the characteristics of PLA is a significant aspect that influences the biodegradability of the bio composites. A higher rate of corrosion was accounted for when PLA films were exposed to raised temperatures and relative dampness simultaneously. The decrease in mechanical properties can be ascribed to the hydrolysis of ester linkages of PLA. The characterization presumed that albeit the explored bio-plastics for product items, it had comparable properties to polystyrene (PS) in the as-obtained condition, the biodegradable bio-plastics were more delicate to UV exposure and the properties were further traced in comparison to the petroleum based polymers. The mechanical strength of the PLA can be considered to decline fundamentally following the exposure to the surrounding medium.

Gorrasi et al. (2013) considered the impact of photo degradation on thermal, mechanical, and electrical conduct of their customized hybrid carbon nanotube-reinforced PLA bio nano composites. They noticed an extraordinary decrease in Young's modulus of slick PLA after UV exposure over the long run because of the chain reactions of the macro-molecular interfaces.

In another UV-exposure investigation of bio-composites revealed by Morlat-Therias et al. (2008) the PLA was supported with calcium sulfate to create bio-composites; the impact of filler substance and molecule size on maturing conduct was likewise examined. The PLA bio-composites showed development of comparative photo-products as seen in the degraded PLA. The pace of debasement of PLA was found to increment with the expanding filler stacking, just as, with the more modest $CaSO_4$ filler particles inclusion in PLA.

Pucciariello et al. (2004) have carried out work on lignin based bio composites and have characterized them. They recommended that the presence of phenolic cycles in lignin could go about as a cell reinforcement which results in decreasing the UV-corrosion process. However, the hydrophilic nature of lignocellulosic bio-fiber in bio composites could advance hydrolytic debasement; which would at that point result in decrease in mechanical performance. Like PLA, Poly Butylene Adipate (PBAT) is likewise inclined to UV-maturing. Zhu et al. (2019) arranged bio-composite films of PBAT-supported with Nano silica-reinforcements. Their outcomes appeared that the PBAT bio-composite film arranged through synthetic grading method displayed

predominant UV maturing obstruction as contrasted with the bio-composite arranged by actual blending. Shahroze et al. (2021), have worked on the mechanical, interfacial and thermal properties of silica aerogel-infused flax/epoxy composites and have found that the thermomechanical aging process has influenced the characteristics of the composites, thereby ascertaining the fact that the aging is a major phenomenon effecting the performance of bio composites.

Further, Krishnasamy et al. (2019), have worked on the effects of stacking and aging on the characteristics of hybrid green composites and have reported that the hybrid composite configurations along with optimum conditions of aging and stacking have enhanced the static, dynamic mechanical and thermal characteristics of the sisal/hemp reinforced green composite. In continuation to the works on the effects of stacking, Senthilkumar et al. (2021), have also worked on the performance of sisal/hemp based bio composites and have reported that the aging of the composites under accelerated weathering conditions have impacted the characteristics and durability of these composites, and thus, the treatment of hybrid composites is a major attribute influencing the performance of the green composites. Also, Senthilkumar et al. (2020) have worked on the creep and recovery behavior of sisal/hemp composites and have analyzed the effect of layering sequence, accelerated weathering and temperature on the bio composites, from the findings of their research, it is evident that the creep and recovery behavior of these composites have drastically improved owing to the interstitial bonding brought about by the thermal treatment and accelerated weathering to the interlayered sequence of the bio composites.

From, the reviews of the works of several researchers on the bio composites, it is herewith evident that not much research has been carried out on the degradability of bio composites and the significance of aging on their durability. Thus, this chapter can serve as a base for further researches on the physicochemical variations that can be brought about in the bio composites owing to aging under varying physical, thermal, chemical and environmental conditions and mechanical forces.

5 Conclusions and Future Perspective

The bio composites are fast gaining prominence due to the fast dwindling supplies of petro polymers, which are becoming costlier day by day. However their degradation conduct under different ecological conditions is a significant factor in evaluating their lifetime. This review is an attempt to cover the examinations directed and investigations carried out on bio-composites for their durability. The aging of bio composites under different set of conditions and appropriate selection of biopolymers for matrix phase and natural fibers for reinforcements along with surface modifications have resulted in promising results especially with respect to the prolonging of degradation owing to better aging and subsequent evolution of passive resistance of the bio composites to erosion, wear, tear, mechanical, thermal, oxidative and biological degradations.

Thus, the bio composites subjected to suitable aging process, followed by their eco sustainable characters can help bio composites replace conventional petro-polymers for a varied set of applications, right from automotive, aerospace to biological and biomedical fields.

References

Brown EE, Laborie MPG (2007) Bioengineering bacterial cellulose/poly (ethylene oxide) nanocomposites. Biomacromol 8:3074–3081

Behera AK, Avancha S, Kumar Basak R, Sen R, Adhikari B (2012) Fabrication and characterizations of biodegradable jute reinforced soy based green composites. Carbohydr Polym 88:329–335

Buffum K, Pacheco H, Shivkumar S (2015) Environmental effects on the properties of biopolymer service-ware products. Polym-Plast Technol Eng 54(5):506–514. https://doi.org/10.1080/03602559.2014.935410

Calmon A, Guillaume S, Bellon-Maurel V, Feuilloley P, Silvestre F (1999) Evaluation of material biodegradability in real conditions—development of a burial test and an analysis methodology based on numerical vision. Environ Polym Degrad 7:157–166

Cao X, Dong H, Li C (2007) New nanocomposite materials reinforced with flax cellulose nanocrystals in waterborne polyurethane. Biomacromol 8:899–904

Chang BP, Mohanty AK, Misra M (2020) Studies on durability of sustainable bio based composites: a review. RSC Adv 10:17955–17999. https://doi.org/10.1039/c9ra09554c

Corbière-Nicollier T, Gfeller Laban B, Lundquist L, Leterrier Y, Månson J-AE, Jolliet O (2001) Life cycle assessment of biofibres replacing glass fibres as reinforcement in plastics. Resour Conserv Recycl 33(4):267–287. https://doi.org/10.1016/S0921-3449(01)00089-1

Diener J, Siehler U (1999) Okologischer vergleich von NMT-und GMT Bauteilen. Angew Makromol Chem 272(Nr. 4744):1–4

Dai CA, Liu MW (2006) The effect of crystallinity and ageing enthalpy on the mechanical properties of gelatin films. Mater Sci Eng 423:121–127

Duigou AL, Davies P, Baley C (2009) Seawater ageing of flax/poly(lactic acid) biocomposites. Polym. Degrad. Stabil. 94:1151–1162

Gorrasi G, Milone C, Piperopoulos E, Lanza M, Sorrentino A (2013) Hybrid clay mineral-carbon nanotube-PLA nanocomposite films. Preparation and photo degradation effect on their mechanical, thermal and electrical properties. Appl Clay Sci 71:49–54

Hakkarainen M (2002) Aliphatic polyesters: abiotic and biotic degradation and degradation products. Adv Polym Sci 157:113–138

Ho KG, Pometto AL (1999) Temperature effects on soil mineralization of polylactic acid plastic in laboratory respirometers. Environ Polym Degrad 7:101–108

Hassan CM, Peppas NA (2000) Structure and applications of poly(vinyl alcohol) hydrogels produced by conventional crosslinking or by freezing/thawing methods, in Biopolymers/PVA Hydrogels/Anionic Polymerization Nano composites. Adv Polymer Sci 153:37–65

Jarerat A, Tokiwa Y (2001) Degradation of poly (L-lactide) by a fungus. Macromol Biosci 1:136–140

Joshi S, Drzal L, Mohanty A, Arora S (2004) Are natural fiber composites environmentally superior to glass fiber reinforced composites? Compos A Appl Sci Manuf 35:371–376. https://doi.org/10.1016/j.compositesa.2003.09.016

Krishnasamy S, Thiagamani SMK, Muthukumar C, Tengsuthiwat J, Nagarajan R, Siengchin S, Brintha NC (2019) Effects of stacking sequences on static, dynamic mechanical and thermal properties of completely biodegradable green epoxy hybrid composites. Mater Res Express 6(10):105351

Li SM, Garreau H, Vert M (1990) Structure–property relationships in the case of the degradation of massive poly (a-hydroxy acids) in aqueous media. Part II. Degradation of lactide–glycolide copolymers: PLA37.5GA25 and PLA75GA25. Mater Sci Mater Med 1(3):131–139

Lourdin D, Colonna P, Brownsey GJ, Noel TR, Ring SG (2002) Structural relaxation and physical ageing of starchy materials. Carbohydr Res 337:827–833

Lawton JW, Doane WM, Willett JL (2006) Ageing and moisture effects on the tensile properties of starch/poly (hydroxyester ether) composites. J Appl Polym Sci 100:3332–3339

Liu Z, Erhan SZ (2008) "Green" composites and nanocomposites from soybean oil. Mater Sci Eng A 483–484:708–711

Morlat-Therias S, Fanton E, Gardette J-L, Dintcheva NT, La Mantia FP, Malatesta V (2008) Photo chemical stabilization of linear low density poly ethylene/ clay nano composites. Polym Degrad Stab 93:1776–1780

Orliac O, Rouilly A, Silvestre F, Rigal L (2003) Effects of various plasticizers on the mechanical properties, water resistance and ageing of thermomoulded films made from sunflower proteins. Ind Crops Prod 18:91–100

Osawa S, Tsukegi T, Ogawa T, Urai T (2000) Biodegradation behavior of molded poly(L-lactic acid)/starch blend in a land-fill test. Mater Life 12:199–205

Patel M, Bastioili C, Marini L, Wurdinger E (2002) Environmental assessment of bio-based polymers and natural fibers. Utrecht University, Netherlands

Pranamuda H, Tokiwa Y, Tanaka H (1997) Polylactide degradation by an Amycolatopsis sp. Appl Environ Microbiol 63:1637–1640

Pucciariello R, Villani V, Bonini C, D'Auria M, Vetere T (2004) Physical properties of straw lignin-based polymer blends. Polymer 45:4159–4169

Reddy N, Yang Y (2011) Completely biodegradable soy protein–jute biocomposites developed using water without any chemicals as plasticizer. Ind Crops Prod 33:35–41

Shogren RL, Jasberg BK (1994) Aging properties of extruded high-amylose starch. J Environ Polym Degrad 2:99–109

Sharmin N, Khan RA, Salmieri S, Dussault D, Bouchard J, Lacroix M (2012) Modification and characterization of biodegradable methylcellulose films with trimethylolpropane trimethacrylate (TMPTMA) by y radiation: effect of nano crystalline cellulose. J Agric Food Chem 60(2):623–629

Srubar WV, Pilla S, Wright ZC, Ryan CA, Greene JP, Frank CW, Billington SL (2012) Mechanisms and impact of fiber–matrix compatibilization techniques on the material characterization of PHBV/oak wood flour engineered biobased composites. Compos Sci Technol 72(6):708–715. https://doi.org/10.1016/j.compscitech.2012.01.021

Senthilkumar K, Subramaniam S, Ungtrakul T, Kumar TSM, Chandrasekar M, Rajini N, Parameswaranpillai J (2020) Dual cantilever creep and recovery behavior of sisal/hemp fibre reinforced hybrid biocomposites: Effects of layering sequence, accelerated weathering and temperature. J Ind Text. 1528083720961416

Senthilkumar K, Ungtrakul T, Chandrasekar M, Kumar TSM, Rajini N, Siengchin S, Ayrilmis N (2021) Performance of sisal/hemp bio-based epoxy composites under accelerated weathering. J Polym Environ 29(2):624–636

Shahroze RM, Chandrasekar M, Senthilkumar K, Kumar TSM, Ishak MR, Rajini N, Ismail SO (2021) Mechanical, interfacial and thermal properties of silica aerogel-infused flax/epoxy composites. Int Polym Proc 36(1):53–59

Takagi H, Ochi S (2004) Biodegradability of hemp fibre-reinforced green composites. In: Proceedings of 2nd international workshop on green composites, Ube, Japan

Taylor CA, Amiri A, Webster DC, Ulven CA (2016) Long-term behavior of bio-composites for structural applications. In: Proceedings of the composites and advanced materials conference; CAMX: Anaheim, CA, USA. https://doi.org/10.13140/RG.2.2.33964.87682

Torres A, Li SM, Roussos S, Vert M (1999) Microbial degradation of a poly (lactic acid) as a model of synthetic polymer degradation mechanisms in outdoor conditions. ACS Symp Ser 723:218–226

Urayama H, Kanamori T, Kimura Y (2002) Properties and biodegradability of polymer blends of poly (L-lactide)s with different optical purity of the lactate units. Macromol Mater Eng 287:116–121

Wang B, Sain M (2007) Isolation of nanofibres from soybean source and their reinforcing capability on synthetic polymers. Compos Sci Technol 67:2521–2527

Wu CS, Liao H-T (2012) Polycaprolactone-based green renewable Eco composites made from rice straw fiber: characterization and assessment of mechanical and thermal properties. Ind Eng Chem Res 51(8):3329–3337

Yu J, Qiu Z (2011) Isothermal and nonisothermal cold crystallization behaviors of biodegradable poly(L-lactide)/ octavinyl-polyhedral oligomeric silsesquioxanes nanocomposites. Ind Eng Chem Res 50(22):12579–12586

Zimmermann T, Pohler E, Geiger T (2004) Cellulose fibrils for polymer reinforcement. Adv Eng Mater 6:754–761

Zhu S, Chen Y, Tang Y, Li Q, Zhong B, Zeng X, Xie D, Jia Z, Jia D (2019) A novel nanosilica-supported ultraviolet absorber for the preparation of robust biodegradable plastic film with high ultraviolet aging resistance. Polym Compos 40:4154–4161

Influence of Moisture Absorption on Mechanical properties of Biocomposites reinforced Surface Modified Natural Fibers

M. Ramesh, L. Rajeshkumar, D. Balaji, and V. Bhuvaneswari

Abstract Recent experimentations witnessed natural fibers as a strong alternative reinforcing element for the synthetic fibers due to their biodegradable and ecofriendly nature. Yet natural fibers are characterized by an inherent disadvantage of poor bonding at the interface of fiber and matrix with that of matrix material which renders substandard mechanical and physical properties of the natural fiber composites. Moisture absorption behavior of the natural fibers is one another demerits of using the natural fibers, since this behaviour may pose the natural fibers to absorb moisture from the surrounding environment owing to their hydrophilic nature. Surface modification renders solution to this problem also by making the surface modified natural fiber to be hydrophobic. Various treatment methods of the natural fibers and its reinforcement in polymeric matrices were dealt in detail in the current chapter. Alongside, the effect of moisture absorption of the natural fibers upon the mechanical and physical properties of the natural fiber reinforced composite materials are also discussed. It was observed from different studies that various characteristics like force of adhesion at the interfacial region between the natural fiber and the polymeric matrix enhanced due to surface modification since the surface area of contact increases which in turn enhanced the mechanical behaviour of the composites and minimized the moisture absorption of the natural fiber composites.

Keywords Natural fibers · Surface modification · Biocomposites · Moisture absorption · Mechanical properties

M. Ramesh (✉)
Department of Mechanical Engineering, KIT-Kalaignarkarunanidhi Institute of Technology, Coimbatore, Tamil Nadu 641402, India

L. Rajeshkumar · D. Balaji · V. Bhuvaneswari
Department of Mechanical Engineering, KPR Institute of Engineering and Technology, Coimbatore, Tamil Nadu 641407, India

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_2

1 Introduction

Natural fibers are the order of today's experimental materials owing to their various benefits like biodegradability, ease of availability, less in cost and better ability to be recycled. Yet, the moisture absorption behaviour of the natural fibers is considered to be an alarming factor for their usage which lowers the adhesion between matrix and natural fibers and their compatibility (Bhoopathi et al. 2015; Ramesh 2018). Natural fibers possess few more demerits like inherent incompatibility with matrix and poor wettability. Possible reason for the incompatibility between matrix and fiber could be the lowest magnitude of adhesive forces existing between the untreated fibers and the matrix (Vimal et al. 2015). Hence in order to improve the fiber and matrix adhesion, fiber surface treatments has become necessary to make the modifications in the surface of the fiber. Fiber surface modification with various chemicals in different concentrations may assist to obtain enhanced fiber matrix adhesion (Jayaramudu et al. 2009; Li et al. 2007). As the surface of the fibers were turned to possess more roughness, their adhesion with the matrix increases thus rendering better resultant characteristics.

2 Surface Treatment of Natural Fibers

Surface treatment of the natural fibers may make the natural fibers to dodge the poor surface adhesion and render a better bonding with the matrix element upon surface modification. Various physical and chemical surface modification practices are under existence currently out of which chemical treatment of fiber plays a major role. Surface modification methods like alkaline, benzoylation, permanganate and acetylation treatments are widely carried out to enhance the moisture absorption and mechanical characteristics of the end composites formed out of natural fibers (Ramesh et al. 2017a; Ramesh 2016). Surface modification removes micro constituents like pectin, lignin, hemicellulose and cellulose thereby indirectly enhancing the aforementioned properties. Most of the researches during the current days focused in using silane treatment for natural fibers (Ramesh et al. 2017b). SiH_4 is the chemical formula for silane and they are the commonly used coupling agents for the stabilization of reinforced fibers and the polymeric matrices by blending them. Silane coupling agents remove all the hydroxyl groups in the cellulose at the interfacial region of matrix and the fiber. Silanes were formed from the hydroxyl alcoholic elements with moisture presence and the formed silanol then undergoes reaction with fiber hydroxyl group resulting in stronger covalent bonds along with the cell membrane surface. It was stated by the experimenters that the fiber cramping was minimized by polymeric chains of hydrocarbon due to the formation of cross-linking structure owing to the silane treatment and a covalent bond is established between matrix and fiber (Agrawal et al. 2000).

3 Moisture Absorption of Natural Fibers

Moisture absorption nature of the natural fibers render a hydrophilic nature of fibers and when such fibers were reinforced in hydrophobic matrix it results in poor interfacial characteristics owing to the presence of cellulosic group with higher hydroxyl group (Alvarez et al. 2003). Few experiments employed E-glass and date palm fibers to fabricate hybrid epoxy composites and the fibers were treated to evaluate their moisture absorption behaviour. Date palm fibers were extracted from the meshes around the stem of the palm trees and the fibers were manually extracted from the mesh after which they were washed with distilled water to get rid of dirt and dust. Then the fibers were dried in hot air oven at a temperature of 80 °C for a period of 24 h. Followed by that the fibers were chopped to a length of 2 mm, washed with 3:1 ratio of acetone and ethanol solution respectively and then by distilled water so that the oil, wax and chlorophyll contents existing in the date palm leaf fibers. Finally, 1% sodium hydroxide solution was used to treat the date palm fibers and were dried at atmospheric conditions for 24 h. By making the fiber to undergo alkali treatment, the hydrogen bonding of the fibers were disintegrated thus enhancing the roughness of the fiber surface. Another important aspect of alkali treatment was that it makes the fibers to be devoid of oils, lignin and wax that existed in the external surface of the fiber cell wall. Additionally, the glass fibers were also chopped to a length of 2 mm from continuous glass fiber roves for fiber treatment with the aid of an electronic controlled fiber cutting machine for better accuracy and were dried at 80 °C for a period of 24 h. Such surface modified fibers when used in composite manufacturing, they possessed minimum moisture absorption according to the experimental results (Swain et al. 2018).

4 Mechanical Properties

The experiments were carried out on the hemp fibers whose surface were modified by fungal treatment and reinforced in polyester matrix to evaluate the moisture absorption behavior. Results showcased that the surface modified fibers exhibited enhanced acidic-basic properties and possessed better hydrophobic characteristics. Meanwhile, the treated fibers exhibited better mechanical properties when compared with its counterparts (Ramesh et al. 2020a). It was stated in many studies that the strong adhesion at the interfacial region between matrix and fibers plays a major role in controlling the performance of natural fiber reinforced polymer composites which would be predominant in case of hydrophilic fibers. Experiments conducted using Grewia optiva fibers which had more polar groups on the surface revealed that the untreated fibers possessed hydrophobic nature, weak bonding at the fiber matrix interface and poor fiber wettability with matrix. Various treatments like benzoylation, grafting of vinyl compounds, alkali and silane coupling agents were carried over on the fibers to reduce the fiber hydrophilicity (Gulati and Sain 2006). Results indicated

that the untreated fiber composites had a higher dielectric constant when compared with the treated fiber composites. This was attributed to the moisture absorption of the natural fibers from the surrounding and the hydrophilicity rendered increased conductivity (Singha et al. 2013). Hence the surface modification of the Grewia optiva fibers rendered minimum dielectric constant for the resultant bio-composites which was attributed to the reduced polar group orientation in case of the treated fiber. Various aforementioned treatments on Grewia optiva fibers made the fibers to be hydrophobic since the A-OH active groups of the fibers in their backbone were blocked by the surface modification (Kulkarni et al. 1981; Singha and Rana 2013).

Few experimenters tried to characterize the treated and untreated banana fiber reinforced polyester composites with respect to their physical, chemical and mechanical characteristics as banana fibers possess various better properties such as better stiffness, strength and appreciable fiber length along with good moisture absorption characteristics. It was stated from the results that the alkali treated banana fibers exhibited better mechanical and moisture absorption behaviour due to the absence of hemicellulose in the surface of the treated fiber (Balaji et al. 2020). Jute fibers reinforced in thermoplastic polyurethane matrix was manufactured with the aid of twin-screw extruder machine with a fiber volume fraction of 30%. Before making the composites, the fibers were oven dried at 100 °C for 8 h period to get rid of moisture interference at the time of composite extrusion. Fibers were treated with benzoyl chloride and the parameters used for extrusion of fibers as 100 rpm screw speed, 200 °C as processing temperature and 5 min of mixing time. It was observed from the results that the treated fibers were much hydrophobic when compared with the untreated fibers (Sathish et al. 2018). Studies on bamboo fiber reinforced epoxy composites were carried out to evaluate the mechanical and moisture absorption behaviour of the composites. Bamboo fibers were treated with sodium hydroxide to remove the micro constituents like lignin, wax, hemicellulose, oil and inorganic salts that were encompassed around the surface of the bamboo fiber and then the formed composites were subjected to mechanical and moisture absorption properties evaluation. Owing to the rough fiber surface morphology, the flexural and moisture absorption behaviour of the bamboo fiber composites enhanced and an appreciable chemical and mechanical interlocking was also induced due to chemical treatment. It was also observed that the surface modified bamboo fibers had better interfacial adhesion along with increased hydrophobicity due to the conversion of polymeric bonds into monomers and exposure short crystallites of bamboo fiber (Singha and Rana 2012; Barathkumar and Gokulprakash 2018; Salem et al. 2020; Kushwaha and Kumar 2010; Saravana Kumar et al. 2017; Indraja et al. 2014; Petinakis et al. 2013).

Natural fibers of flax were reinforced with PLA matrix and the mixture was compounded in a melt mixer of model Haake Rheomix at a temperature of 185 °C. Before compounding the matrix with the reinforcement, PLA matrix was dried at 90 °C for a period of 2 h in order to reduce the degradation of PLA matrix by hydrolytion. After compounding and fabricating the composites, the moisture content of the composites containing treated and untreated fibers were 1% to 5% (Phuong et al. 2010). Mechanical characteristics of the natural fiber reinforced composites were influenced by various factors like moisture absorption ability of the fiber, fiber

loading and fiber length. It was also noticed that at a low absorption of moisture and at optimum loading condition and length the natural fiber composites had enhanced mechanical characteristics. On the other hand, moisture absorption of the natural fibers influenced the thermal behaviour of the composites. Thermal stability of the composites dropped in case of untreated fiber composites while the composites with treated fibers had better thermal stability. It was stated by the authors that when flame retardants were added as fillers to the above composites, their thermal stability increased further (Sathish et al. 2017).

Various researchers stated that the conductivity of cellulose based natural fibers was due to the hydrophilic nature of the composites. As the hydroxyl group of the natural fibers turned them to be hydrophilic, their moisture absorption rate increases which paved way for the enhanced conductivity of the natural fiber reinforced polymeric composites. It was also noted from the earlier experiments that the alkaline treatment of the natural fibers reduced their dielectric constant and hence the conductivity values which could be attributed to the reduction of orientation polarization of the composites containing alkaline treated natural fibers. As mentioned earlier blockage of active OH group of the natural fibers by the alkaline compounds rendered minimum moisture absorption characteristics of the natural fibers (Yan et al. 2012). Sisal fibers reinforced in polylactic acid matrix were subjected to dielectric constant evaluation and the results showed that the treated sisal fiber composites had better dielectric constant when compared with untreated dielectric constant which could be due to the lignocellulosic constituents present in the sisal fibers. This could also be attributed to the heterogeneous nature of the sisal fiber composites and the chemical constituents present in it. Treated sisal fibers had 43–88% of cellulose, 10–21% of moisture, 10–14% of hemicellulose and 5–12% of lignin content as per the test results (Ramesh and Rajeshkumar 2018).

Dimensional instability and swelling were noted to be end effects of high moisture absorption of fibers and reduced mechanical characteristics and these anomalies resulted due to the weak interfacial adhesion existed in between hydrophobic matrix and hydrophilic fibers. Natural fiber reinforced composites were converted into high performance materials by various physical and chemical surface modifications which indirectly enhances the interfacial characteristics between the natural fiber and matrix (Yan et al. 2012; Sethy 2011; Orue et al. 2015). Hydrophobicity of the natural fibers can be enhanced by the surface modification through chemicals which also improves the fiber matrix compatibility. Bonding between the fiber and the matrix is also enhanced due to the chemical modification of fiber surface structures which also minimizes the moisture absorption behaviour of the natural fibers. Optimal fiber characteristics could be obtained through the selection of appropriate process parameters and fiber volume fraction. Fiber inherent characteristics like chemical composition, morphology, crystal structure and surface chemistry decides the ultimate properties of the composites and the matrix properties like functionality and nature also emphasizes the same (Singh and Samanta 1163; Sigha and Rana 2013; Sathish et al. 2019). Biodegradation of plastic matrix resulting in its fragmentation would take place in suitable conditions like oxygen availability, metallic elements presence, moisture absorption, temperature, humidity and the value of pH which

ends up with harmless residue generation which would also be non-toxic (Karthi et al. 2020; Mohanty et al. 2005). Cellulose natural fibers were surface modified by acetylene and the process of modification is termed as esterification treatment and is known to be the better method for the cellulose fibers. Moisture that was present in the natural fibers were taken out by the active CH_3–COO acetyl group of the acetylene by undergoing a reaction with the hydroxyl group of the hydrophilic fiber. This renders a better dimensional stability to the natural fibers thereby reducing their hydrophilic nature and improving the dispersion of fiber within the matrix material. As the hydroxyl group of the natural fibers were replaced by the acetyl group during the acetylation, fibers turned more hydrophobic after the acetylation treatment (Chigondo et al. 2013).

4.1 Cyclic Moisture Absorption and Desorption

Few experiments were conducted over the Luffa fibers reinforced in PLA matrix and their hot and cold water absorption and desorption cycles along with few mechanical characteristics like impact and flexural strengths were evaluated. Heat treated Luffa fibers in volume fractions of 5%, 10%, 15% and 20% were reinforced within the PLA matrix and the test were conducted. Luffa fiber composites which exhibited maximum impact and flexural strengths were taken for the analysis of water absorption and desorption where the composites were subjected to a total of 56 cycles of cold and hot water desorption and absorption. Strength of the composites were evaluated after every 14 water absorption and desorption cycles. It was observed from the results that the reduction of flexural and impact strength occurred during absorption and desorption of water and meanwhile impact strength of the Luffa fiber composites faced a major reduction than the flexural strength. SEM images of the Luffa-PLA bio composites were used for the analysis of their microstructure (Sujaritjun et al. 2013). Figure 1 shows the SEM images of the moisture absorbed samples at different time intervals. The water absorbed matrix layer is clearly visible, which is reported that there has been a maximum amount of water immersed in the first two hours after immersion. It swelled, the the surfaces of the composite specimens are shown. The presence of water molecules within the sample are also visible (Ramesh et al. 2016).

4.2 Polylactic Based Composites

Few experimental results exhibited that the tensile strength and stiffness of the unreinforced polylactic acid (PLA) based composites were not upto the mark for any load carrying application. Hence the use of natural firs which were less in cost, biodegradable, less in weight with high stiffness were recommended as reinforcements particularly for manufacturing methods like 3D printing of natural composites. It was stated that alkali, acid or silane treatments were most often used for the surface modification

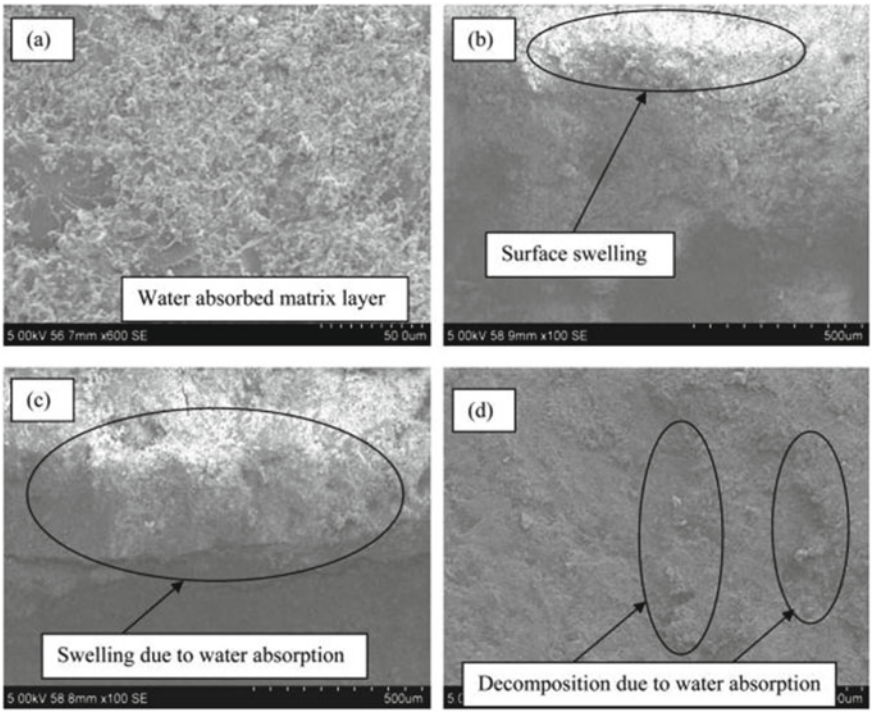


Fig. 1 SEM images of the moisture absorbed composite samples after **a** 2 h, **b** 3 h, **c** 4 h, and **d** 5 h (Ramesh et al. 2016)

of the natural fibers in order to improve their interfacial adhesion between matrix and the fiber. Few experiments were carried out on the epoxy modified pine fibers reinforced in PLA matrix which were manufactured by impregnation method and the fiber volume fraction was maintained as 30%. When compared with the unreinforced PLA, epoxy modified pine fibers exhibited an increase of tensile strength and Young's modulus by 20% and 82% respectively which was purely due the surface modification of pine fibers by epoxy treatment. It was also found from the results that 1 wt.% of epoxy modification resulted in less void formation in pine-PLA composites when compared with the pine/PLA composites without epoxy surface modification. SEM images, as depicted in Fig. 2, showcases the penetration of epoxy partially into the interior structural pores of the pine fibers which rendered an improved fiber matrix adhesion. It was concluded by the authors that epoxy modification was found to a simple yet effective method of surface modification to obtain better bio composite properties. Figure 2 denotes the various stages in water absorption of pine fibers with PLA biocompoistes and the morphology of treated fibers which had enhanced moisture resistance (Faruk and Sain 2014; Zhao et al. 2020).

Figure 3 shows the various processing methods and morphology of untreated and treated pine fibers along with the physical properties of various unreinforced

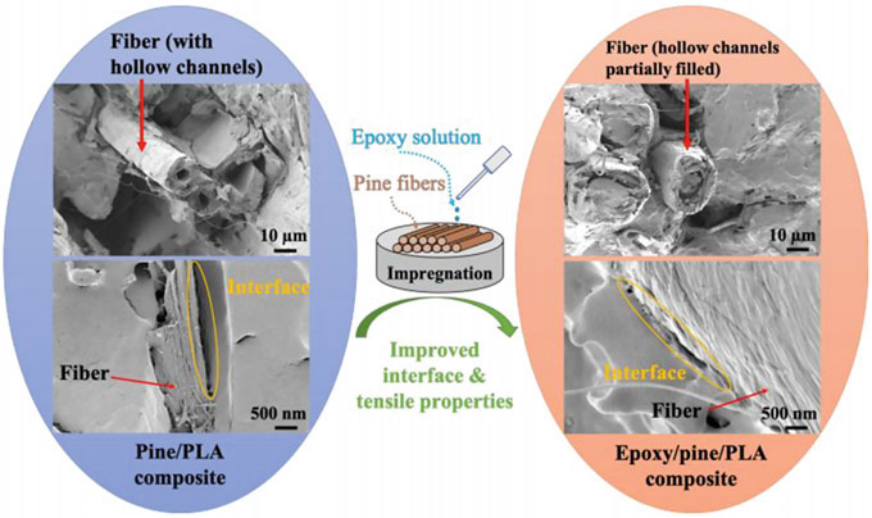


Fig. 2 Moisture absorption behavior of bio composites with natural fibers (Zhao et al. 2020)

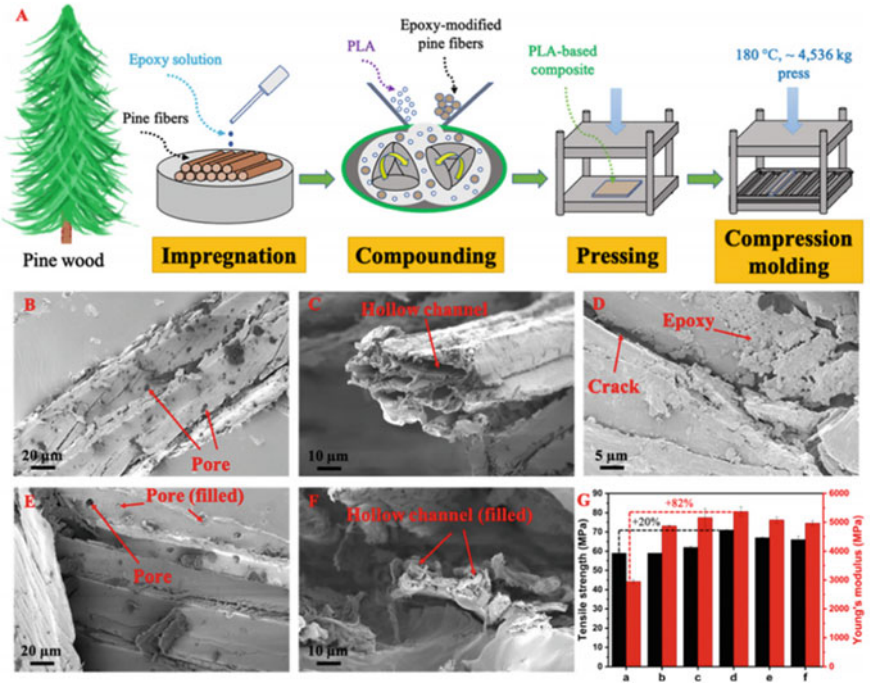


Fig. 3 **a** Processing of PLA based biocompoistes, SEM morphology of **b** Pine fiber surface, **c** Pine fibers cross section, **d**, **e** Epoxy treated pine fiber surfaces, **f** Epoxy treated pine fiber cross section, **g** Variation of tensile strength and Young's modulus of PLA-pine-epoxy composites (Zhao et al. 2020)

and PLA/epoxy reinforced pine fiber composites. Figure 3g denotes the variation of tensile strength and Young's modulus of unreinforced PLA (A), PLA reinforced with pine fibers (B), PLA reinforced with pine fibers treated with 0.5, 1, 2 and 4 parts of epoxy (C, D, E, F respectively).

Usually the thermal stability of natural fiber reinforced polymer composites were carried out in a thermogravimetric analyzer of model Q500 in a nitrogen atmosphere at a 20 mL/min flow rate of purge gas. Natural fiber composite samples were heated to temperatures in between 35 and 70 ºC at a rate of heating of 10 ºC per minute and was maintained at a temperature of 70 ºC for a time of 20 min in order to get rid of the moisture absorbed by the natural fibers. Again the samples were heated at a rate of 10 ºC/min for a maximum of 700 ºC to assess their behavior. Few experimental results showed that the use of PLA/natural fiber composites face few constraints in temperature related applications owing to their lower flammability resistance and high moisture absorption ability. Diammonium Phosphate (DAP) was one among the commonly used chemical used for the modification of natural fiber surface to improve the flammability resistance of PLA/natural fiber bio composite. Few aspects like low tensile strength, high flammable behavior and moisture absorption hindered the application of PLA/natural fiber composites. Through experimentation, various researchers proposed that this could be improved by various chemical modification methods (Zhao et al. 2020; Ramesh et al. 2020b). Figure 4 denotes the variation of decomposition temperature and peak temperature for the natural fiber reinforced PLA composites.

Few experiments were carried out with PLA matrix reinforced with date palm fibers which were fabricated using a twin screw extruder of Leistriz LSM 34 co-rotator type having an aspect ratio of 29 and a screw diameter of 34 mm. PLA pellets

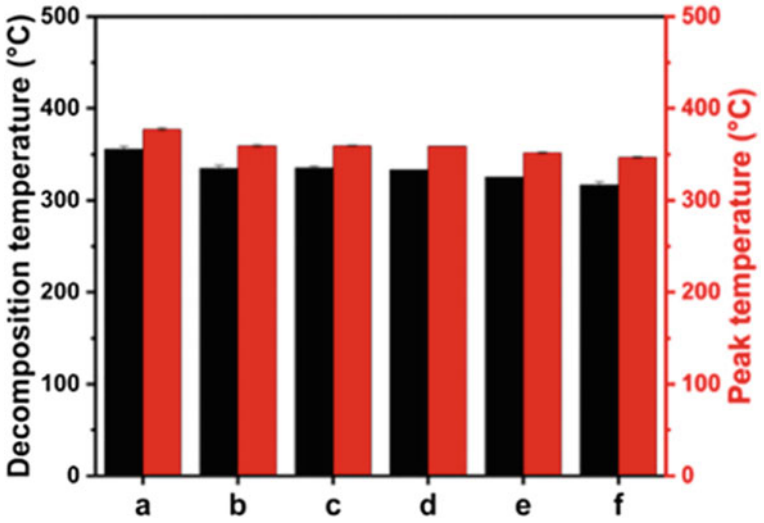


Fig. 4 Variation of decomposition and peak temperature (Zhao et al. 2020)

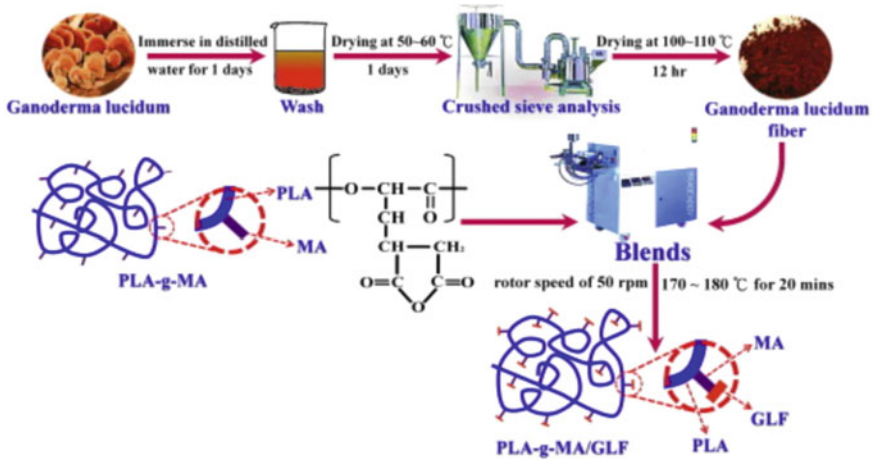


Fig. 5 Ganoderma lucidum fibres reinforced in PLA matrix (Chin-San 2014)

were oven dried at 70 ℃ for 3 h with a hot air blow and the date palm/PLA ingredients were fed into the extruder hopper with a volumetric feeder at a rate of 4 kg per hour. Venting port at the extruder machine made the mixture devoid of volatile compounds and residual moisture. After extrusion, the mixture was made into pellets by a rotating cutter and the extruded elements were then cooled by feeding them into a water bath (Goriparthi et al. 2012). Cosmetic application of the PLA was observed to be mainly due to the retaining of moisture by the lactate which in turn was due to the hydrophilic nature of the lactic acid. Ethyl lactate possess an appreciable solvency with various polymeric elements and oils which made them suitable for the preparation of antiacne compounds (Chin-San 2014). Experiments were also conducted by few researchers with Ganoderma lucidum fibers reinforced in PLA matrix. Water absorption behavior of the above natural composites were investigated and determined that the surface modification of Ganoderma fibers rendered a hydrophobic composite when compared with the untreated composites. Figure 5 shows the process of washing the Ganoderma lucidum fibers, treating them and blending them with PLA matrix along with its chemical structure after the surface modification with acetic acid blended in a twin screw extruder (Suprakas and Mosto 2005).

4.3 Kenaf Fiber Composites

Fibers existing in nature plays a significant role for producing green composite for both manufacturing and investigation areas due to its viability. Relations with water and other elements which are convenient for thermodynamic property in natural fiber is a crucial part for the effective outside usage. So for these reasons investigation of both absorption and adsorption nature of kenaf or glass polyester mixture composite

with various stacking order by using water as a medium is a major aim of this task. At the same time investigating the mechanical characteristics of the fiber is also essential part here. Twenty days required for the composite which need to wet completely at actual temperature for conducting moisture absorption experiment. At equilibrium the content of moisture (M_m), coefficient of diffusion (D_x) and water transport mechanism were the unique factors investigated through this test. Fickian's diffusion law used to calculate water transport mechanism of mixed composites in which polymer relaxation time (t_r) is higher than the characteristic solvent diffusion time (t_d). Mechanical characteristics like tensile and flexure strength of the protective layer of the composites were derived by using both absorption and adsorption method. The quality of being physically strong was calculated that got reduced with addition of water intake and depends on the arrangement of long thin parts of a kenaf fibre at the protective layer (Suprakas and Mosto 2005). Coefficient (n), coefficient of diffusion (d_x) and moisture gain percentage were the major influencing factors for moisture uptake investigation for various laminates. Those influencing factors were arranged in a column.

Moisture uptake for several composites was explained in the below image with root square value of time (H_r). at the initial stage, moisture uptake curve is linear, later maintained a value and saturated at the final time period. Few observations have been done that, glass fiber composite possesses a value of 2.314% which is less value of moisture gain and attained the saturation level beyond 288 h. Kenaf composite possesses a larger value of 10.560% for moisture gain and attained the saturation level beyond 432 h. Observations carried out for mixed composite of kenaf /glass and found the moisture gain value which is intermediate of those two composites. Hybrid composite of glass and kenaf fiber results improved moisture gain value than the hybrid composite of kenaf and glass fiber. The reason for this variation is protective layer acting in glass kenaf fiber restricts the dispersion of water particles since it is acting as a protective layer. Fickian's diffusion used to find the absorption of moisture for experimental composites which is having a coefficient (n) nearer to 0.5 which depicts clearly in the table. Transferability of the particles which can dissolve in to the solution of the polymer composite is explained by the coefficient of diffusion. It was observed that diffusion coefficient is linearly proportional to value of moisture gain and found maximum in protective layer of kenaf fiber which is not in a case of glass fiber since the fiber of glass oppose the humidity content (Sorrentino et al. 2007). Decrease of stability of the fibers has been studied by considering tensile and bending characteristics of those fibers with the inclusion of three levels in the below images. It was observed that in glass fibers, maximum elongation stability is more and if we include kenaf means it gets reduced slightly. Kenaf fiber composite possess a reduced elongation stability compare to other fiber composites. The reason for this change is if the laminate strength is more, then it can merge with glass fiber correctly (Mishra et al. 2020).

Figure 6 denotes the weight loss of the natural fibers due to moisture absorption and the variation of ultimate tensile strength of the natural/synthetic fibers reinforced polymer composites. Absorption of moisture is also one of the reasons for decrement of stability of the fiber composites. In kenaf fiber composites, around fifty one

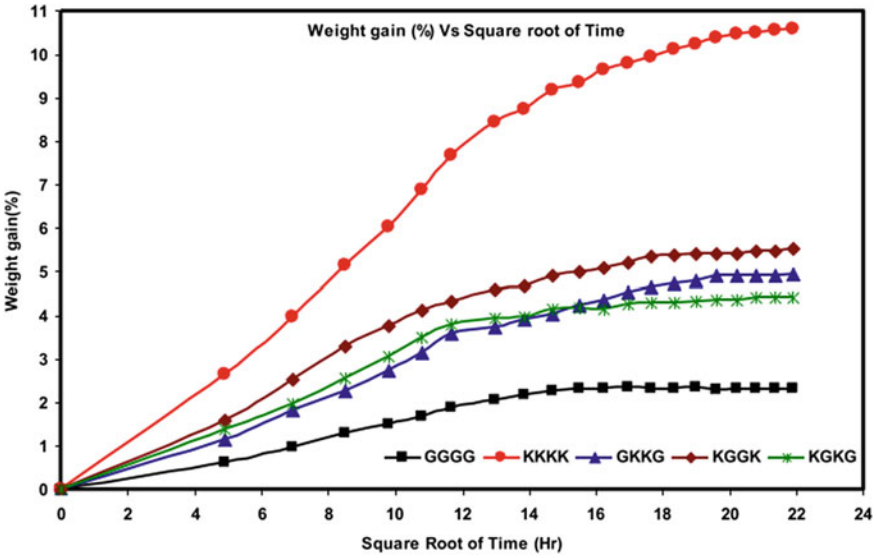


Fig. 6 Effect of Moisture absorption on the weight loss/gain (Mishra et al. 2020)

percentage of stability reduction was found but if we merge this fiber in to glass fiber, the stability reduction attain the value of thirty seven percentages. Reason for more strength reduction in kenaf fiber composite is bulging of fiber which yield the formation of shear stress in the boundary of the fiber matrix could be the factor for weaken bonding. After dryness, some amount of elongation stability of the composites was retained. This residual strength is more in glass fiber comparatively with both kenaf and kenaf glass fiber composite. In glass fiber returning back of tensile strength is obtained up to the value of 95% which is not in case of kenaf/glass hybrid composite which can obtain only with the value of 87.22%. The reason for this problem is process of becoming older is the nature of kenaf fiber. Plasticizer role is used to regaining the strength of the fiber composite which is used to soft, flexible, increase plasticity, reduce viscosity and friction in processing. This plasticizer role is done by water which could be extracted after dehydration (Prabhu et al. 2020). Figure 7a, b explains the bending strength and bending modulus of composite samples at the same three various levels. Related nature of lowering in stability and modulus and their revival are also explained (Mishra et al. 2020; Gurunathan et al. 2015).

Scanned electron microscopy (SEM) was used to examine the failure state of the broken parts of the composites with the magnification value of × 350. Figure 8a explains the fracture surface of tensile test specimen. In this figure, elongation and empty space of fibers while removing it visualized clearly. Figure 8b explains the rupture of vascular fiber bundles and empty spaces because of fiber pull out at fracture surface of flexural test sample (Mishra et al. 2020; Alomayri et al. 2014).

Through all discussions and investigations, the following conclusions were derived. Protective layer of all composites for transferring the moisture uses Fickian's

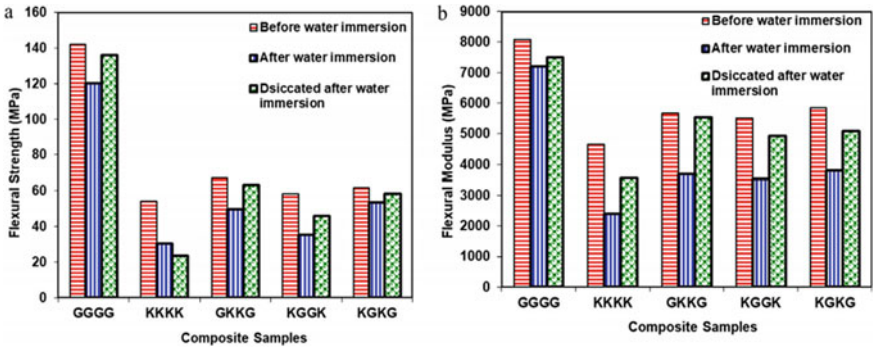


Fig. 7 **a** Variation of flexural strength w.r.t. composite samples; **b** variation of flexural modulus w.r.t. composite samples (Mishra et al. 2020)

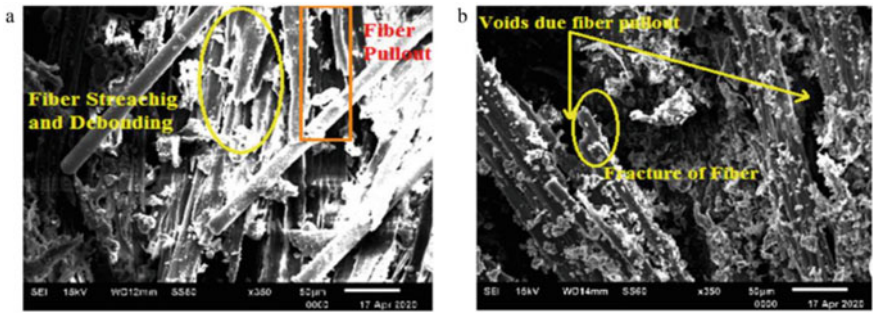


Fig. 8 **a** Fiber stretching and debonding; **b** fracture surfaces of composite samples (Mishra et al. 2020)

law in which the coefficient value is nearer to 0.5. Maximum value of 7.140×10^8 cm^2/s as a diffusion coefficient is attained by kenaf fiber. Even if that is the case, continuous inclusion of fiber glass decreases the amount of taking up of water. Humiliation of mechanical characteristics is found because of moisture absorption but of merging of glass fiber enhances the reduction as-well-as enhanced the retaining of stability up to 87.22% after the process of drying. Major factors for decrement of stability and tensile constants of fiber composites are based on the pulling out of fiber and de-bonding of fiber–matrix inter-phase (Gokulkumar et al. 2019).

4.4 Pineapple Leaf Fiber Composites

Pineapple leaf fibers (PALF) are being currently used as natural fiber reinforcements widely due to its abundant availability in many regions around the globe. Unique properties including biodegradability, environmental friendly end products,

less in cost and weight pose the usage of hybrid fiber reinforced composites to a greater extent. Few experiments were carried out earlier to evaluate the moisture absorption and mechanical characteristics of PALF-G fibers reinforced hybrid composites reinforced in epoxy matrix and the influence of fiber stacking sequence had been analyzed. Tensile, flexural and accelerated moisture absorption tests were conducted for three different stacking sequence such as GPPG, PGPG and PGGP which were used to fabricate the hybrid PALF-G fibers reinforced epoxy composites and the experiments were also carried out in individual PALF and G fiber composites. Fickian diffusion theory was used to evaluate the moisture absorption characteristics of the composites and SEM was used for the characterization of fracture surface morphology of the specimen. Results portrayed that individual PALF composites absorbed larger quantity of moisture than the hybrid composites which in turn degraded the mechanical characteristics of the individual PALF composites while the hybrid composites possessed higher mechanical properties. It was also noticed from the results that the fiber stacking sequence had an appreciable effect over the moisture absorption behaviour of the composites. Mechanical test results indicated that the tensile and flexural behaviour of PALF-G hybrid composites were higher than the individual composites due to the lower moisture absorption of hybrid composites and when compared with unreinforced epoxy composites, the tensile and flexural strength was 153% and 119% higher for the fiber reinforced composites respectively. Amongst the various stacking sequence, PGPG sequence exhibited better mechanical characteristics with their tensile and flexural strength as 120.19 MPa and 169.17 MPa respectively when compared with other sequences. It could be noticed from the SEM images that hybrid composites with PGPG sequence displayed better bonding at the composite interface between matrix and fiber when compared with the other sequences (Ramesh and Rajesh Kumar 2020; Mochane et al. 2019; Wu 2014).

Moisture absorption behaviour of the PALF-G hybrid composites were evaluated by using the composite specimens of length 50 mm adopting ASTM D5229 standards. A water resistant epoxy coating was applied at each end of the specimen and were sealed with the paint. Specimens were then oven dried at a temperature of 50 ºC for a period of 24 h until all the moisture present in the specimen evaporates and the specimens were atmospheric cooled. Specimens were weighed before and after drying in the oven and the mass values were noted as M_r and M_o respectively. Specimens were then drowned in a bath of water at a temperature of 60 ºC and were measured for their weight at regular interval of time until saturated state was reached (Kharrat et al. 2019). Moisture absorption rate was determined by the following Eq. 1:

$$M_f = \frac{M_t - M_0}{M_0} \times 100 \tag{1}$$

where M_t = Mass of the Specimen after time of exposure t, M_o = Mass of specimen before immersing in water bath. Following equation denoted the Fick's law of

diffusion that could be applied to the composite specimen for evaluating its moisture absorption behaviour.

$$M(T,t) = (M_m - M_i)\left(1 - \exp\left[-7.3\left(\frac{D_Z \times t}{h^2}\right)^{0.75}\right]\right) + M_i \quad (2)$$

Experiments conducted in using PALF-G hybrid fibers reinforced in epoxy matrix to determine their moisture absorption behaviour along with the determination of mechanical properties such as tensile and flexural characteristics revealed that the effect of hybridization of fibers had significant effect on the above behaviour and enhanced them. It was also seen that the stacking sequence of the fiber laminates showed greater impact over the composite properties. Fick's law of diffusion could effectively predict the moisture absorption behaviour of the hybrid and individual fiber reinforced composites. The stacking sequence with alternate laminates of PALF and G fibers (PGPG) exhibited lowest moisture absorption which was 10.35% less than the moisture absorption rate of other compositions. Overall from the above discussion it could be seen that the PALF-G hybrid composites with PGPG stacking sequence exhibited better moisture absorption, tensile and flexural properties with better adhesion at the interfacial region in between epoxy matrix and PALF-G hybrid composite reinforcements (Datta et al. 1995; Karimzadeh et al. 2020).

5 Conclusion

Broad preamble to actual fiber strengthened composites, the proportion of actual fiber, and modification of surface of the natural fiber and the chemical treatments effect of on natural fiber composites are discussed. Several experiments clearly illustrate the mechanical characteristics of all natural fibers strengthened composites namely; tensile and bending, elongation percentage and finally absorption of water etc. are extensively enhanced. Comparison of several characteristics between surface modified natural fiber and un-treated fiber has been done. Among that, improved tensile and bending strength identified in alkali surface modified natural fiber composites with untreated composites. Sticking bond between natural fiber and matrix got enhanced in case of surface modified fibers and water amalgamation characteristics of natural fiber reinforced composites got decreased. Surface modified fiber composite proven the better tensile properties compared with un-treated fibres. Surface modified fibers has proven enhanced tensile properties comparator combined surface modified fiber which is deriving good property enhancement than the single surface modified method in which alkali method is exceptional. Silane treated surface modified fiber composites possess good improvement in case of impact strength characteristics. Fat, lignin and pectin are the natural fiber impurities can be eliminated easily by using surface modifications of the natural fibers.

References

Agrawal R, Saxena NS, Sharma KB, Thomas S, Sreekala MS (2000) Activation energy and crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde composites. Mater Sci Eng, A 277(1–2):77–82

Alomayri T, Assaedi H, Shaikh FUA, Low IM (2014) Effect of water absorption on the mechanical properties of cotton fabric-reinforced geopolymer composites. J Asian Ceramic Soc 2(3):223–230

Alvarez VA, Ruscekaite RA, Vazquez A (2003) Mechanical properties and water absorption behavior of composites made from a biodegradable matrix and alkaline-treated sisal fibers. J Compos Mater 37(17):1575–1588

Balaji D, Ramesh M, Kannan T, Deepan S, Bhuvaneswari V, Rajeshkumar L (2020) Experimental investigation on mechanical properties of banana/snake grass fiber reinforced hybrid composites. Mater Today Proc. https://doi.org/10.1016/j.matpr.2020.09.548

Vonoth R, Gokulnath KS, Barathkumar KJ, Ahildarshan K, Gokulprakash E (2018) A study of banana fiber: a review. Int J Sci Res Develop 6(09):127–131

Bhoopathi R, Deepa C, Sasikala G, Ramesh M (2015) Experimental investigation on mechanical properties of hemp-banana-glass fiber reinforced composites. Appl Mech Mater 766:167–172

Chigondo F, Shoko P, Nyamunda BC, Guyo U, Moyo M (2013) Maize stalk as reinforcement in natural rubber composites. Int J Sci Technol Res 2(6):2277–8616

Chin-San W (2014) Preparation, characterisation, and biocompatibility of Ganoderma lucidum fibre-based composites with polylactic acid. Compos Sci Technol 103:1–9

Datta R, Tsai SP, Bonsignore P, Moon SH, Frank JR (1995) Technological and economic potential of poly (lactic acid) and lactic acid derivatives. FEMS Microbiol Rev 16(2–3):221–231

Faruk O, Sain M (2014) Biofber reinforcement in composites materials. Woodhead Publ Ser 51:454–487

Gokulkumar S, Thyla PR, Prabhu L, Sathish S (2019) Measuring methods of acoustic properties and influence of physical parameters on natural fibers: a review. J Nat Fibers. https://doi.org/10.1080/15440478.2019.1598913,1-20

Goriparthi BK, Suman KNS, Rao NM (2012) Efect of fber surface treatments on mechanical and abrasive wear performance of polylactide/jute composites. Compos Part A Appl Sci Manuf 43:1800–1808

Gulati D, Sain M (2006) Fungal-modification of natural fibers: a novel method of treating natural fibers for composite reinforcement. J Polym Environ 14(4):347–352

Gurunathan T, Mohanty S, Nayak SK (2015) A review of the recent developments in biocomposites based on natural fbres and their application perspectives. Compos Part A Appl Sci Manuf 77:1–25

Indraja Y, Kumar GS, Rao HR (2014) Development and study of properties of natural fiber reinforced polyester composites. Int J Eng Sci Res Technol 410–414

Jayaramudu J, Reddy KO, Maheswari CU, Reddy DJP, Rajulu AV (2009) Tensile properties and thermal degradation parameters of Polyalthia cerasoides natural fabric reinforcement. J Reinf Plast Compos 28(18):2177–2181

Karimzadeh A, Yahya MY, Abdullah MN, Wong KJ (2020) Effect of stacking sequence on mechanical properties and moisture absorption characteristic of hybrid PALF/glass fiber composites. Fibers Polym 21(7):1583–1593

Karthi N, Kumaresan K, Sathish S, Gokulkumar S, Prabhu L, Vigneshkumar N (2020) An overview: Natural fiber reinforced hybrid composites, chemical treatments and application areas. Mater Today Proc 27(3):2828–2834

Kharrat F, Chaari R, Khlif M, Hilliou L, Covas JA, Haboussi M, Nouri H, Bradai C (2019) The effect of the process on mechanical properties of polylactic acid-date palm leaf fibers composite films produced by extrusion blowing. J Renew Mater 7(9):891–901

Kulkarni AG, Satyanarayana KG, Rohatgi PK (1981) Electrical resistivity and dielectric strength of plant fibres. J Mater Sci 16(6):1719–1726

Kushwaha PK, Kumar R (2010) Effect of silanes on mechanical properties of bamboo fiber-epoxy composites. J Reinf Plast Compos 29(5):718–724. https://doi.org/10.1177/0731684408100691

Li X, Tabil LG, Panigrahi S (2007) Chemical treatments of natural fiber for use in natural fiber-reinforced composites: a review. J Polym Environ 15(1):25–33

Mishra C, Deo CR, Baskey S (2020) Influence of moisture absorption on mechanical properties of kenaf/glass reinforced polyester hybrid composite. Mater Today Proc. https://doi.org/10.1016/j.matpr.2020.08.100

Mochane MJ, Mokhena TC, Sadiku ER, Ray SS, Mofokeng TG (2019) Green polymer composites based on polylactic acid (PLA) and fibers. In: Green biopolymers and their nanocomposites. Springer, Singapore, pp 29–54

Mohanty AK, Misra M, Drzal LT (2005) Natural fibers, biopolymers, and biocomposites. Taylor & Francis Group, Boca Raton, Florida

Orue A, Jauregi A, Peña-Rodriguez C, Labidi J, Eceiza A, Arbelaiz A (2015) The effect of surface modifications on sisal fiber properties and sisal/poly (lactic acid) interface adhesion. Compos Part B Eng 73:132–138

Petinakis E, Yu L, Simon G et al. (2013) Natural fiber bio-composites incorporating poly (lactic acid). In: Masuelli M (ed) Fiber reinforced polymers—the technology applied for concrete repair. InTech, pp 41–59. https://doi.org/10.5772/52253

Phuong NT, Sollogoub C, Guinault A (2010) Relationship between fiber chemical treatment and properties of recycled pp/BFCs. J Reinf Plast Compos 3244–3256. https://doi.org/10.1177/0731684410370905

Prabhu L, Krishnaraj V, Gokulkumar S, Sathish S, Sanjay MR, Siengchin S (2020) Mechanical, chemical and sound absorption properties of glass/kenaf/waste tea leaf fiber-reinforced hybrid epoxy composites. J Ind Text. https://doi.org/10.1177/1528083720957392

Ramesh M (2016) Kenaf (*Hibiscus cannabinus* L.) fibre based bio-materials: a review on processing and properties. Prog Mater Sci 78:1–92

Ramesh M (2018) Flax (*Linum usitatissimum* L.) fibre reinforced polymer composite materials: a review on preparation, properties and prospects. Prog Mater Sci 102:109–166

Ramesh M, Palanikumar K, Reddy KH (2016) Influence of fiber orientation and fiber content on properties of sisal-jute-glass fiber-reinforced polyester composites. J Appl Polym Sci. https://doi.org/10.1002/APP.42968

Ramesh M, Palanikumar K, Reddy KH (2017a) Plant fibre based bio-composites: sustainable and renewable green materials. Renew Sustain Energy Rev 79:558–584

Ramesh M, Deepa C, Aswin US, Eashwar H, Mahadevan B, Murugan D (2017b) Effect of alkalization on mechanical and moisture absorption properties of Azadirachta indica (Neem tree) fiber reinforced green composites. Trans Indian Inst Met 70(1):187–199

Ramesh M, Rajesh Kumar L (2020) Bioadhesives. In: Green adhesives preparation, properties and applications. Wiley, pp 145–164

Ramesh M, Rajeshkumar L (2018) Wood flour filled thermoset composites. Thermoset Compos Prep Prop Appl Mater Res Forum 38:33–65. https://doi.org/10.21741/9781945291876-2

Ramesh M, Deepa C, Rajesh Kumar L, Sanjay MR, Siengchin S (2020a) Life-cycle and environmental impact assessments on processing of plant fibres and its bio-composites: a critical review. J Indus Textiles 1528083720924730. https://doi.org/10.1177/1528083720924730

Ramesh M, Rajesh Kumar L, Khan A, Asiri AM (2020b) Self-healing polymer composites and its chemistry. In: Self-healing composite materials. Woodhead Publishing, pp 415–427

Salem TF, Tirkes S, Akar AO, Tayfun U (2020) Enhancement of mechanical, thermal and water uptake performance of TPU/jute fiber green composites via chemical treatments on fiber surface. E-Polymers 20(1):133–143

Saravana Kumar A, Maivizhi Selvi S, Rajeshkumar L (2017) Delamination in drilling of sisal/banana reinforced composites produced by hand lay-up process. Appl Mech Mater 867:29–33

Sathish S, Kumaresan K, Prabhu L, Vigneshkumar N (2017) Experimental investigation on volume fraction of mechanical and physical properties of flax and bamboo fibers reinforced hybrid epoxy composites. Polym Polym Compos 25:229–236

Sathish S, Kumaresan K, Prabhu L, Gokulkumar S (2018) Experimental investigation on mechanical and FTIR analysis of flax fiber/epoxy composites incorporating SiC, Al_2O_3 and graphite. Roman J Mater 48:476–482

Sathish S, Kumaresan K, Prabhu L, Gokulkumar S (2019) Experimental investigation of mechanical and morphological properties of flax fiber reinforced epoxy composites incorporating SiC and Al_2O_3. Mater Today Proc. https://doi.org/10.1016/j.matpr.2019.09.106,1-5

Sethy SR (2010) A study on mechanical behavior of surface modified natural fiber based polymer composites. B. Tech Thesis. Department of Mechanical Engineering, National Institute of Technology, Rourkela, India, 2011

Sigha AS, Rana A (2013) Effect of Aminopropyltriethoxysilane (APS) treatment on properties of mercerized lignocellulosic grewia optiva fiber. J Polym Environ 21:141–150

Singh TJ, Samanta S (2014) Characterization of natural fiber reinforced composites-bamboo and sisal: a review. IJRET: Int J Res Eng Technol. eISSN: 2319-1163|PISSN: 2321–7308

Singha AS, Rana AK (2012) Ce (IV) ion–initiated and microwave radiation–induced graft copolymerization of acrylic acid onto lignocellulosic fibers. Int J Polym Anal Charact 17(1):72–84

Singha AS, Rana AK (2013) Effect of Aminopropyltriethoxysilane (APS) treatment on properties of mercerized lignocellulosic grewia optiva fiber. J Polym Environ 21(1):141–150

Singha AS, Rana AK, Jarial RK (2013) Mechanical, dielectric and thermal properties of Grewia optiva fibers reinforced unsaturated polyester matrix-based composites. Mater Des 51:924–934

Sorrentino A, Gorrasi G, Vittoria V (2007) Potential perspectives of bio-nanocomposites for food packaging applications. Trends Food Sci Technol 18:84–95

Sujaritjun W, Uawongsuwan P, Pivsa-Art W, Hamada H (2013) Mechanical property of surface modifed natural fber reinforced PLA biocomposites. Energy Proc 34:664–672

Suprakas SR, Mosto B (2005) Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. Prog Mater Sci 50:962–1079

Swain PTR, Das SN, Jena SP (2018) Manufacturing and study of thermo-mechanical behaviour of surface modified date palm leaf/glass fiber reinforced hybrid composite. Mater Today: Proc 5(9):18332–18341

Vimal R, Subramanian KHH, Aswin C, Logeswaran V, Ramesh M (2015) Comparisonal study of succinylation and phthalicylation of jute fibres: study of mechanical properties of modified fibre reinforced epoxy composites. Mater Today: Proc 2:2918–2927

Wu CS (2014) Preparation, characterisation, and biocompatibility of Ganoderma lucidum fibre-based composites with polylactic acid. Compos Sci Technol 102:1–9

Yan L, Chouw N, Yuan X (2012) Improving the mechanical properties of natural fiber fabric reinforced epoxy composites by alkali treatment. J Reinf Plast Compos 425–437. https://doi.org/10.1177/0731684412439494

Zhao X, Li K, Wang Y, Tekinalp H, Larsen G, Rasmussen D, Ginder RS, Wang L, Gardner DJ, Tajvidi M, Webb E (2020) High-strength polylactic acid (PLA) biocomposites reinforced by epoxy-modified pine fibers. ACS Sustain Chem Eng 8(35):13236–13247

Effect of Water Absorption on the Tensile, Flexural, Fracture Toughness and Impact Properties of Biocomposites

Jyotishkumar Parameswaranpillai, Jenny Jacob, Midhun Dominic C.D., Chandrasekar Muthukumar, Senthil Muthu Kumar Thiagamani, Aswathy Jayakumar, Suchart Siengchin, and Sabarish Radoor

Abstract The study on the effect of water aging gives information on the performance of composites at diverse operational conditions. The natural fibers absorb water/moisture and hence the addition of natural fibers in the polymer matrix caused an increase in water/moisture uptake at different environmental operational conditions. This literature survey presented the effect of water aging on the tensile, flexural, fracture toughness, and impact properties of the biocomposites. The mechanical properties of the natural fiber-reinforced biocomposites are reported to drop with water aging. This is caused by the degradation of the fiber/polymer interface due to water hydrolysis. The chemical, physical, and hybridization methods can be adapted to reduce the water uptake of natural fiber-reinforced biocomposites.

Keywords Biocomposites · Water absorption · Hybridization · Mechanical properties · Fracture toughness

J. Parameswaranpillai (✉) · J. Jacob
Department of Bioscience, Mar Athanasios College for Advanced Studies Tiruvalla, Pathanamthitta, (MACFAST)Kerala, India

M. Dominic C.D.
Department of Chemistry, Sacred Heart College, Kochi, Kerala, India

C. Muthukumar
Department of Aeronautical Engineering, Hindustan Institute of Technology & Science, Kelambakkam, Chennai 603103, India

S. M. K. Thiagamani
Department of Mechanical Engineering, Kalasalingam Academy of Research and Education, Krishnankoil, Tamil Nadu 626126, India

A. Jayakumar · S. Siengchin · S. Radoor
Natural Composites Research Group Lab, King Mongkut's University of Technology, North Bangkok (KMUTNB), Bangkok, Thailand

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_3

Abbreviations

AFM	Atomic force microscopy
DSC	Differential scanning calorimetry
FS	Flexural strength
FTIR	Fourier-transform infrared spectroscopy
FT	Fracture toughness
T_g	Glass transition temperature
IS	Impact strength
OM	Optical microscopy
RT	Room temperature
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TS	Tensile strength
TM	Tensile modulus
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

1 Introduction

Eco-friendly materials are increasingly using for advanced engineering composite industries due to the environmental concerns caused by the non-biodegradable fibers and polymers. Therefore, researchers prefer either biodegradable polymer (polylactic acid, polyvinyl alcohol, polysaccharides, bioepoxy, and biobased polyethylene) (Varghese et al. 2020; Ahmed et al. 2021; Radoor et al. 2021; Thomas et al. 2021a; Rangappa et al. 2021; Rojas-Lema et al. 2021) or natural filler (plant-based, animal-based, and bacterial-based fillers) (Vinod et al. 2020; Zwawi 2021; Mahmud et al. 2021; Mohd Nurazzi et al. 2017; Thomas et al. 2021b, c), for the manufacturing of polymer composite components for automobile, civil engineering, aerospace, water purification, sensors, toys, and household applications. Glass and carbon fibers were commonly used for composite manufacturing (Hassan et al. 2021; Sun et al. 2021). However, these synthetic fibers cannot be recycled, and are hazardous to the environment causing toxicity to human health, animals, aquatic life. To overcome these defects plant-based natural fibers are widely employed for the development of green composite (Moudood et al. 2019). Plant fibers are commonly isolated from banana, pineapple, cotton, flax, hemp, jute, kenaf, sisal, abaca, and wood (Peças et al. 2018; Sanjay et al. 2019; Radoor et al. 2020; Thyavihalli Girijappa et al. 2019). In recent years plant fibers are the regularly used in polymer composite applications (Thyavihalli Girijappa et al. 2019; Alama et al. 2020; Hasan et al. 2020).

On one hand, the advantages of natural fibers are easy availability, renewable resource, biodegradability, low cost, lightweight, low emitting of CO_2 gas, and environmental friendliness (Tajuddin et al. 2016; Célino et al. 2014). On the other

hand, polymer composites fabricated from natural fibers have low cost and increased biodegradability (Syduzzaman et al. 2020). Natural fiber-based composites have been recommended for the manufacturing of interior parts in the automobile, aerospace, and construction industry (Peças et al. 2018; Akampumuza et al. 2017; Ilyas et al. 2019; Fan 2017). Thus, an upsurge in the usage of natural fibers in engineering polymer composites has been observed in recent years as a substitute for traditional synthetic non-biodegradable fillers. The natural fibers also have many disadvantages such as hydrophilicity, poor moisture/water resistance, poor compatibility with polymer matrices, swelling, low fire resistance, and low durability (Namvar et al. 2014). These factors limit the outdoor applications of natural fiber-modified polymer composites.

The natural fiber is composed of cellulosic (cellulose) and noncellulosic components (hemicellulose, lignin, pectin, wax, and other impurities). The amorphous components in the plant fibers are responsible for water absorption (Célino et al. 2014). Therefore, when natural fiber or natural fiber-reinforced composites exposed to water/moisture or other solvents during the operational conditions absorb moisture. This may cause the swelling of the fiber and composites. The absorption of water in natural fiber-based composites is due to (i) hydrogen bonding between cellulose fibers and moisture (ii) diffusion of water molecules into the microscopic pores or voids generated/formed during the fabrication process (iii) capillary movement of water molecules through the fiber/matrix interface, and (iv) transport of water molecules through the crack sites caused by the swelling of the fibers (Moudood et al. 2019; Muñoz and García-Manrique 2015; Masoodi and Pillai 2012). The absorption of water in the composites caused fiber polymer debonding and may deteriorate the properties of the biocomposites. The moisture absorption effect on the fiber-matrix interface is shown in Fig. 1 (Azwa et al. 2013).

Several methods have been adopted to improve the natural fiber/polymer matrix compatibility. This method includes the physical treatments, chemical treatments, coatings, and hybridization with synthetic fibers (Sanjay et al. 2019; Mukhopadhyay and Fangueiro 2009; Godara 2019; Pothan and Thomas 2004; Abdel-Hakim et al. 2021). The physical and chemical methods will reduce the hydrophilicity of the fibers and hence have better compatibility with the polymer matrices. The widely accepted physical treatments of natural fibers are steam explosion, plasma treatment, ultraviolet irradiation treatment, corona treatment, and ozone treatment (Sanjay et al. 2019; Mukhopadhyay and Fangueiro 2009). The chemical methods such as alkali treatment, acetylation, silane, benzoylation, potassium permanganate, etc., are the preferred methods (Sanjay et al. 2019). Chemical treatment in high-pressure autoclave is a widely accepted method for the synthesis of nanocellulosic fibers with high crystallinity (Dominic et al. 2021). Polymer coating on fiber is employed to reduce moisture absorption and to enhance fiber-polymer compatibility (Abdel-Hakim et al. 2021). A recent study on polyfurfuryl alcohol coating over flax/phenolic composites was reported to present enhanced water resistance and improved mechanical performance (Mokhothu and John 2017).

The properties of the modified natural fibers can be characterized by using methods such as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD)

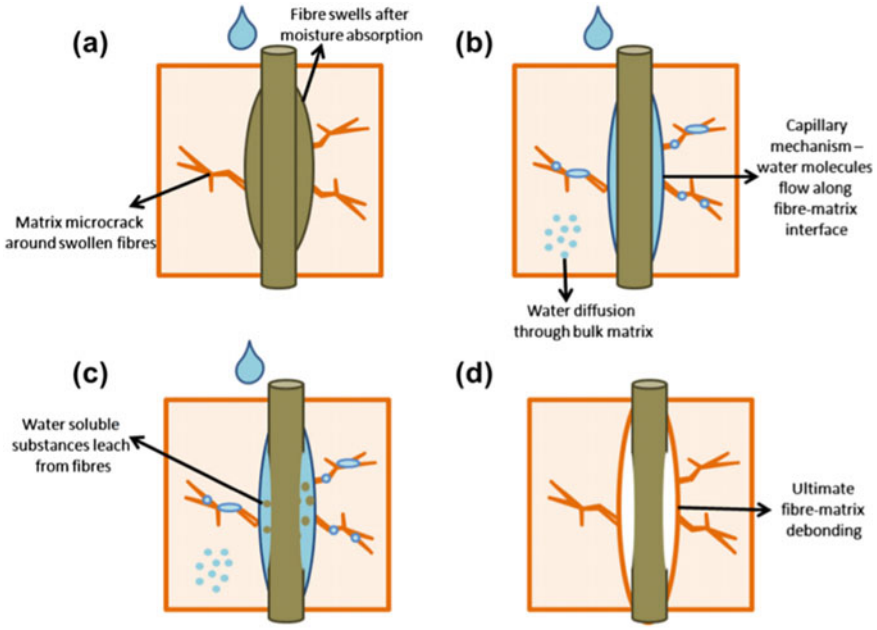


Fig. 1 Moisture absorption effect on the fiber-matrix interface (Azwa et al. 2013) (Reproduced with thanks from Elsevier, License number: 5087561104303)

spectrometry, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), and optical microscopy (OM) (Thomas et al. 2021b; Sanjay et al. 2019; Chen et al. 2014; Chandrasekar et al. 2017). The FTIR spectra of untreated and treated fibers showed many characteristic peaks of the functional groups present. From the changes in the peak position, the structural changes in the fibers during the chemical treatments can be evaluated. The diminishing peak position of natural fibers at approximately 2846 cm^{-1}, and 1739 cm^{-1} after the treatments correspond to the progressive removal of amorphous phases such as lignin and hemicellulose from natural fiber. The increase in peak intensity at approximately 897 cm^{-1}, for the chemical treated fiber corresponds to the increase in the cellulosic content, indicating the increasing percentage of pure cellulose (Thomas et al. 2021b). Further, the XRD spectra can be used for the study of the increase in the cellulosic content and the increase in percentage crystallinity of the treated plant fiber. For natural fibers, the peaks at 2θ values at approximately 16° and 23° corresponding to 200 and 110 planes of cellulose I structure were reported (Thomas et al. 2021b; Chen et al. 2011). The minimum in intensity between 200 and 110 planes corresponds to the amorphous phase. The removal of the amorphous phase is reported to cause an increase in the intensity of these peaks. From the peak intensity values corresponding to 200 plane and amorphous phases, the percentage crystallinity of

the untreated and treated fibers can be measured (Chen et al. 2011). It is reported that the crystallinity of the fibers will increase with chemical treatments.

Polarised OM can be used as a tool for the evaluation of the size of the fibers, it can also be used to observe the crystalline regions of the modified natural fibers (Senthilkumar et al. 2019). The electron microscopic images such as TEM and SEM images can be used for the evaluation of the changes in the morphology of the fibers during the chemical treatments (Thomas et al. 2021b). Further AFM is used for the evaluation of the length (l), diameter (d), and roughness of the fibers before and after chemical treatments. It is reported that the l/d ratio of the fibers will increase after the chemical treatments (Jonoobi et al. 2015). Thermal studies such as TGA and DSC are used for the characterization of the natural fibers. The report suggests that the thermal stability of the treated fibers depends on the type of treatment. The DSC results also showed the removal of the amorphous phase from the treated fibers (Kabir et al. 2010, 2013). The single fiber test can be used for the evaluation of the strength of the treated fibers, which is an indirect measurement of crystallinity. The studies have shown that for the treated fibers the crystallinity is more, and therefore higher strength was observed (Hossain et al. 2013).

The natural fibers were widely used along with biodegradable and non-biodegradable plastics such as polypropylene (Kim et al. 2008), polyamides (Arcaya et al. 2009), polyethylene (Bazan et al. 2020), polylactic acid (Oksman et al. 2003; Wahit et al. 2012), poly (ε-caprolactone) (Wahit et al. 2012), poly (butylene adipate-co-terephthalate) (Ferreira et al. 2019), etc., for the fabrication of advanced composites. The composites were mostly manufactured by injection molding, extrusion and thermoforming (Kumar and Singh 2020). The structural and non-structural compounds for interior engineering applications can be manufactured by the combination of thermoplastic and natural fibers. The thermosetting polymers such as bioepoxy (Senthilkumar et al. 2021), polyesters (Haghdan and Smith 2015), etc., are also modified with natural fibers for semi-structural applications. The thermosetting composites can be manufactured by hand lay-up, resin transfer molding (RTM), and vacuum molding (Kumar and Singh 2020). In the following section, the mechanical properties of water-aged biocomposites are discussed.

2 Water Absorption and Mechanical Properties

2.1 Epoxy Composites

Epoxy and bioepoxy resins are widely accepted polymers for engineering applications such as coating, adhesives, and composites. Synthetic fibers are used normally for the fabrication of epoxy composites. Due to ill effects caused by the synthetic fibers, the natural fibers especially plant fibers are preferred over synthetic fibers for the manufacturing of advanced composites. However, the water absorption of

natural fibers is their main drawback limiting their applications in the outdoor environment. The water absorption in polymer composites may follow Fickian, non-Fickian behavior. In the Fickian model, the water absorption is rapid and then a saturation level is achieved (Grace and Altan 2012). At room temperature (RT), most of the natural fiber-modified polymer composites follow the Fickian model of water absorption (Assarar et al. 2011). Kim and Seo (2006) fabricated sisal fiber textile-reinforced epoxy and vinyl ester composites and studied the effect of water aging on the tensile properties and FT of the composites. The samples were water immersed for 216 h and later dried for 24 h, the test was repeated for 5 cycles. Even though the sisal textile was silane treated, still the water penetrates/diffuses through the composite, because of the (i) hollow structure of the sisal fiber, (2) void content generated in the composite during the fabrication process, and (iii) through the fiber/matrix interface. Among the composite prepared vinyl ester showed lower water absorption compared to epoxy composites. The researchers point out that this could be due to several factors affecting the absorption of water in the composites such as void content, fiber/matrix adhesion, polymer chain relaxation, temperature, type of polymer matrix and crosslink density. The tensile strength (TS), and FT of both sisal textile-reinforced epoxy and vinyl ester composites showed a gradual drop with an increase in water absorption cycle, and the lowest strength and toughness were observed for the composites at the 5^{th} cycle. Figure 2 shows the tensile stress/strain curve of the epoxy/sisal composite at different water aging cycles. The drop in strength and toughness of the composites was due to the degradation of the fibers, resulting in the weakening of the fiber-polymer interface caused by the water absorption.

Assarar et al. (2011) studied and compared the durability of flax–fiber reinforced and glass–fiber reinforced epoxy composite. The water immersion was carried out for up to 20 days. The water absorption is more for natural fiber reinforced composites. This is because of the hollow structure of natural fibers. It was observed that both the

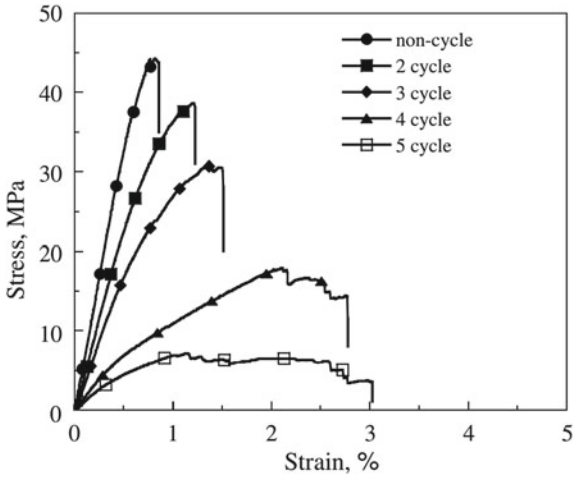


Fig. 2 Tensile stress/strain curve of the epoxy/sisal composites at different water aging cycles (Kim and Seo 2006) (Reproduced with thanks from Elsevier, License number: 5087570010389)

flax–fiber and glass–fiber reinforced epoxy composite showed a drop in tensile properties with water aging. This is due to the degradation of the fiber/matrix interface of the epoxy composites during the water aging process. The drop in tensile stress and young's modulus is more evident in flax/epoxy composites than glass/epoxy composites with water aging. In a similar work, Yan et al. (2015) studied the influence of seawater treatment, water, and alkaline solution, on the tensile and flexural properties of bidirectional woven flax fiber reinforced epoxy composites. The weight gain vs. immersion time in the composites at different conditions for up to one year is shown in Fig. 3a. The composite showed a saturation effect after 8 months irrespective of the different test conditions. The weight gain is maximum for alkali-treated followed by water and seawater. The TS, tensile modulus (TM), flexural strength (FS), and flexural modulus (FM) of the composites drop after the aging studies. The drop in mechanical properties follows the order: alkali > seawater > water. This is because the degradation of the fiber-matrix interface is more in alkali-treated samples. Figure 3b shows the TS of control and aged (1 year) composites.

Maslinda et al. (2017) fabricated and studied the effect of water aging on the mechanical properties of individually woven, interwoven kenaf(K)/jute(J) and kenaf/hemp(H) fiber composites. For water absorption and water aging studies, the composites were immersed in tap water for 1400 h. The composites KK, JJ, and HH showed the highest water absorption. However, the interwoven hybrid composites showed lower water absorption. The results indicated that the interwoven fiber composites have better water resistance. From the mechanical data, the interwoven KJ and KH composites showed the best properties due to hybridization (before and after aging studies). However, upon water saturation, all the composites studied showed a drop in TS, TM, FS, and FM, while the tensile strain and flexural strain were increased. The drop in TS, FS, TM, and FM was due to the ingress of water molecules into the composite causing the debonding of fiber and matrix. On the other hand, the % strain was increased because of the plasticization of the polymer matrix caused by the water molecules.

Moudood et al. (2019) studied the environmental effects on the tensile and flexural properties of flax fiber/bioepoxy composites. The pure bioepoxy and flax composites were subjected to (i) immersion test (water saturation (WS)), (ii) humidity tests (humidity saturation (HS)), and (iii) freeze–thaw (F/T) cycle tests. The effects of WS, water-saturated completely dried (WSD), HS, F/T cycling, and water-saturated and freeze–thaw (WSF/T) cycling on the tensile and flexural properties were tested. The TS of the composite showed a marginal drop at different environmental conditions. However, the composites showed a major drop in young's modulus and an increase in strain at break, for WS, and WSF/T samples, due to the plasticization effect of water molecules present in the sample. Interestingly, the WSD samples showed Young's modulus and strain at break comparable to the "as manufactured composites. That means the softening and plasticization effect of water molecules disappear after the removal of water by drying. Similarly, the FS and FM of water-saturated samples showed the lowest values caused by the softening and plasticization due to the water molecules in bioepoxy/flax composites and showed a reversible trend after drying.

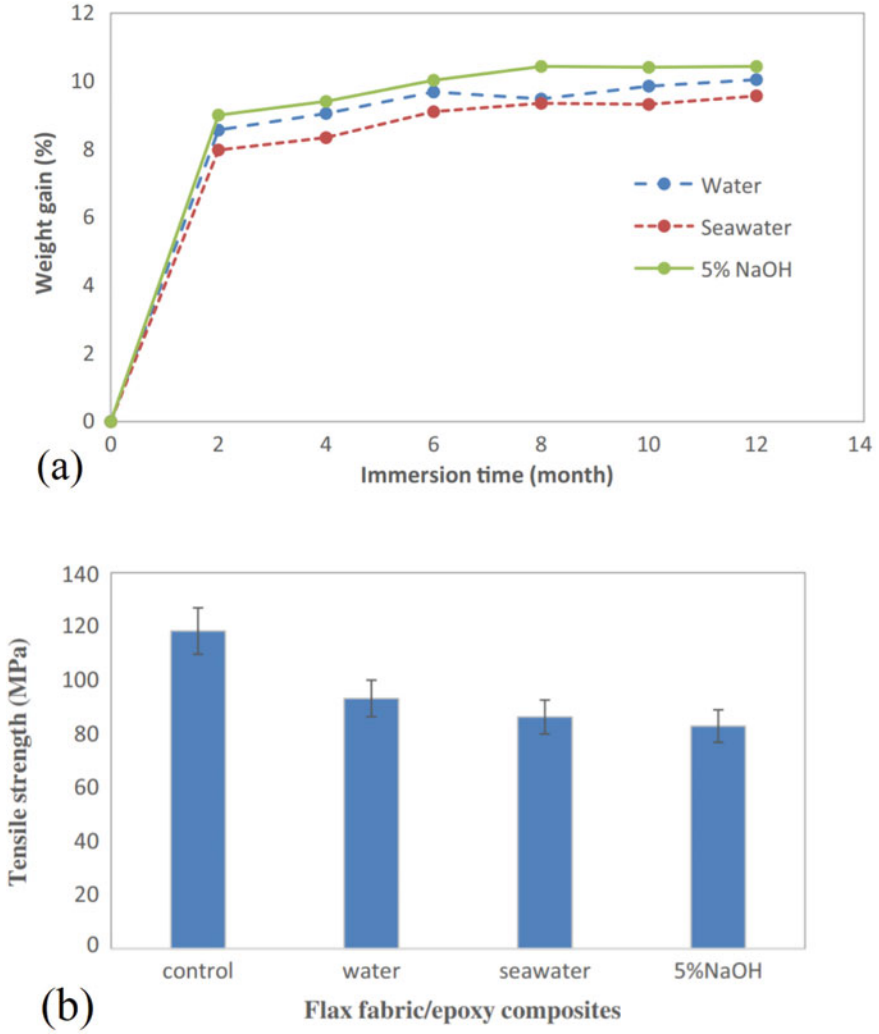


Fig. 3 **a** weight gain in the flax fabric/epoxy composites at different environmental conditions for 1 year, **b** TS of control and aged (1 year) composites (Yan and Chouw 2015) (Reproduced with thanks from Elsevier, License number: 5087570349325)

Thus, the results showed that the flax/bioepoxy composites are operational at most environmental conditions, excluding underwater applications.

Chaudhary et al. (2020) fabricated woven fabric-based epoxy composites. The woven fabrics such as jute, hemp, and flax fiber were used. The composites jute/epoxy, flax/epoxy, hemp/epoxy, jute/hemp/epoxy, hemp/flax/epoxy, jute/hemp/flax/epoxy were fabricated. The tensile and flexural properties of the composites, water-saturated for 1 year were taken. All the composites showed

a reduction in mechanical properties after water saturation. Among the various composites studied, flax/epoxy composite showed the minimum reduction in TS, TM, and FS, due to the better fiber/matrix adhesion. Thus, studies reported a drop in TS, FS, TM, and FM with water aging, however, Muñoz et al., (Muñoz and García-Manrique 2015) in an interesting working reported an improvement in TS and FS with water aging. The tensile and flexural properties of water immersed (water-saturated) flax fiber-reinforced bioepoxy composites and dry composites were studied by the researchers. The composites were prepared by RTM. The composites with 6-layer flax, and 8-layer flax corresponding to 40 vol% and 55 vol% respectively were prepared. The TS and % strain of composites with 40 and 55 vol% fiber after 768 h water immersion showed an increase. The increase in fiber volume also reported an increased TS. The FS of 40 vol% fiber-reinforced composites showed an increase after water immersion, but 55 vol% fiber-reinforced decrease after water immersion may due to the breakage of swallowed fibers during bending. The increase in the TS and FS of the samples was due to the swelling of the fibers which results in filling the gap between the fiber and epoxy interface.

2.2 Polybenzoxazine Composites

Zhang et al. (2021) examined the effect of water absorption of polybenzoxazine composites on the tensile and flexural properties. Three different composites were prepared, untreated bamboo modified polybenzoxazine, treated bamboo modified polybenzoxazine, and hybrid polybenzoxazine composites contain both treated bamboo/glass fibers. The water absorption test was carried out at 25 °C and 80 °C for 20 days. As expected, the water absorption is highest for the untreated bamboo modified polybenzoxazine, followed by treated bamboo modified polybenzoxazine, then hybrid polybenzoxazine composites contain both bamboo/glass fibers and the least for pure polybenzoxazine. This is because the untreated fibers have poor interaction with polymer, the treated fibers have good interaction with polymer matrix, and in the case of hybrid composites containing 15 wt% bamboo and 5 wt% water absorption is least due to the presence of hydrophobic glass fibers. The tensile and flexural properties of the dry and saturated composites were tested. All the samples prepared, shows a drop in TS, TM, FS, and FM with water aging. The drop is highest for the untreated composites followed by treated, and hybrid composites (depends on the fiber-matrix interaction). Also, the drop is highest at 80 °C for 20 days of aging due to the weakening of the fiber/matrix interface.

2.3 Polyester Composites

Dhakal et al. (2007) examined the effect of water aging on the tensile and flexural properties of unsaturated polyester/hemp fiber composites. The water aging test was

performed at RT and at 100 °C. The water uptake is more at 100 °C. At RT, the water absorption is based on Fickian behavior, and high temperature non-Fickian. The TS and FS of the composites were reduced after water aging at RT for 888 h, caused by the degradation of the fiber-matrix interface. Sugiman et al. (2021) studied the effect of nano $CaCO_3$ on the properties of bamboo fiber-modified polyester composites. The concentration of bamboo was fixed at 25 wt%, while that of nano $CaCO_3$ was 1, 3, and 5 wt.%. Water aging studies were carried out for up to 112 days at RT. The water uptake of the composite was reduced by approximately 16% with the incorporation of 3 wt.% nanofiller. The mechanical properties of unaged, aged samples were tested for the hybrid nanocomposites. The TS, elastic modulus, FS, FM, and impact strength (IS) were improved with the incorporation of nanofillers in the composites. The TS, FS, and IS are highest for 1wt.% nanofiller-based composites, and the drop in strength of the composites at higher filler content could be due to the agglomeration of the nanofillers. The water aging reduces the TS, FS, TM, and FM of the composites due to the debonding of the matrix from fiber caused by the deterioration of the fiber/matrix interface. However, it should be pointed that the drop in tensile and flexural properties for 112 days is comparable to 24 days of aging. These results point out that the degradation of the fiber/matrix interface is the greatest in the first 24 days of water aging. On the other hand, the IS increases with aging due to the debonding and fiber pull-out.

2.4 Vinyl Ester Composites

Almansour et al. (2017) fabricated vinyl ester/flax composites and flax/basalt reinforced vinyl ester hybrid composites (stitched and unstitched) were prepared. In flax reinforced vinyl ester composites six layers of flax fiber mat were used for the fabrication of the composites. On the other hand, in the hybrid composites of flax/basalt vinyl ester composites, four layers of flax fiber mat were placed inside and two layers of basalt were placed outside. The hybrid composites absorbed less water and also showed better FT in dry and wet conditions. In a similar work Živković et al. (2017) fabricated flax/vinyl ester composites, basalt/vinyl ester composites, and flax/basalt fiber reinforced vinyl ester hybrid composites and examined the effect of moisture uptake (saltwater) on the impact resistance. The researchers reported an increase in impact resistance for the statured composites.

2.5 Polypropylene Composites

Deng et al. (2010) studied the tensile properties of natural fiber mat reinforced PP (NMT) composites before and after water aging. The water aging was carried out at different water temperatures 20, 40, and 65 °C for 40 days. The 40 days aged samples at 65 °C were further frozen at −18 °C. The water absorption is highest at 65 °C.

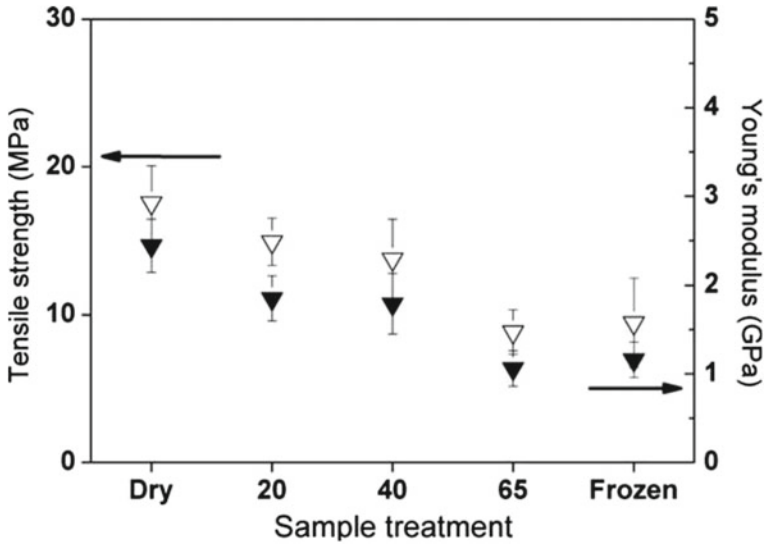


Fig. 4 TS and YM values of the dry NMT sample and treated NMT sample (40 days) at different water temperatures (20, 40, and 65 °C) (Deng et al. 2010) (Reproduced with thanks from Elsevier, License number: 5087570708086)

Compared to glass, natural fiber mat reinforced PP showed high water absorption. The TS and YM of the composites before and after aging were taken. The TS and YM values of the dry NMT sample and treated NMT sample (40 days) at different water temperatures (20, 40, and 65 °C) are shown in Fig. 4. The water-aged NMT composites have lower strength and modulus compared to the pure dry samples. Espert et al. (2004) studied the effect of water aging on the mechanical properties of PP and PP/EVA-based composites containing kraft cellulose fibers, sisal fibers, coir fibers, and luffa sponge fibers. The fiber content used was 10, 20, and 30 wt%. The composites were water aged at three different temperatures 23, 50, and 70 °C. The fiber content, temperature, and type of matrix have a significant impact on water absorption. The water absorption is more at higher fiber content. Also, the absorption or wetting of the composites is faster at higher aging temperature, or in other words, the saturation times is faster at higher temperatures. The TS, TM, and EB of the composites is reduced for the water-saturated samples due to the degradation caused by the fiber-matrix interface.

2.6 Geopolymer Composites

Alomayri et al. (2014) fabricated geopolymer composites (inorganic aluminosilicate polymers) based on cotton fabrics. The mechanical properties of the geopolymer were increased with the addition of cotton fabrics. The water absorption test was

performed at RT for 133 days. The water absorption rate of the composites increased with fabric content. This is because the cellulose is hydrophilic. The composites subjected to water absorption showed a drop in the mechanical properties, due to the hydrophilicity of the cellulose. The cellulose swelled and generate microcracks in the matrix, later it degrades resulting in a poor matrix-fiber interface.

2.7 Biodegradable Composites

Matveeva et al. (2000) studied the plasticizing effect of water molecules in biopolymers and formulated an equation to predict the glass transition temperature (T_g) of biopolymers. The T_g and plasticizing effect is important for food technology and bioscience. This is because the physical and mechanical properties of biopolymers depend on their T_g. Alvarez et al. (2004) fabricated polymer blends based on cellulose derivatives and starch. The blends were modified with 0 to 15 wt% short sisal fibers. The composites were further studied for the effect of moisture content on the mechanical properties. It was observed that the composites have higher moisture absorption compared to pure blend due to the presence of sisal fibers. The composite modulus at different moisture content and relative humidity were studied. The modulus showed a gradual drop with an increase in moisture content and relative humidity.

3 Conclusion

Biocomposites are increasingly preferred for advanced applications. However, the incorporation of natural fibers in the polymer matrix caused an increase in moisture uptake during the different operational conditions. The natural fiber-reinforced biocomposites showed a drop in mechanical properties with water aging. The fibers are hydrophilic, while most of the polymers are hydrophobic, this caused poor compatibility with the polymer matrix. The poor compatibility, voids, type of filler, type of polymer influence the diffusion of water into the polymer composite. At RT, the ingress of water through the natural fiber reinforced polymer composites mostly follows the Fickian model. The drop in mechanical properties is caused by the debonding of the fiber from the polymer matrix. The chemical and physical methods can remove the hydrophilic groups present in the natural fibers and hence the modified fibers can reduce the water uptake. The hybridization of synthetic fibers with natural fibers, and polymer coatings are also widely accepted methods to improve the performance of the composites at different external environmental conditions.

References

Abdel-Hakim A, El-Wakil AEAA, El-Mogy S, Halim S (2021) Effect of fiber coating on the mechanical performance, water absorption and biodegradability of sisal fiber/natural rubber composite. Polymer Int

Ahmed J, Mulla MZ, Vahora A, Bher A, Auras R (2021) Morphological, barrier and thermomechanical properties of high-pressure treated polylactide graphene oxide reinforced composite films. Food Packaging Shelf Life 29:100702

Akampumuza O, Wambua PM, Ahmed A, Li W, Qin XH (2017) Review of the applications of biocomposites in the automotive industry. Polym Compos 38(11):2553–2569

Alama MA, Sapuanb SM, Yaa HH, Hussaina PB, Azeema M, Ilyasb RA (2020) Application of biocomposites in automotive components: a review. Biocompos Synthetic Compos Autom Appl 1

Almansour FA, Dhakal HN, Zhang ZY (2017) Effect of water absorption on Mode I interlaminar fracture toughness of flax/basalt reinforced vinyl ester hybrid composites. Compos Struct 168:813–825

Alomayri T, Assaedi H, Shaikh FUA, Low IM (2014) Effect of water absorption on the mechanical properties of cotton fabric-reinforced geopolymer composites. J Asian Ceramic Soc 2(3):223–230

Alvarez VA, Fraga AN, Vazquez A (2004) Effects of the moisture and fiber content on the mechanical properties of biodegradable polymer–sisal fiber biocomposites. J Appl Polym Sci 91(6):4007–4016

Assarar M, Scida D, El Mahi A, Poilâne C, Ayad R (2011) Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: flax–fibres and glass–fibres. Mater Des 32(2):788–795

Azwa ZN, Yousif BF, Manalo AC, Karunasena W (2013) A review on the degradability of polymeric composites based on natural fibres. Mater Des 47:424–442

Bazan P, Nosal P, Kozub B, Kuciel S (2020) Biobased polyethylene hybrid composites with natural fiber: mechanical, thermal properties, and micromechanics. Materials 13(13):2967

Célino A, Fréour S, Jacquemin F, Casari P (2014) The hygroscopic behavior of plant fibers: a review. Front Chem 1:43

Chandrasekar M, Ishak MR, Sapuan SM, Leman Z, Jawaid M (2017) A review on the characterisation of natural fibres and their composites after alkali treatment and water absorption. Plast, Rubber Compos 46(3):119–136

Chaudhary V, Bajpai PK, Maheshwari S (2020) Effect of moisture absorption on the mechanical performance of natural fiber reinforced woven hybrid bio-composites. J Nat Fibers 17(1):84–100

Chen W, Yu H, Liu Y, Hai Y, Zhang M, Chen P (2011) Isolation and characterization of cellulose nanofibers from four plant cellulose fibers using a chemical-ultrasonic process. Cellulose 18(2):433–442

Chen W, Abe K, Uetani K, Yu H, Liu Y, Yano H (2014) Individual cotton cellulose nanofibers: pretreatment and fibrillation technique. Cellulose 21(3):1517–1528

de Arcaya PA, Retegi A, Arbelaiz A, Kenny JM, Mondragon I (2009) Mechanical properties of natural fibers/polyamides composites. Polym Compos 30(3):257–264

Deng H, Reynolds CT, Cabrera NO, Barkoula NM, Alcock B, Peijs T (2010) The water absorption behaviour of all-polypropylene composites and its effect on mechanical properties. Compos B Eng 41(4):268–275

Dhakal HN, Zhang ZA, Richardson MOW (2007) Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. Compos Sci Technol 67(7–8):1674–1683

Dominic CDM, Joseph R, Begum PMS, Kumar AS, Jeemol PA, Jose T, Padmanabhan D, Formela K, Siengchin S, Parameswaranpillai J, Saeb MR (2021) Cellulosic bionanocomposites based on acrylonitrile butadiene rubber and *Cuscuta reflexa*: adjusting structure-properties balance for higher performance. Cellulose

Espert A, Vilaplana F, Karlsson S (2004) Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties. Compos A Appl Sci Manuf 35(11):1267–1276

Fan M (2017) Future scope and intelligence of natural fibre based construction composites. In: Advanced high strength natural fibre composites in construction. Woodhead Publishing, pp 545–556

Ferreira FV, Pinheiro IF, Mariano M, Cividanes LS, Costa JC, Nascimento NR, Kimura SP, Neto JC, Lona LM (2019) Environmentally friendly polymer composites based on PBAT reinforced with natural fibers from the amazon forest. Polym Compos 40(8):3351–3360

Godara SS (2019) Effect of chemical modification of fiber surface on natural fiber composites: a review. Mater Today: Proc 18:3428–3434

Grace LR, Altan MC (2012) Characterization of anisotropic moisture absorption in polymeric composites using hindered diffusion model. Compos A Appl Sci Manuf 43(8):1187–1196

Haghdan S, Smith GD (2015) Natural fiber reinforced polyester composites: a literature review. J Reinf Plast Compos 34(14):1179–1190

Hasan KM, Horváth PG, Alpár T (2020) Potential natural fiber polymeric nanobiocomposites: a review. Polymers 12(5):1072

Hassan A, Khan R, Khan N, Aamir M, Pimenov DY, Giasin K (2021) Effect of seawater ageing on fracture toughness of stitched glass fiber/epoxy laminates for marine applications. J Marine Sci Eng 9(2):196

Hossain SI, Hasan M, Hasan MN, Hassan A (2013) Effect of chemical treatment on physical, mechanical and thermal properties of ladies finger natural fiber. Adv Mater Sci Eng

Ilyas RA, Sapuan SM, Norizan MN, Atikah MSN, Huzaifah MRM, Radzi AM, Ishak MR, Zainudin ES, Izwan S, Azammi AN Jumaidin R (2019) Potential of natural fibre composites for transport industry: a review. In: Prosiding Seminar Enau Kebangsaan, vol 2019, pp 2–11

Jonoobi M, Oladi R, Davoudpour Y, Oksman K, Dufresne A, Hamzeh Y, Davoodi R (2015) Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: a review. Cellulose 22(2):935–969

Kabir MM, Wang H, Lau KT, Cardona F (2013) Effects of chemical treatments on hemp fibre structure. Appl Surf Sci 276:13–23

Kabir MM, Wang H, Cardona F, Aravinthan T (2010) Effect of chemical treatment on the mechanical and thermal properties of hemp fibre reinforced thermoset sandwich composites. Incorp Sustain Practice Mech Struct Mater 439–444

Kim HJ, Seo DW (2006) Effect of water absorption fatigue on mechanical properties of sisal textile-reinforced composites. Int J Fatigue 28(10):1307–1314

Kim SJ, Moon JB, Kim GH, Ha CS (2008) Mechanical properties of polypropylene/natural fiber composites: comparison of wood fiber and cotton fiber. Polym Testing 27(7):801–806

Kumar R, Singh R (2020) Processing of conducting polymers for sensors applications: a state of art review and future applications. https://doi.org/10.1016/B978-0-12-820352-1.00019-5

Mahmud S, Hasan KF, Jahid MA, Mohiuddin K, Zhang R, Zhu J (2021) Comprehensive review on plant fiber-reinforced polymeric biocomposites. J Mater Sci 1–34

Maslinda AB, Majid MA, Ridzuan MJM, Afendi M, Gibson AG (2017) Effect of water absorption on the mechanical properties of hybrid interwoven cellulosic-cellulosic fibre reinforced epoxy composites. Compos Struct 167:227–237

Masoodi R, Pillai KM (2012) A study on moisture absorption and swelling in bio-based jute-epoxy composites. J Reinf Plast Compos 31(5):285–294

Matveev YI, Grinberg VY, Tolstoguzov VB (2000) The plasticizing effect of water on proteins, polysaccharides and their mixtures. Glassy state of biopolymers, food and seeds. Food Hydrocolloids 14(5):425–437

Mohd Nurazzi N, Khalina A, Sapuan SM, Dayang Laila AHAM, Rahmah M, Hanafee Z (2017) A review: fibres, polymer matrices and composites. Pertanika J Sci Technol 25(4)

Mokhothu TH, John MJ (2017) Bio-based coatings for reducing water sorption in natural fibre reinforced composites. Sci Rep 7(1):1–8

Moudood A, Rahman A, Khanlou HM, Hall W, Öchsner A, Francucci G (2019) Environmental effects on the durability and the mechanical performance of flax fiber/bio-epoxy composites. Compos B Eng 171:284–293

Mukhopadhyay S, Fangueiro R (2009) Physical modification of natural fibers and thermoplastic films for composites—a review. J Thermoplast Compos Mater 22(2):135–162

Muñoz E, García-Manrique JA (2015) Water absorption behaviour and its effect on the mechanical properties of flax fibre reinforced bioepoxy composites. Int J Polymer Sci

Namvar F, Jawaid M, Tanir PM, Mohamad R, Azizi S, Khodavandi A, Rahman HS, Nayeri MD (2014) Potential use of plant fibres and their composites for biomedical applications. BioResources 9(3):5688–5706

Oksman K, Skrifvars M, Selin JF (2003) Natural fibres as reinforcement in polylactic acid (PLA) composites. Compos Sci Technol 63(9):1317–1324

Peças P, Carvalho H, Salman H, Leite M (2018) Natural fibre composites and their applications: a review. J Compos Sci 2(4):66

Pothan LA, Thomas S (2004) Effect of hybridization and chemical modification on the water-absorption behavior of banana fiber–reinforced polyester composites. J Appl Polym Sci 91(6):3856–3865

Radoor S, Karayil J, Rangappa SM, Siengchin S, Parameswaranpillai J (2020) A review on the extraction of pineapple, sisal and abaca fibers and their use as reinforcement in polymer matrix. Express Polymer Lett 14(4):309–335

Radoor S, Karayil J, Jayakumar A, Parameswaranpillai J, Siengchin S (2021) An efficient removal of malachite green dye from aqueous environment using ZSM-5 zeolite/polyvinyl alcohol/carboxymethyl cellulose/sodium alginate bio composite. J Polymers Environ 1–14

Rangappa SM, Parameswaranpillai J, Yorseng K, Pulikkalparambil H, Siengchin S (2021) Toughened bioepoxy blends and composites based on poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) triblock copolymer and sisal fiber fabrics: a new approach. Construct Build Mater 271:121843

Rojas-Lema S, Ivorra-Martinez J, Lascano D, Garcia-Garcia D, Balart R (2021) Improved performance of environmentally friendly blends of biobased polyethylene and kraft lignin compatibilized by reactive extrusion with dicumyl peroxide. Macromol Mater Eng 2100196

Sanjay MR, Siengchin S, Parameswaranpillai J, Jawaid M, Pruncu CI, Khan A (2019) A comprehensive review of techniques for natural fibers as reinforcement in composites: preparation, processing and characterization. Carbohyd Polym 207:108–121

Senthilkumar K, Ungtrakul T, Chandrasekar M, Kumar TSM, Rajini N, Siengchin S, Pulikkalparambil H, Parameswaranpillai J, Ayrilmis N (2021) Performance of sisal/hemp bio-based epoxy composites under accelerated weathering. J Polym Environ 29(2):624–636

Senthilkumar K, Chandrasekar M, Rajini N, Siengchin S, Rajulu V (2019) Characterization, thermal and dynamic mechanical properties of poly (propylene carbonate) lignocellulosic Cocos nucifera shell particulate biocomposites. Mater Res Express 6(9):096426

Sugiman S, Setyawan PD, Maryudi M, Madnasri S (2021) Water absorption, tensile, flexural and impact properties of aged bamboo fibre/nano $CaCO_3$-modified unsaturated polyester composites. J Appl Sci Eng 24(2):239–251

Sun Q, Zhou G, Meng Z, Jain M, Su X (2021) An integrated computational materials engineering framework to analyze the failure behaviors of carbon fiber reinforced polymer composites for lightweight vehicle applications. Compos Sci Technol 202:108560

Syduzzaman M, Al Faruque MA, Bilisik K, Naebe M (2020) Plant-based natural fibre reinforced composites: a review on fabrication, properties and applications. Coatings 10(10):973

Tajuddin M, Ahmad Z, Ismail H (2016) A review of natural fibers and processing operations for the production of binderless boards. BioResources 11(2):5600–5617

Thomas SK, Begum PS, Midhun Dominic CD, Salim NV, Hameed N, Rangappa SM, Siengchin S, Parameswaranpillai J (2021) Isolation and characterization of cellulose nanowhiskers from Acacia caesia plant. J Appl Polym Sci 138(15):50213

Thomas SK, Parameswaranpillai J, Krishnasamy S, Begam PS, Nandi D, Siengchin S, George JJ, Hameed N, Salim NV, Sienkiewicz N (2021) A comprehensive review on cellulose, chitin, and starch as fillers in natural rubber biocomposites. Carbohydrate Polym Technol Appl 100095
Thomas SK, Parameswaranpillai J, Krishnasamy S, Begam PS, Nandi D, Siengchin S, George JJ, Hameed N, Salim NV, Sienkiewicz N (2021) A comprehensive review on cellulose, chitin, and starch as fillers in natural rubber biocomposites. Carbohydrate Polym Technol Appl 100095
Thyavihalli Girijappa YG, Mavinkere Rangappa S, Parameswaranpillai J, Siengchin S (2019) Natural fibers as sustainable and renewable resource for development of eco-friendly composites: a comprehensive review. Front Mater 6:226

Varghese SA, Siengchin S, Parameswaranpillai J (2020) Essential oils as antimicrobial agents in biopolymer-based food packaging-A comprehensive review. Food Biosci 100785

Vinod A, Sanjay MR, Suchart S, Jyotishkumar P (2020) Renewable and sustainable biobased materials: an assessment on biofibers, biofilms, biopolymers and biocomposites. J Cleaner Prod 258:120978

Wahit MU, Akos NI, Laftah WA (2012) Influence of natural fibers on the mechanical properties and biodegradation of poly (lactic acid) and poly (ε-caprolactone) composites: a review. Polym Compos 33(7):1045–1053

Yan L, Chouw N (2015) Effect of water, seawater and alkaline solution ageing on mechanical properties of flax fabric/epoxy composites used for civil engineering applications. Constr Build Mater 99:118–127

Zhang K, Liang W, Wang F, Wang Z (2021) Effect of water absorption on the mechanical properties of bamboo/glass-reinforced polybenzoxazine hybrid composite. Polym Polym Compos 29(1):3–14

Živković I, Fragassa C, Pavlović A, Brugo T (2017) Influence of moisture absorption on the impact properties of flax, basalt and hybrid flax/basalt fiber reinforced green composites. Compos B Eng 111:148–164

Zwawi M (2021) A review on natural fiber bio-composites; surface modifications and applications. Molecules 26(2):404

Effect of Compatibilizer on the Aging and Degradation Mechanism of the Natural Fiber-Reinforced Thermoplastic Composites

C. Ganesan, M. Chandrasekar, M. S. Nisha, and S. Subha

Abstract Natural fiber-reinforced composites have received significant attention in recent years due to their distinct properties which include reduced carbon dioxide emission, lightweight, reduced tool wear, etc. This chapter provides an outline of the influence of different compatibilizers on the aging characteristics and degradation mechanisms of the natural fiber reinforced thermoplastic composites. Different compatibilization techniques and their effect on various properties which include mechanical, thermal, hygrothermal, chemical has been discussed. It was found that the Compatibilizers play a major role in improving interfacial characteristics and their performance will be decided by the miscibility of its components. The severity of degradation under hygrothermal aging will be lower for composites with compatibilizers and helps in retaining mechanical and thermal properties.

Keywords Compatibilizer · Thermoplastics · Natural fibres · Aging

1 Introduction

Fiber reinforced composites play a substantial role in recent decades in replacing the usage of traditional materials in various industries ranging from aerospace to sports equipments. Even though advanced fibers such as glass, carbon, aramid, etc. exhibit better properties, replacing them with an eco-friendly alternative such as natural fiber has been under investigation for the past few decades. In particular, the use of lignocellulosic fibers as reinforcement in the polymer matrix has benefits such as improved specific strength and specific modulus (Chattopadhyay et al. 2011; Atiqah et al. 2020). The natural fibers are biodegradable which can be obtained

C. Ganesan (✉)
Amity Institute of Aerospace Engineering, Amity University, Noida, Uttar Pradesh 201301, India

M. Chandrasekar · M. S. Nisha · S. Subha
Department of Aeronautical Engineering, Hindustan Institute of Technology and Science, Chennai 603103, India

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_4

from renewable sources, and they are abundant in nature and cost-effective as well (Dissanayake et al. 2009; Senthilkumar et al. 2021).

Plant fiber-based composites that have found industrial applications are based on sisal (Huber et al. 2012; Senthilkumar et al. 2020), kenaf (Ochi 2008), bamboo (Deshpande et al. 2000), flax (De Prez et al. 2018; Shahroze et al. 2021) and hemp (Beaugrand and Berzin 2013). Scientists from different countries have developed different natural fibers for applications in automobile parts and other industries (Sun 2018). These applications were further extended to insulation materials such as blowing insulation, for ceiling panels that act as a thermal insulator, sound insulation material and acoustic soundproof (Müssig 2010).

Degradation of bio composite material due to the hydrophilic nature of the natural fiber under various environmental conditions such as temperature, moisture, humidity, various microorganisms, radiations can affect the performance and load-carrying capability of these composites (Tokiwa et al. 2009; Krishnasamy et al. 2019). This drawback can be overcome by the addition of a compatibilizer in thermoplastic-based composites. The upcoming sections focus on explaining the theory of compatibilization and the response of various natural fiber reinforced thermoplastic composites to aging conditions.

2 Theory of Compatibilization

The process of transforming a multiphase polymer solution into a commercially viable component is known as compatibilization. In principle, if a molecule contains a part that is soluble in one phase whilst the other is soluble in the other, it will act as a compatibilizer. As a result, the compatibilizer would be positioned around the interface which minimizes interfacial tension between materials and allows smoother dispersion while blending them with a thermoplastic matrix. Hence, this characteristic provides a degree of stability and leads to improved interfacial bonding (Ajitha and Thomas 2020). The compatibilizers can be classified into non-reactive and reactive types as discussed below.

2.1 Non-reactive Compatibilizers

Compatibilizers of the form AB copolymers are most widely used in this process for immiscible blends of polymer A and polymer B. A further choice is to use a copolymer composed of segments with distinct connections or solubility with one or more of the ingredients. The miscibility of a compatibilizer's corresponding blocks or components in each phase, as well as the compatibilizer's molecular weight, decides its performance. When a compatibilizer is inserted into an immiscible blend, it may switch to the interface between the components, allowing one end of the compatibilizer to connect with one part of the blend while the other end interacts with

the other part of the blend. This behavior of compatibilizers aid in the reduction of scattered phase proportions, thus strengthening the blend composition and enhancing polymeric adhesion with the reinforcement.

2.2 Reactive Compatibilization

Another kind of compatibilization is reactive compatibilization, which occurs when copolymers react in situ to form a solid interface. During the reactive compatibilization process, a copolymer spontaneously forms at the interface between two insoluble polymers, where it is required to regulate morphology. Reactive compatibilization includes many reactions such as (a) transreactions, (b) Reactive graft, block, or lightly cross-linked copolymer formation, (c) ionically bound structure formation and (d) mechanical and chemical mixing. The above-mentioned mechanisms can result in chain breakage and recombination, resulting in copolymer formation. Another effective technique for immiscible blend compatibilization is the use of nanofillers (Saleem and Baker 1990; Markham 1990; Xanthos and Dagli 1991; Song and Baker 1992; Liu et al. 1993; Utracki 2002; Brown 2003).

2.3 Mechanical and Thermal Properties

Hydroxyl and other polar groups in the natural fibers which makes them hydrophilic in are the principal cause of weak wear resistance between the polymer matrix and the fiber. Since the hydrophilic fractions of the fibers have a free hydroxyl group, they have poor wetting characteristics with the hydrophobic matrix, leading to inferior performance of the composites under various mechanical loads (Wu 2009). However, the efficiency of natural fiber composites can be enhanced by the use of compatibilizers and binding agents.

Malleated polypropylene (MAPP) was used to enhance the compatibility between kenaf fiber reinforcement and matrix which improve the impact strength significantly. Because of improved adhesion between fiber and polymer molecules, the crystallization was slower which resulted in reduced crystalline temperature and reduced crystallity for higher molecular weight blends and vice versa for lower molecular weight blends. Because of the improved stress transfer interface caused by the stronger possible covalent bonding between the anhydride group and the hydroxyl groups of the kenaf, MAPP, and PP, the failure strain and tensile strength were higher than the composite without MAPP.

Wu reported that acrylic acid grafted polylactic acid (AA-g-PLA) reinforced with sisal fiber (SF) demonstrated higher tensile strength, durability, and lesser biodegradability than PLA/SF due to the better compatibility between SF and PLA. Maleic anhydride grafted PLA/coir fiber-based composites yielded comparatively better performance than the PLA/coir-based composites (Wu 2009). After exposing the

composites to the bacteria named *Burkholderia cepacia*, it was discovered that the biodegradation intensity of PLA-g-MA/coir was higher than PLA but lower than PLA/coir while the biodegradability improved with the increment in coir fiber wt%. After 21 days, the weight loss percentages of PLA, PLA/coir, and PLA-g-MA/coir is approximately 15, 80, and 75%, respectively.

The temperature modulus, softening temperature and creep properties were improved due to the improved adhesion between the polypropylene matrix and kenaf due to the addition of MAPP (Feng et al. 2001). Thermoplastic elastomer (TPNR) has many advantages in properties like elasticity, damping, characteristics and thermal stability. TPNR is a combination of natural rubber and thermoplastic that can be used for applications including household appliances and automotive parts (Tanrattanakul and Bunkaew 2014; Bhattacharya et al. 2020). Because of the strong chemical interaction between the phases, properties such as tensile strength, hardness, elongation at break, and tear strength were substantially improved when MNR, NR-g-PMMA, and ENR-50 were used as compatibilizers. "The TPNR with ENR-50 and MNR as compatibilizers demonstrated a higher enticing force due to the presence of epoxide and anhydride groups in the ENR and MNR molecules as they interacted with the PBAT molecule" (Kalkornsurapranee et al. 2020).

3 Degradation

3.1 Chemical Degradation

When polymers/fibers are exposed to chemicals such as acids, bases, solvents, and other chemicals, chemical oxidation occurs.

3.2 Thermal Degradation

Thermal degradation is the decay of a polymer's molecular structure caused by temperature change. This happens at the melting temperature of thermoplastic polymers, as the state of the polymer is shifted from solid to liquid. The polymer backbone chain components detach and react with one another, modifying the polymer's properties.

3.3 Mechanical Degradation

Mechanical degradation refers to the macroscopic changes that happen in polymer materials as a outcome of compression, stress, and shear forces.

3.4 Photodegradation

Photodegradation happens as polymers undergo physical and chemical modifications as a result of ultraviolet or visible light exposure, causing Norrish and/or crosslinking reactions.

3.5 Hygrothermal Degradation

Hygrothermal deterioration refers to the significant loss of a material's weight and mechanical properties caused by moisture and temperature (Balakrishnan et al. 2011).

4 Aging Effects

Inácio et al. (2018) investigated the effect of maleic anhydride grafted polypropylene on the physical and mechanical properties of the bamboo/recycled talc/ethylene-propylene-diene monomer composites subjected to aging in a hot air chamber at 90 °C for 7 days. From their results, it can be observed that the addition of MAPP had an encouraging effect on the tensile strength, fatigue life and flexural properties while the impact energy, tensile modulus and strain at break from the tensile test showed a decreasing trend for the aged composite specimens. The reduction in impact energy was believed to be due to the weakening of the bond between the polymeric chains and the compatibilizer. Furthermore, incorporation of MAPP resulted in a marginal increase in thermal degradation temperature of the aged composites as indicated from their TGA results (Inácio et al. 2018).

Pinewood waste/Low-density polyethylene scrap waste-based composites incorporated with 2.5 wt% of maleic anhydride grafted polyethylene were subjected to accelerated weathering for 48, 168, 672, 720, 1344 and 4032 h. Their results indicate that deterioration in modulus of elasticity, ultimate tensile strength and elongation deteriorated at 4032 h compared to 720 h for the pure polymer without the reinforcement. The decline in tensile properties under the accelerated aging was caused by the formation of microcracks in the aged specimens due to the residual stress generated within the polymer and chemical changes within the polymer due to aging. The pinewood fibers in the composite absorbed the incident UV irradiation such that the severity on the composite due to aging was lower compared to the pure polymer (Moreno et al. 2018).

Badji et al. investigated the effects of natural weathering under climatic conditions and natural weathering under glass by subjecting the hemp/PP/MAPP in proportions of 10/87.3/2.7 and 30/67.1/2.1 in terms of wt% for 12 months. According to them, Young's modulus decreased with the aging time for both the pure polymer and composite specimens. However, composites exhibited superior elastic modulus

over the pure polymer irrespective of aging since hemp fibers imparted stiffening effect to the composite. Among the aging type, the composite specimens exposed to glass weathering showed more variation in elastic modulus than the naturally weathered specimens. The composites reinforced with hemp fibers showed yellowing due to aging over the pure PP which was also confirmed by the higher value of lightness evolution measured for composites than the pure PP. Higher color variation in composites was mainly due to oxidation occurring in hemp fiber exposed to weathering. Lightness evolution reached saturation and remained constant after 9 and 12 months of exposure under natural weathering and under glass weathering. This is due to the formation of holocellulose on the fiber surface over the increased exposure time. The composites exposed to natural weather under climatic conditions exhibited microcracks as well as hollow spots indicating fiber removal compared to the microcracks in the exposure time. Moreover, average surface roughness increased with the exposure time for the weathered specimens and the surface roughness values were comparatively higher for naturally weathered specimens than the under glass weathering (Badji et al. 2018).

Hydrothermal aging characteristics of the sisal/polylactide composites incorporated with 2.5 wt% maleic anhydrides (MAH) and 0.3 wt% of dicumyl peroxide (DCP) was investigated by immersing the composite specimens in 65, 75 and 85 °C hot water until saturation. The composites added with MAH and DCP had a smooth surface (Fig. 1b) compared to the rough surface for the control specimen without the compatibilizer (Fig. 1a). The composites incorporated with MAH and DCP also showed reduced water uptake. The severity of the degradation under hydrothermal aging was lower for the composites incorporated with compatibilizer (Fig. 1d) as could be noted from the lesser number of microcracks over the composites without compatibilizer (Fig. 1c) (Gil-Castell et al. 2014).

Hamour et al. exposed acetylated alfa fiber/PP composites added with 5 wt% MAH to hydrothermal aging at a temperature of 65 °C under a relative humidity of 75% up to 1000 h. Both the onset temperature and residue % obtained from the thermogravimetric analysis was found to decline for the aged specimens. Similarly, crystallinity index (CI) calculated from the X-ray diffraction spectra and young's modulus also decreased for the aged specimens compared to the pristine. The drop in CI was believed to be due to the chain scission which can lead to reduced molecular weight representing an increase in the rigidity of the polymer while the decrease in modulus of elasticity was caused by the plasticization effect of MAH. The plasticization effect for aged composites with MAH was also visible from the lower storage modulus obtained from the dynamic mechanical analysis (Hamour et al. 2015).

Hemp/high-density polyethylene (HDPE) composites added with MAH grafted polyethylene were exposed to water aging and accelerated aging (moisture, temperature and UV radiation). The composite specimens exposed to accelerated aging showed higher tensile strength and modulus of elasticity than the unexposed specimens. In the case of the water aging, the ultimate tensile strength of the composite did not change much while there was a drop in young's modulus. The fiber/matrix interface was severely affected for water aging despite the occurrence of coupling

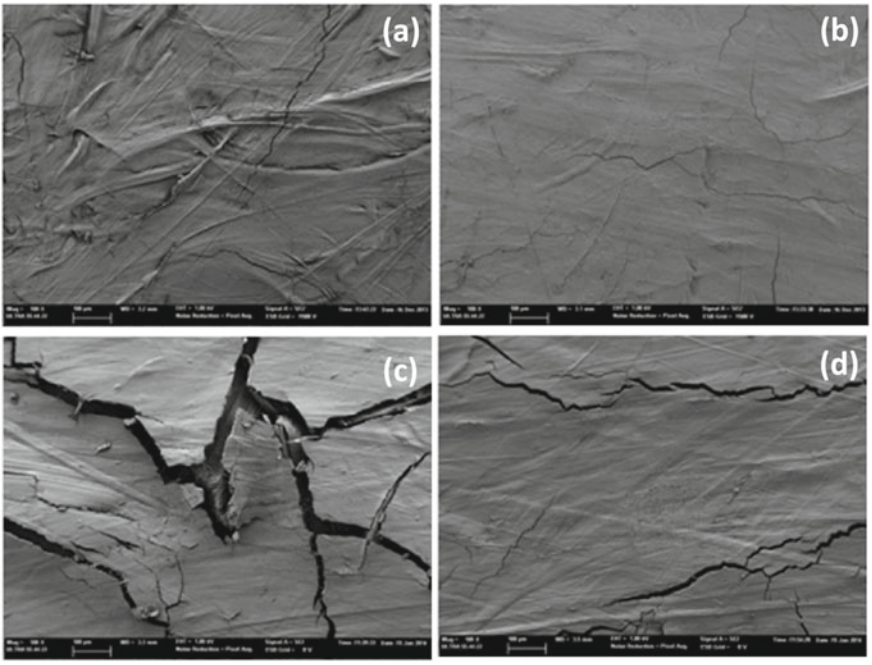


Fig. 1 Sisal/polylactide composites **a** Smooth surface on dry specimen without compatibilizer, **b** Rough surface on the dry specimen incorporated with MAH and DCP, **c** Microcracks in hydrothermally aged specimens without compatibilizer and **d** Microcracks in hydrothermally aged specimens with MAH and DCP (Re-used with permission from Elsevier, License number 5053070771941) (Gil-Castell et al. 2014)

agent compared to the accelerated aging in which the fiber/matrix interface remained intact due to the presence of coupling agent (Sergi et al. 2019).

According to Fajardo et al., Bamboo/PP composites infused with 3 wt% MAPP and 3 wt% of citric acid exhibited better thermal stability and a lower drop in tensile properties than the composites without compatibilizer exposed to the natural climatic weathering for 1 year. The increased retention in tensile properties for composites with MAPP and citric acid is mainly due to the better compatibility between the fiber and matrix (Fajardo Cabrera de Lima et al. 2020). In their study by Bajwa et al., oak wood fiber/cotton burr and stem/guayule bagasse reinforced HDPE with 1 wt% MAPE were exposed to accelerated weathering under UV irradiation and condensation cycles for 2200 h. Flexural strength, flexural rigidity and impact strength were found to decrease while the compressive strength improved for the aged specimens. However, the addition of MAPE helped retain the mechanical properties better than the composites without MAPE. The degradation in the fiber-matrix interface was lower due to the occurrence of coupling agent according to the study (Bajwa et al. 2015).

5 Applications

Natural fiber-reinforced composites are in higher demand for various applications that concern environmental sustainability. The market growth of natural fiber composites from 2014 to 2020 is almost 28% (Rwawiire et al. 2015). The automobile product such as door panels, roof, seat backboard, dashboard and trunks are being manufactured using natural fiber-reinforced composites. According to this literature (Liu and Dai 2007), the annual requirement for natural fibers exceeds 45,000 tons every year. The major reason for using natural fiber for the automobile is their biodegradability and easier recycling of material (Wilson 2017). According to the European community's 2000/53/EC "End of life vehicles" program, 95% of automobile products must be recyclable. Similarly, the Japanese government has also recommended that 95% of automobile products should be recyclable (Sun 2018). All automobile manufacture should comply with this requirement to sustain themselves in the market.

A product like outdoor bed boards, park benches, fences, indoor decors and building templates are manufactured based on wood-plastic composite. Such applications are produced on large scale by China-based manufactures and later, many countries like North America, Germany and India have elevated the production of natural fiber-reinforced composites (Dammer et al. 2017). Besides that, natural fibers have applications in storage and transportation containers, office and household goods.

6 Conclusion

Compatibilization in the natural fiber composites plays a fine role in improving their properties particularly the interfacial characteristics in addition to their positive contribution in improving the quality of the environment. This chapter discussed numerous compatibilization techniques and their effects on mechanical, thermal, hygrothermal, and chemical properties. Some of the important findings are summarised as follows.

- Compatibilizer allows smoother dispersion while blending with a thermoplastic matrix and provides a degree of stability which leads to improved interfacial bonding.
- The compatibilizer's performance will be decided by the miscibility of its corresponding components in each phase, as well as its molecular weight.
- The principal cause of poor wear resistance between the polymer matrix and the fiber is the Hydroxyl and the other polar groups present in the natural fibers which makes them hydrophilic.
- Composite with MAPP has higher failure strain and tensile strength than the composite without MAPP due to the improved stress transfer interface caused by the stronger possible covalent bonding between the anhydride group and the hydroxyl groups of the kenaf, MAPP, and PP.

- The temperature modulus, softening temperature and creep properties were improved due to the improved adhesion between the polypropylene matrix and kenaf due to the addition of MAPP.
- The incorporation of MAPP resulted in a marginal increase in thermal degradation temperature of the aged composites.
- The severity of the degradation under hydrothermal aging was lower for the composites incorporated with compatibilizer over the composites without compatibilizer
- Flexural strength, flexural rigidity and impact strength were found to decrease while the compressive strength improved for the aged specimens. However, the addition of MAPE helped retain the mechanical properties better than the composites without MAPE

Recent developments in natural fibers with compatibilizers can be used in a variety of industries, including biomedicine, agriculture, aerospace, manufacturing, automotive, construction and electrical applications. Many natural-based fibers can be designed to have enhanced mechanical and thermal properties, as well as to be deliberately or accidentally degraded under suitable environmental conditions.

References

Ajitha AR, Thomas S (2020) Introduction. In: Compatibilization of polymer blends. Elsevier, pp 1–29

Atiqah A, Chandrasekar M, Senthil Muthu Kumar T, et al (2020) Characterization and interface of natural and synthetic hybrid composites. In: Encyclopedia of renewable and sustainable materials. Elsevier, pp 389–400

Badji C, Beigbeder J, Garay H et al (2018) Exterior and under glass natural weathering of hemp fibers reinforced polypropylene biocomposites: impact on mechanical, chemical, microstructural and visual aspect properties. Polym Degrad Stab 148:104–116

Bajwa DS, Bajwa SG, Holt GA (2015) Impact of biofibers and coupling agents on the weathering characteristics of composites. Polym Degrad Stab 120:212–219

Balakrishnan H, Hassan A, Imran M, Wahit MU (2011) Aging of toughened polylactic acid nanocomposites: water absorption, hygrothermal degradation and soil burial analysis. J Polym Environ 19:863–875. https://doi.org/10.1007/s10924-011-0338-9

Beaugrand J, Berzin F (2013) Lignocellulosic fiber reinforced composites: influence of compounding conditions on defibrization and mechanical properties. J Appl Polym Sci 128:1227–1238. https://doi.org/10.1002/app.38468

Bhattacharya AB, Chatterjee T, Naskar K (2020) Automotive applications of thermoplastic vulcanizates. J Appl Polym Sci 137:49181. https://doi.org/10.1002/app.49181

Brown SB (2003) Reactive compatibilization of polymer blends. In: Utracki LA (ed) Polymer blends handbook. Springer, Netherlands, Dordrecht, pp 339–415

Fajardo Cabrera de Lima L del P, Santana RMC, Chamorro Rodríguez CD (2020) Influence of coupling agent in mechanical, physical and thermal properties of polypropylene/bamboo fiber composites: under natural outdoor aging. Polymers 12:929

Chattopadhyay SK, Khandal RK, Uppaluri R, Ghoshal AK (2011) Bamboo fiber reinforced polypropylene composites and their mechanical, thermal, and morphological properties. J Appl Polym Sci 119:1619–1626. https://doi.org/10.1002/app.32826

Dammer L, Carus M, Iffland K et al (2017) Current situation and trends of thebio-based industries in Europe with a focus on bio-based materials. Nova Institute, Germany

De Prez J, Van Vuure AW, Ivens J et al (2018) Enzymatic treatment of flax for use in composites. Biotechnol Rep 20:e00294. https://doi.org/10.1016/j.btre.2018.e00294

Deshpande AP, Bhaskar Rao M, Lakshmana Rao C (2000) Extraction of bamboo fibers and their use as reinforcement in polymeric composites. J Appl Polym Sci 76:83–92. https://doi.org/10.1002/(SICI)1097-4628(20000404)76:1%3c83::AID-APP11%3e3.0.CO;2-L

Dissanayake NPJ, Summerscales J, Grove SM, Singh MM (2009) Life cycle impact assessment of flax fibre for the reinforcement of composites. J Biobased Mat Bioenergy 3:245–248. https://doi.org/10.1166/jbmb.2009.1029

Feng D, Caulfield DF, Sanadi AR (2001) Effect of compatibilizer on the structure-property relationships of kenaf-fiber/polypropylene composites. Polym Compos 22:506–517. https://doi.org/10.1002/pc.10555

Gil-Castell O, Badia JD, Kittikorn T et al (2014) Hydrothermal ageing of polylactide/sisal biocomposites. Studies of water absorption behaviour and physico-chemical performance. Polym Degrad Stab 108:212–222

Hamour N, Boukerrou A, Djidjelli H, et al (2015) Effects of MAPP compatibilization and acetylation treatment followed by hydrothermal aging on polypropylene alfa fiber composites. Int J Polym Sci

Huber T, Müssig J, Curnow O et al (2012) A critical review of all-cellulose composites. J Mater Sci 47:1171–1186. https://doi.org/10.1007/s10853-011-5774-3

Inácio ALN, Nonato RC, Bonse BC (2018) Mechanical and thermal behavior of aged composites of recycled PP/EPDM/talc reinforced with bamboo fiber. Polym Testing 72:357–363. https://doi.org/10.1016/j.polymertesting.2018.10.035

Kalkornsurapranee E, Koedthip D, Songtipya P et al (2020) Influence of modified natural rubbers as compatibilizers on the properties of flexible food contact materials based on NR/PBAT blends. Mater Des 196:109134. https://doi.org/10.1016/j.matdes.2020.109134

Krishnasamy S, Thiagamani SMK, Muthukumar C et al (2019) Effects of stacking sequences on static, dynamic mechanical and thermal properties of completely biodegradable green epoxy hybrid composites. Mater Res Express 6:105351. https://doi.org/10.1088/2053-1591/ab3ec7

Liu XY, Dai GC (2007) Surface modification and micromechanical properties of jute fiber mat reinforced polypropylene composites. Express Polym Lett 1:299–307. https://doi.org/10.3144/expresspolymlett.2007.43

Liu NC, Xie HQ, Baker WE (1993) Comparison of the effectiveness of different basic functional groups for the reactive compatibilization of polymer blends. Polymer 34:4680–4687. https://doi.org/10.1016/0032-3861(93)90701-B

Markham RL (1990) Introduction to compatibilization of polymer blends. Adv Polym Technol 10:231–236. https://doi.org/10.1002/adv.1990.060100307

Moreno DDP, Hirayama D, Saron C (2018) Accelerated aging of pine wood waste/recycled LDPE composite. Polym Degrad Stab 149:39–44

Müssig J (ed) (2010) Industrial applications of natural fibres: structure, properties and technical applications. Wiley, Chichester, UK

Ochi S (2008) Mechanical properties of kenaf fibers and kenaf/PLA composites. Mech Mater 40:446–452. https://doi.org/10.1016/j.mechmat.2007.10.006

Rwawiire S, Tomkova B, Militky J et al (2015) Development of a biocomposite based on green epoxy polymer and natural cellulose fabric (bark cloth) for automotive instrument panel applications. Compos B Eng 81:149–157. https://doi.org/10.1016/j.compositesb.2015.06.021

Saleem M, Baker WE (1990) In situ reactive compatibilization in polymer blends: effects of functional group concentrations. J Appl Polym Sci 39:655–678. https://doi.org/10.1002/app.1990.070390316

Senthilkumar K, Subramaniam S, Ungtrakul T et al (2020) Dual cantilever creep and recovery behavior of sisal/hemp fibre reinforced hybrid biocomposites: effects of layering sequence, accelerated weathering and temperature. J Ind Text. https://doi.org/10.1177/1528083720961416

Senthilkumar K, Ungtrakul T, Chandrasekar M et al (2021) Performance of sisal/hemp bio-based epoxy composites under accelerated weathering. J Polym Environ 29:624–636. https://doi.org/10.1007/s10924-020-01904-7

Sergi C, Tirillò J, Seghini MC et al (2019) Durability of basalt/hemp hybrid thermoplastic composites. Polymers 11:603

Shahroze RM, Chandrasekar M, Senthilkumar K et al (2021) Mechanical, interfacial and thermal properties of silica aerogel-infused flax/epoxy composites. Int Polym Proc 36:53–59. https://doi.org/10.1515/ipp-2020-3964

Song Z, Baker WE (1992) In situ compatibilization of polystyrene/polyethylene blends using aminomethacrylate-grafted polyethylene. J Appl Polym Sci 44:2167–2177. https://doi.org/10.1002/app.1992.070441213

Sun Z (2018) Progress in the research and applications of natural fiber-reinforced polymer matrix composites. Sci Eng Compos Mater 25:835–846. https://doi.org/10.1515/secm-2016-0072

Tanrattanakul V, Bunkaew P (2014) Effect of different plasticizers on the properties of bio-based thermoplastic elastomer containing poly(lactic acid) and natural rubber. Express Polym Lett 8:387–396. https://doi.org/10.3144/expresspolymlett.2014.43

Tokiwa Y, Calabia B, Ugwu C, Aiba S (2009) Biodegradability of plastics. IJMS 10:3722–3742. https://doi.org/10.3390/ijms10093722

Utracki LA (2002) Compatibilization of polymer blends. Can J Chem Eng 80:1008–1016. https://doi.org/10.1002/cjce.5450800601

Wilson A (2017) Vehicle weight is the key driver for automotive composites. Reinf Plast 61:100–102. https://doi.org/10.1016/j.repl.2015.10.002

Wu C-S (2009) Renewable resource-based composites of recycled natural fibers and maleated polylactide bioplastic: characterization and biodegradability. Polym Degrad Stab 94:1076–1084. https://doi.org/10.1016/j.polymdegradstab.2009.04.002

Xanthos M, Dagli SS (1991) Compatibilization of polymer blends by reactive processing. Polym Eng Sci 31:929–935. https://doi.org/10.1002/pen.760311302

Effects of Hygrothermal Aging on the Mechanical Properties of the Biocomposites

Athul Joseph, Vinyas Mahesh, Vishwas Mahesh, Dineshkumar Harursampath, and M. A. R. Loja

Abstract The need for bio-based composites or biocomposites has been increasing over recent years as a measure for sustainable development and to minimize the use of petrochemical-based plastics to reduce global warming. However, the properties of biocomposites are hugely influenced by the environmental parameters because of their inherent material properties. Therefore, in this chapter, the coupled effect of temperature and moisture on the overall mechanical properties of biocomposites is discussed under the framework of hygrothermal ageing. The variation in the parameters of hygrothermal ageing such as the relative humidity, temperature, and ageing time have different effects based on the type of composite, its composition, and the properties of the constituent materials of the composites. These variables may either enhance or deteriorate the properties of such composites. This chapter aims to provide a consolidated understanding of the effects of these variables on the mechanical properties of the biocomposites such as the tensile strength, compressive strength and modulus, flexural rigidity, impact toughness, dynamical mechanical properties such as the storage modulus, loss modulus and the damping coefficient,

A. Joseph · V. Mahesh · D. Harursampath
Department of Aerospace Engineering, Indian Institute of Science (IISc), Bangalore 60012, India

V. Mahesh (✉)
Department of Mechanical Engineering, National Institute of Technology, Silchar 788010, Assam, India

V. Mahesh
Department of Industrial Engineering and Production, Siddaganga Institute of Technology, Tumkur 572103, India

M. A. R. Loja
CIMOSM – Centro de Investigação em Modelação e Optimização de Sistemas Multifuncionais; ISEL, IPL – Instituto Politécnico de Lisboa, Av. Conselheiro Emídio Navarro 1, 1959-007 Lisboa, Portugal

Institute of Earth Sciences, University of Évora, Colégio Luís António Verney, 7002-554 Évora, Portugal

IDMEC, Instituto Superior Técnico – Universidade de Lisboa, Av. Rovisco Pais, 1, 1049-01 Lisboa, Portugal

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_5

fatigue properties, shear properties, and many others. The sections in this chapter are designed to discuss the effects of hygrothermal parameters on the said properties exclusively. Additionally, care has been exercised to include biocomposites used in a wide variety of applications including those used in tissue engineering, aerospace components, automobile components, structural components, and many others.

Keywords Hygrothermal · Ageing · Biocomposites · Mechanical properties · Temperature · Moisture · Ageing period

1 Introduction to Biocomposites and Their Importance in the Context of the Modern Materials

Composite materials have been extensively used in various engineering frontiers for many years. However, it is only recently that natural alternatives for such materials have received considerable attention. Such a development is largely due to the rise in the global environmental issues that have disrupted the planet's natural course of existence rendering extreme discomfort in recent times and the upcoming years. This is one of the driving forces behind the predominant importance laid on the development of biomaterials and biocomposites for a wide variety of applications. Therefore, bio-based composites or biocomposites may be defined as the composites that are produced from either partially or fully eco-friendly (green) materials (Smitthipong et al. 2014). This includes a wide array of plant fibres, naturally available polymers, ground plant powders etc. While green composites are extremely beneficial in the context of environmental safety, they are often characterized by poor mechanical performances and thermal instabilities. Hence, most research conducted today focus on obtaining partially eco-friendly composites that contain a large portion of biologically- or naturally-derived components along with petroleum-based plastics. However, efforts are being made to obtain green composites that offer the same performance advantages as their petroleum-based counterparts (Avella et al. 2009; Graupner et al. 2009), Kim and Netravali (Kim and Netravali 2012).

As mentioned above, biocomposites have been researched immensely in recent times. Recent studies have also promoted the use of bio-based epoxy resins for engineering applications in the aviation industry, primarily for structural components (Ramon et al. 2018). In addition to this, (Antov et al. 2020) expounded on the developments made in bio-based adhesives that can be used to reduce the harmful effects of formaldehyde and other volatile compounds used in modern adhesives. However, their poor water resistance and lower bonding strength often restrict their application. A similar observation can be made in the case of adhesives used for wood composites application (Ferdosian et al. 2017). Biocomposites made from stone ground wood were used in the production of economically feasible and sustainable "eco-chairs" with properties comparable to those produced by common plastics such as polypropylene (PP) (Julian et al. 2012; Winandy and Morrell 2017). Bio-based sorbents and gelators have been used extensively for oil-spill treatment (Doshi et al.

2018) However, they require significant and often expensive modifications in the properties of their native materials. Bio-based additives are finding increasing applications in the preparation of natural-fibre composites with inclusions like biochar, lignin, animal fibres, and sewage sludge (Väisänen et al. 2017). Another interesting application of biocomposites is the use of polysaccharides for the production of luminescent biomaterials (Pinto et al. 2014). In addition to the prospects of sustainability, these materials are preferred due to their abundance, diversity, and specific properties. One of the most challenging and highly demanding applications of biomaterials and biocomposites are in the field of biomedical engineering, specifically, tissue engineering (Bedian et al. 2017). Materials such as polyhydroxyalkanoate (PHA), chitin, and alginate provide great advantages over conventional materials in terms of their non-toxicity to most cell lines, biodegradability, biocompatibility, and their high structural growth. Packaging including those for food and other sensitive commodities have seen a steady increase in the use of biomaterials and biocomposites (Attaran et al. 2017; Garrison et al. 2016; Helanto et al. 2019; Silva et al. 2020). While there are no single biocomposites that can be recommended for all potential markets and applications, polymers such as polylactic acid (PLA), polybutylene succinate (PBS) and PHA have been extensively researched to derive maximum properties (Babu et al. 2013). The efforts are further exemplified by the use of wood-based fillers and additives. Renewable fibre materials have also been promoted for effective food packaging with improved cost-effectiveness and sustainability solutions (Johansson et al. 2012). In addition to these materials, efforts have been made to expand the library of available biomaterials and biocomposites (Klimek and Wimmer 2017). Such materials can improve other properties of biocomposites such as termite resistance, lower swelling, and cost-effectiveness.

Therefore, due to this huge spectrum of current and prospective applications of biocomposites, they are the solution to today's problems of sustainability. In addition to this, the improvements in the properties of such materials along with cost-effective production can further extend the reach and applicability of such materials. However, as seen in most cases, their usage is limited by their poor thermal properties and their high moisture absorption. This results in increased matrix swelling, poor mechanical properties, and decreased overall material stability. Therefore, in the present chapter, a detailed discussion is carried out to present and encompass the effect of temperature and moisture on the overall mechanical properties of the composites. The mechanical properties of biocomposites including tensile properties, compressive properties, impact toughness, fatigue life, dynamical mechanical properties, indentation resistance, and others have been presented in the sections that follow along with their variations with respect to different hygrothermal parameters.

2 Hygrothermal Ageing and Its Parameters

The word "hygrothermal" has its origins set in ancient: *hygros* meaning moist and *therme* meaning heat. Therefore, hygrothermal ageing refers to the ageing of materials or composites by subjecting them to thermal and moisture fields. This is however slightly different from hydrothermal fields where water is used as the medium instead of moisture. Materials evolve their characteristics with respect to time or usage. The change in these properties is seen as degradation from their physical, chemical, or mechanical stand-point. Such degradation can occur due to natural process, the intensity of usage, and/or by the action of external agents (Schrefler et al. 2018). Ageing is a time-dependent process that alters the properties of materials by the above means. This can result in the improvement or degradation of the desired properties of the material and is highly dependent on the type of material, its chemical nature, its intrinsic material properties, the ageing parameters, and the surrounding media. Consequently, hygrothermal ageing refers to the subjugation of materials to thermal and moisture loads to alter their properties or to assess the changes in their constituent properties as a result of the intervention of temperature and moisture (Martin 2008).

Hygrothermal ageing is defined largely by three parameters: intensity of thermal loads, the extent of moisture uptake, and the ageing time. The intensity of the thermal loads can be adjusted by varying the temperature gradient that exists between the material and the media it is surrounded by. The application of thermal loads to materials has varied responses based on the type of material. The application of thermal loads to metals and alloys can help relieve the stresses within the material that might have existed as a result of their manufacturing or forming processes (Chandrasekar et al. 2017; Majerski et al. 2018). In addition to this, the application of thermal loads to such materials are seen to improve their properties based on the temperature and ageing period (Hu et al. 2018; Zheng et al. 2021). However, for polymers and polymer composites, the application of thermal loads is a sensitive matter. Polymers and polymer composites are characterized by lower thermal stability when compared to metals and ceramics. The application of thermal loads to polymer matrices can alter the shape of the materials when the applied temperature is greater than the glass transition temperature of the material (Firdosh et al. 2015). Polymer materials are largely characterized by covalent bonds that are highly susceptible to heat which is indicated by the low thermal stability of the materials (Firdosh et al. 2015; Yang et al. 2010; Foulc et al. 2005; Rocha et al. 2017; Wang et al. 2016). Consequently, when thermal loads are applied to such materials, it results in extensive bond breakage leading to lower properties. This behaviour is more significantly evident in biomaterials and biocomposites due to the poor bond strength (Wang et al. 2020; Scida et al. 2013). Ceramic materials on the other hand display high thermal stability which is further increased by the use of fine ceramic materials (Smeacetto et al. 2011; Rocha et al. 2010; Mather et al. 2010; Dwivedi et al. 2014).

When metals and alloys are subjected to moisture fields, it might result in chemical reactions between the metal and water molecules leading to the formation of

metal oxides on the surface of the material (Ouyang et al. 2013; Andrade et al. 1994; Galvez et al. 2019; Yamada and Fusayama 1981). This can result in corrosion of the materials which is largely another form of the ageing process. Polymers and polymer composites on the other hand are seen to experience a process called *swelling* where the materials absorb water that results in the expansion in their physical dimensions (Athijayamani et al. 2009; Selzer and Friedrich 1997). This results in lower bond strength and subsequent loss in the mechanical properties of the materials. This effect is more prominent in biocomposites which are usually characterized by high moisture uptake (Van Den Oever et al. 2010; Sombatsompop and Chaochanchaikul 2004; Deo and Acharya 2010). Ceramics display superior immunity against moisture fields. Earlier ceramic materials with porous surface were seen to absorb moisture to an extent. However, modern ceramic materials are capable of functioning in most environments with minimal disruptions or irregularities. Therefore, the upcoming sections aim to discuss the effect of the combination of thermal and moisture loads or *hygrothermal* loads on the functioning and properties of polymer materials, specifically, biomaterials and biocomposites.

3 Influence of Hygrothermal Ageing on the Tensile Properties of Biocomposites

Studies on PLA and PLA/SiC composites show that the moisture absorption and tensile properties of the composites depend on both the temperature and time of ageing (Kakanuru and Pochiraju 2020). Higher temperatures cause saturation at a quicker rate when compared to lower temperatures. After saturation, the materials undergo severe degradation. It is seen that the extensive degradation in PLA rendered it unusable as a result of high moisture absorption. However, PLA/SiC composites exhibited lower disintegration of the structure at higher SiC loadings (>20wt%). However, PLA/SiC composites with 20wt% of SiC exhibited the best tensile properties in unaged condition. Cyclic loading of unidirectional flax-fibre reinforced epoxy biocomposites showed that the tensile properties of the composites decreased as the ageing period increased (Cadu et al. 2019). The composites showed appreciable stability when subjected to hygrothermal loads for upto 26 weeks. However, later on, the maximum strain and ultimate tensile strength decreased drastically. The decrease in the ultimate tensile strength was much lesser at around 12% compared to the 30% decrease in the maximum strain. The modulus of the composites decreased continuously as the ageing period progressed. Figure 1 represents these variations in terms of the percentage of their initial values along the ageing period. The strength parameters of the aged samples are governed by the post-crosslinking rather than the physical plasticization effect that results due to water absorption. Moreover, it is noted that hygrothermal ageing of these samples also affected the transverse mechanical properties as described in Muthukumar (2019), Schoors et al. (2021). Similar observations were recorded for low-density short-flax-fibre reinforced epoxy composites

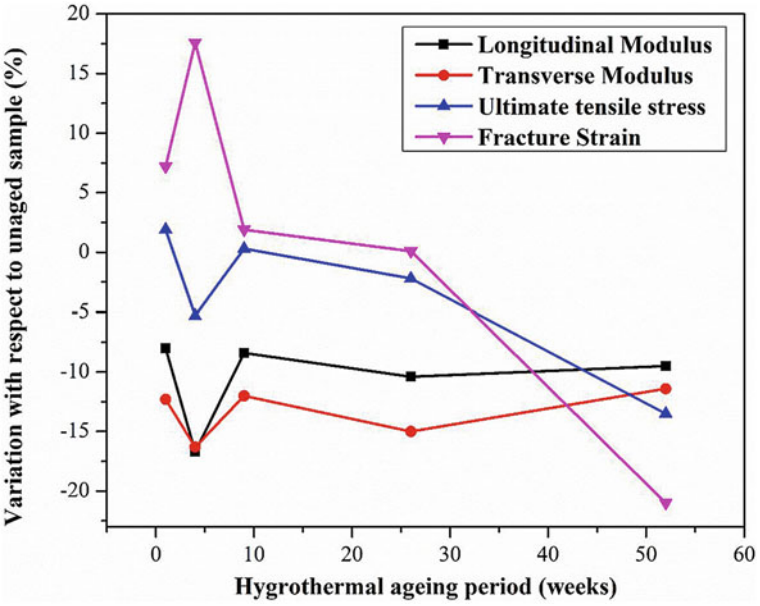


Fig. 1 Variation of the longitudinal elastic modulus, transverse elastic modulus, ultimate tensile strength, and fracture strain of flax-fibre/epoxy composites for the ageing period (Cadu et al. 2019)

by Rabii et al. (2015). The addition of 20wt% of bamboo fibres to polyester decreases the tensile strength of the composites (Azwa and Yousif 2017). However, there is an improvement witnessed in the elastic modulus of the composites. Moreover, the properties are dependent on the concentration of NaOH used for conditioning the composites. When subjected to hygrothermal ageing, the composites show a varied response for different temperature and moisture parameters. Figure 2 represents this variation in terms of the different hygrothermal parameters and conditioning of the composites. The effect of coating the composites treated with 6% NaOH improves the yield strength of the composite at room temperature. However, at elevated temperatures, its influence is very minimal.

The influence of hygrothermal ageing on Kraft fibre reinforced PP composites was evaluated by Beg and Pickering (2008a). The composites were aged for about 238 days at different temperatures. In addition to this, 4wt% maleated PP (MAPP) binders were added to further improve the responses. It is observed that the yield strength, tensile modulus, and fracture strain decrease with the increase in the ageing temperature. However, composites that contained MAPP showed better responses as witnessed in Fig. 3. Similar observations were made for reprocessed wood-fibre composites with MAPP (Beg and Pickering 2008b). The decline in the properties was much lesser for composites that were reprocessed repeatedly. Bio-nanocomposites made from PLA, maleic anhydride (MA), microcrystalline cellulose (MCC) and cellulose nanowhiskers (CNW) were severally affected by hygrothermal parameters

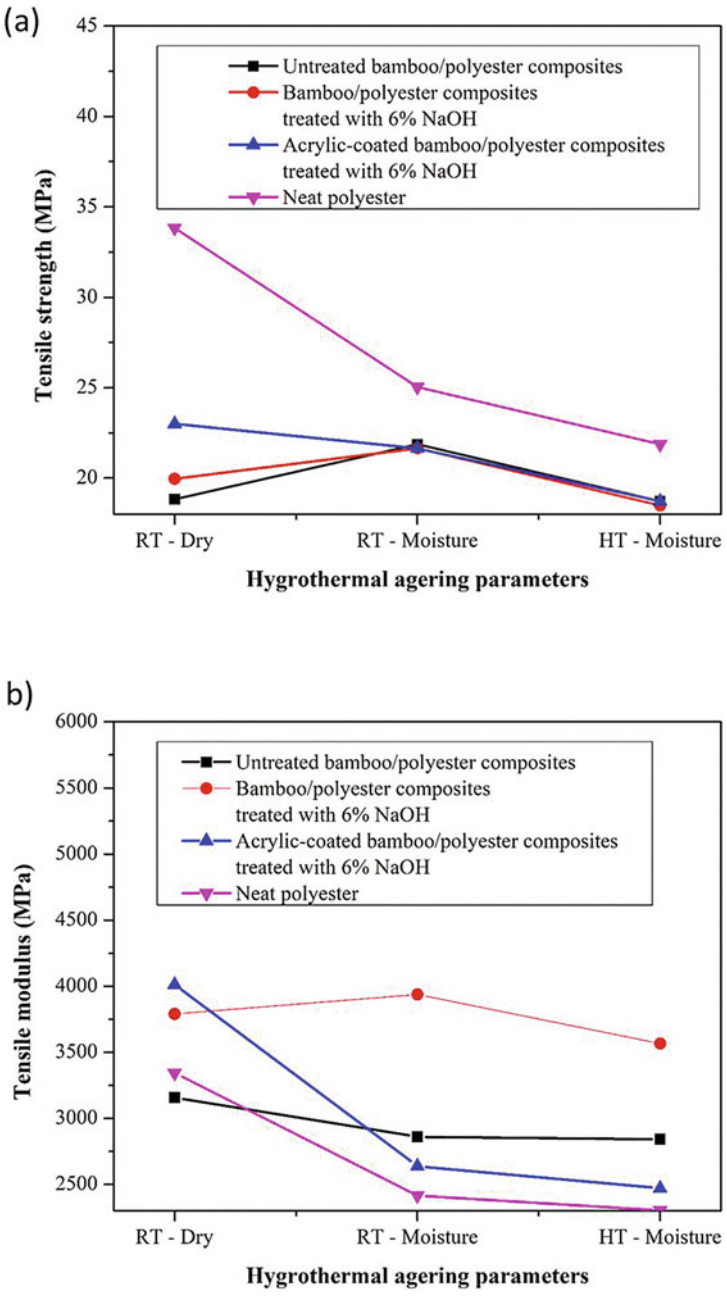


Fig. 2 Variation in the **a** tensile strength and **b** tensile modulus of bamboo fibre/epoxy composites with respect to different hygrothermal ageing parameters (Azwa and Yousif 2017). Where RT—room temperature and HT—high temperature (80 °C)

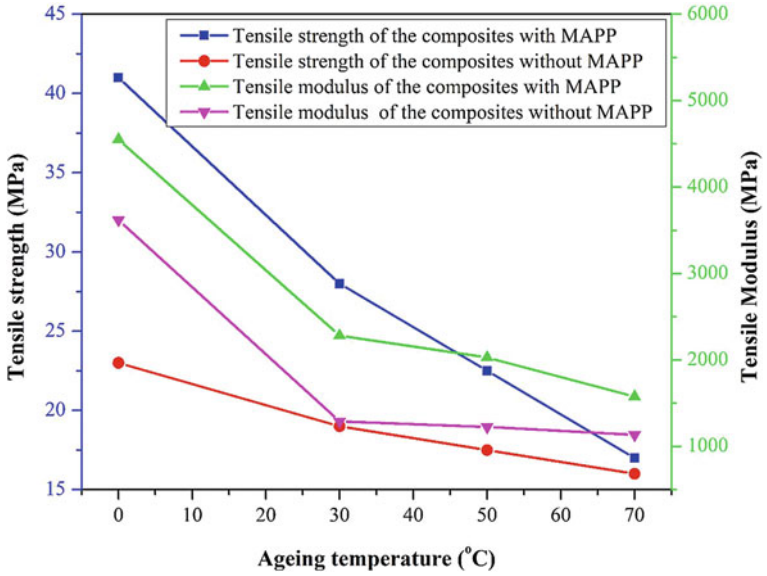


Fig. 3 Variation in the tensile properties of kraft fibre reinforced PP composites with respect to the ageing temperature (Beg and Pickering 2008a)

(Aouat et al. 2019). It is seen that a small change in the ageing temperature can degrade the composites much quickly. Fig. 4 depicts this variation. The evaluation of the bulk mechanical properties of bio-based epichlorohydrin/cardanol adhesive was carried out by Tzatzadakis and Tserpes (2020). The adhesives of these adhesives were comparable to those of commercial structural adhesives. The materials were seen to follow a nonlinear ductile behaviour. On hygrothermally ageing these samples at 70 °C and 85% relative humidity (RH) until saturation, the tensile properties of the composites decreased by a considerable margin. The ageing period varied between 6 to 8 weeks. Once the ageing was complete, a decrease of 13.4 and 34.9% were observed in Young's modulus and tensile strength of the composites. However, the fracture toughness, which is the deciding parameter on the suitability of an adhesive decreased by only 3.2% during the entire ageing period.

It is seen that the adoption of post-curing methods like thermo-pressing can help reduce the standard deviation of the mechanical properties of biocomposites (Cadu et al. 2018). This helps with the reticulation of the resin and with the release of internal stresses in biocomposites. In these methods, time and temperature play an important role in determining the resulting properties. However, in most cases, the temperature applied will be much lesser than the processing temperature of the composites. This renders post-curing duration as the deciding parameter. A higher post-curing temperature and lesser post-curing duration can help maintain the average resultant properties. However, a higher post-curing time is recommended to reduce the standard deviation of the results to ensure repeatability.

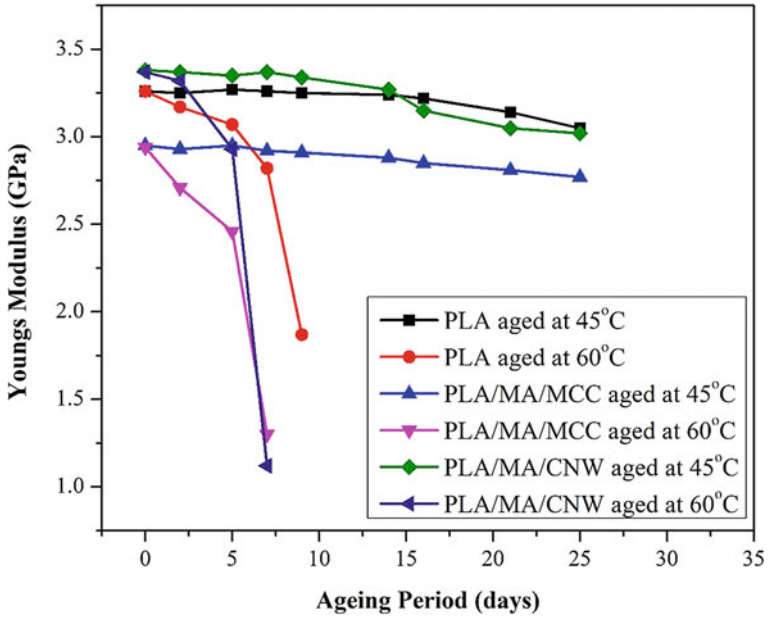


Fig. 4 Variation of Young's modulus for PLA bio-nanocomposites for different hygrothermal ageing temperatures and periods (Aouat et al. 2019)

4 Influence of Hygrothermal Ageing on the Compressive Properties of Biocomposites

The compressive properties of hygrothermal biocomposites made from ammonium dihydrogen phosphate (AHP), dead burned magnesia (MgO), fly ash (FA), crush corn stalk (CS), sodium triphosphate and borax were measured by Ahmad et al. (2019). The composites contained 40 wt%, 33 wt% and 26 wt% of water respectively. It is seen that the compressive strength of the composites increased as the water content in them decreased irrespective of the extent of compaction of the constituent materials. However, for a given concentration of water in the composite, higher levels of compactness gave the best compression properties. Additionally, the moisture uptake of the composites increased with the ageing time for upto 50 h irrespective of the water content in them. Hemp concrete structures were subjected to extreme accelerated conditions over a span of 40 days with successive immersion and drying periods (Benmahiddine et al. 2020a). During this period, the immersion was carried out for 48 h while the drying was carried out at 50 °C for 72 h. This type of ageing can give a clear and more practical understanding of the extremes of the composites when subjected to compressive loads. At the end of the ageing period, the weathered hemp concrete structures were seen to lose about 51% of their initial compressive strength.

Recent studies by Kaur and Jayakumari (2017) evaluated the influence of hygrothermal parameters on the compressive strength of bio-based epoxidized cardanol/cenosphere syntactic foams. Under unaged conditions, the compressive strength of the composites decreased with the increase in the concentration of the nanoparticles. The hygrothermal effect on these materials maintained the same trend while showing variations in terms of the type of media and temperature of ageing. It is noticed that salt-water media improves the properties of composites with 20 and 30 wt% loading of particles. The variations in the compressive strength of the composites with respect to different ageing media and temperatures are depicted in Fig. 5.The compressive properties of concrete reinforced with flax shives subjected to hygrothermal conditions were studied by Benmahiddine et al. (2020b). It is observed that the compressive strength of the composites decreased with the increase in the ratio of water to flax shives concentration. The same trend was observed with the increase in the size of the flax shives. The variation in the compressive strengths of these composites is depicted in Fig. 6. Similar observations were made for bio-concrete composites consisting of magnesium phosphate cement (MPC) and ordinary Portland cement (OPC) (Ahmad and Chen 2020). The composites with MPC exhibited superior compressive properties as a result of the superior compatibility and cohesion with the plant aggregates used in bio-concrete.

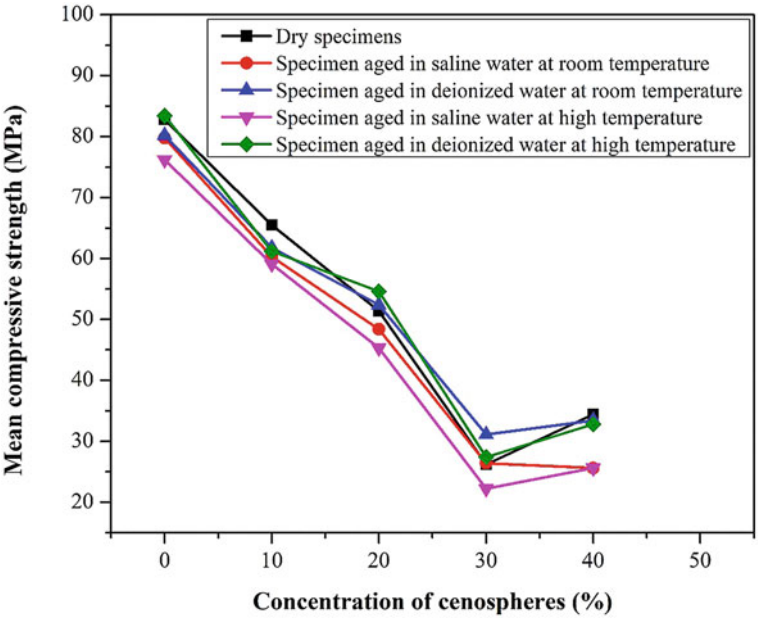


Fig. 5 Variation of the compressive strength of bio-based epoxidized cardanol/cenosphere syntactic foams with respect to different hygrothermal media and temperature (Kaur and Jayakumari 2017)

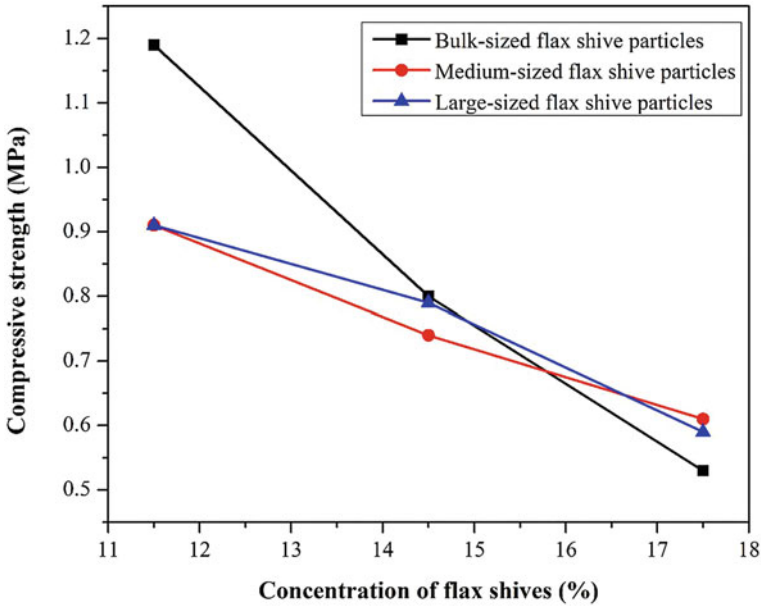


Fig. 6 Variation of the compressive strength of green concrete reinforced with flax shives with respect to the size and concentration of flax shives (Benmahiddine et al. 2020b)

5 Influence of Hygrothermal Ageing on the Flexural Properties of Biocomposites

The flexural properties of biocomposites also showed similar variation in the properties like that of the tensile and compression tests. Studies on the flexural properties of various plant-based composites for maritime applications showed that the flexural properties of glass/epoxy, glass/linseed oil and glass/castor oil composites decreased with the increase in the ageing period (Valgma 2014; Malmstein et al. 2013). However, among these three composites, the glass/linseed oil composites were seen to undergo the highest degradation in the flexural properties after the highest hygrothermal ageing period as represented in Fig. 7. The poor bonding characteristics and the lower glass transition temperature are believed to have contributed largely to this variation. Similar observations were made for PP composites reinforced with bamboo fibres were in the moisture uptake of the composites followed a Fickian-type diffusion (Chunhong et al. 2016). However, when surface treatments such as alkali and alkali-silane treatments were adopted for the composites, the properties varied. A general observation states that the flexural strength of the composites improved with these surface treatments with the highest improvement noted for alkali-silane treatment. However, the flexural modulus of the alkali-treated variants had the least values irrespective of the ageing period, while the alkali-silane treated variants possessed the best flexural moduli.

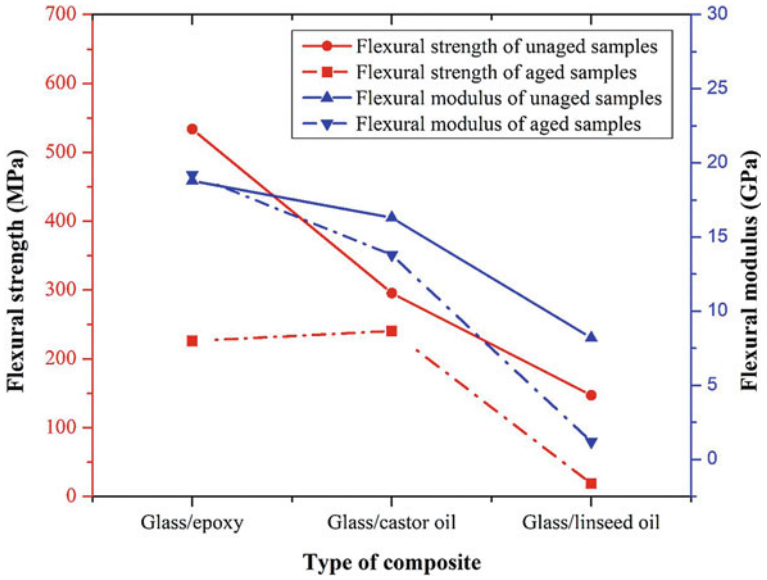


Fig. 7 Variation in the flexural properties of unaged and aged samples of glass/epoxy, glass/castor oil and glass/linseed oil composites (Valgma 2014)

The flexural responses of hygrothermally-aged PP composites reinforced with flax pulps and MAPP binders (E-43 and G-3003) were studied by Retegi et al. (2006). The composites were soaked in distilled for a period of three months at different temperatures such as 30, 50, 70, and 100 °C after pre-drying them in a vacuum at 90 °C. Irrespective of the ageing temperature, the composites that used the G-3003 binder displayed higher flexural strength and modulus when compared to those that used E-43 binders and those that used no binders. However, for a given ageing temperature the flexural strength of the composites increased for upto 4wt% loading of either of the MAPPs. Flax fibre/bio-epoxy composites showed varied flexural responses with respect to different hygrothermal ageing mechanisms (Moudood et al. 2019). The different mechanisms included freeze/thaw cycles, humidity saturation, water saturation, water-saturated and freeze/thaw, and water saturation and drying. Among these mechanisms, the highest retention in the properties of the as-manufactured variants was seen for composites that were water-saturated and then completely dried. The highest decline in the properties was noticed for composites that were simply water-saturated. Hybrid composites were made from jute and basalt fibres were hygrothermally aged in a climate chamber to determine their flexural properties based on their stacking sequences (Fiore et al. 2017). Among the two different modes of stacking sequences (sandwich-model and intercalated-model), it is observed that intercalated composites exhibited the highest flexural strengths which decreased as the ageing period increased. This variation in the flexural properties of the composites is illustrated in Fig. 8. Flax/epoxy composites showed a similar variation where

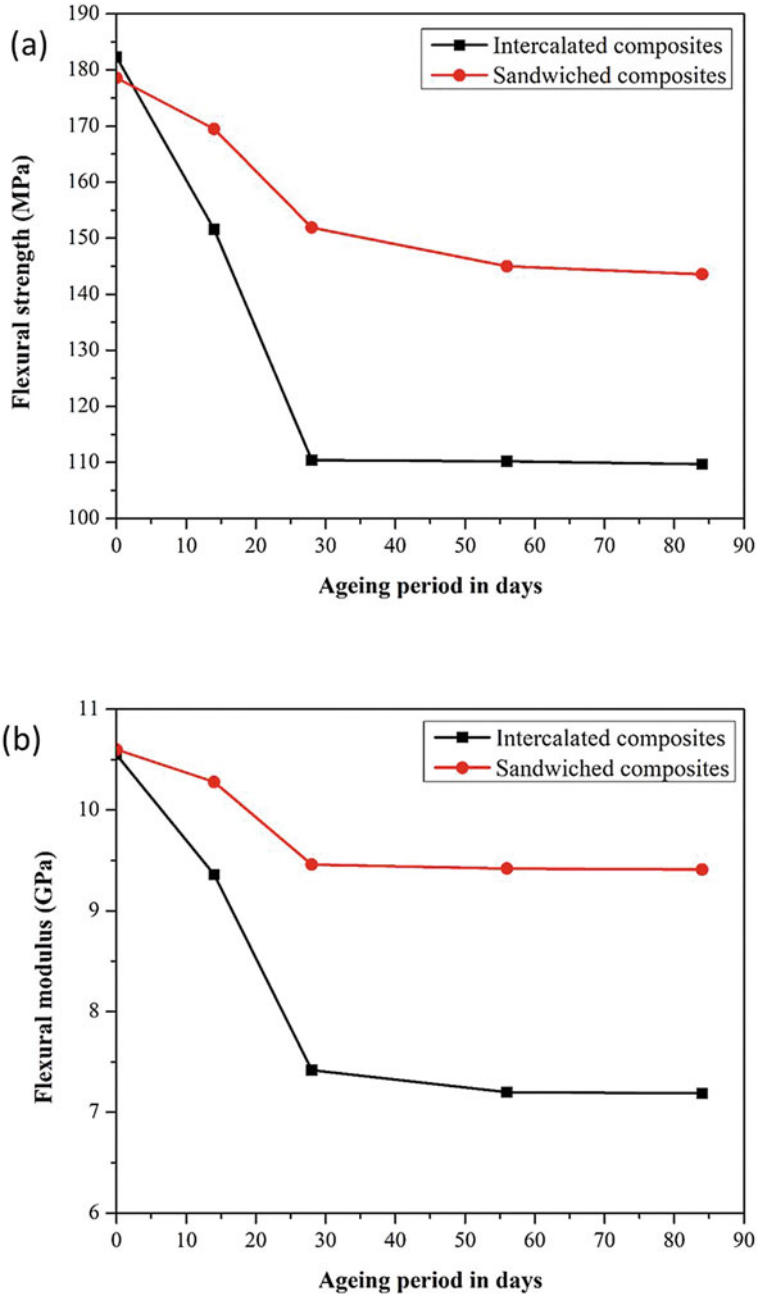


Fig. 8 The influence of stacking sequence and ageing period on the **a** flexural strength and **b** flexural modulus of jute-basalt hybrid composites (Fiore et al. 2017)

a larger dip in the properties was seen for composites exposed to 100% RH over 50% RH (César dos Santos et al. 2020).

6 Influence of Hygrothermal Ageing on the Dynamical Mechanical Properties of Biocomposites

Hygrothermally aged natural fibre reinforced composites made of flax and jute along with epoxy resin were subjected to fatigue studies to determine their critical behaviour (Bambach 2020). It is noted that, between flax and jute fibres, the latter absorbed higher moisture content when subjected to similar conditions of hygrothermal ageing. Both the composites showed an increasing moisture content as the ageing period was increased. The stiffness of jute and flax fibre composite increased upto a load of 0.5 times their initial ultimate compressive stress (UCS) at 10^5 cycles. However, when the number of cycles at 0.5 times the UCS was increased to 10^6, the stiffness reduced to the degeneration and loss in properties of the fibres in the composite. Similar observations are recorded for the UCS of the structures under fatigue loading. However, for jute composites, the properties declined after 0.4 times the UCS at 10^4 cycles. On the other hand, the initial UCS of the composites decreased with the increase in the hygrothermal ageing period. When similar composites were exposed to salt-fog environments, the storage modulus and glass transition temperature decreased while the loss factor increased (Fiore et al. 2020). However, the effects were more pronounced for flax fibres and there was little to no influence of the salt-fog environment on composites with an abundance of jute fibres indicating that the treatment was highly dependent on the chemical properties of the medium under consideration. Though hydrothermal ageing of flax/epoxy composites reduces the static properties of the composites, they are seen to improve the fatigue responses of the composites (Jeannin et al. 2019). The maximum stress of the fatigue tests remains the same as that of the static tests and the other properties at high fatigue cycles also improve. However, these properties can be further improved by incorporating coatings to reduce water absorption.

Accelerated weathering studies on kenaf/sisal reinforced bio-epoxy showed that the dynamical mechanical properties of the composites varied with respect to the stacking sequence and weathering of the composites (Yorseng et al. 2020). The ageing of the composites is seen to decrease the overall modulus of a given composite. However, it effects of weathering vary in intensity as per the different stacking sequences adopted for the composites which are indicated by the variation in the storage modulus and loss modulus of the composites. Similar observations were made for the mobility of the polymer chains in flax fibre/bio-based resin composites which were subjected to hydrothermal ageing under dry and wet conditions (Kollia et al. 2020). The samples tested under dry conditions were seen to exhibit a better glass transition and moduli at lower temperatures. Creep compliance studies on hygrothermally aged all-cellulose-composites (ACC) showed that the values increased with

the increase in the RH and creep temperature (Sallesh 2017). The significant slippage in the composites subjected to higher RH and temperatures were responsible for the observed effect. The ACCs produced via NaOH/urea were seen to possess higher creep compliance over those produced by BmimAc solvents.

7 Influence of Hygrothermal Ageing on the Impact and Shear Responses of Biocomposites

Hygrothermal studies on carbon-fibre-reinforced rosin-based epoxy bio-composites showed that these composites possess very good shear properties when compared to regular carbon-fibre reinforced plastics (CFRPs) (Tserpes et al. 2019; Yang et al. 2020). The composites exhibited a decrease of only 4% in the inter-laminar shear strength (ILSS) with respect to their unaged counterparts when aged at 70 °C and 85% RH until saturation. Similarly, flax/bio-epoxy composites showed varied shear responses with the ageing temperature, RH and ageing period as shown in Benzarti et al. (2018). The composites did not show any serious degradation when aged up to a period of 3 months. After this period, a notable decrease in the global properties is observed for specimens aged at 60 °C at 100% RH due to extensive moisture absorption. Studies on the assessment of environmental resistance of flax/bio-epoxy composites and flax/polyurethane composites showed that the shear deformation of the composites was dependent on the overall moisture absorption of the composites which increased with the ageing period (Cuinat-Guerraz et al. 2016). The observed shear stress curves show two different modes of failure: interlaminar shear/tension at lower values of moisture absorption and inelastic deformation at higher values of moisture absorption. Additionally, among these two composites, flax/polyurethane variants showed higher shear strength values at all ageing periods.

Biocomposites made from montmorillonite (OMMT) filled epoxy/acrylate epoxidized palm oil (AEPO) and hybrid kenaf/glass fibres were experimentally characterized for their mechanical strength (Mustapha 2019). The impact strength of these composites was seen to improve with AEPO loading exhibiting a maximum increment of about 57% from the unreinforced variants. The moisture absorption studies on these composites show that the properties of the composites varied due to the hybridization of the kenaf and glass fibres in the matrix. PLA and composites of PLA reinforced with untreated (AUL) and alkali-treated aligned long hemp (AAL) fibres were hygrothermally aged to determine their impact strength (Islam and Pickering 2010). The samples were aged at different temperatures until their sorption saturation limit was reached. The results reveal that the impact strength of PLA immensely improved with the addition of the fibres. The largest increment was observed for composites with the untreated hemp fibres. Additionally, the impact strength of a given composite improved with the increase in the ageing temperature. Figure 9 represents the effect of the hygrothermal ageing temperature on the impact properties of the composites. Absorption of moisture caused swelling in the fibre surface,

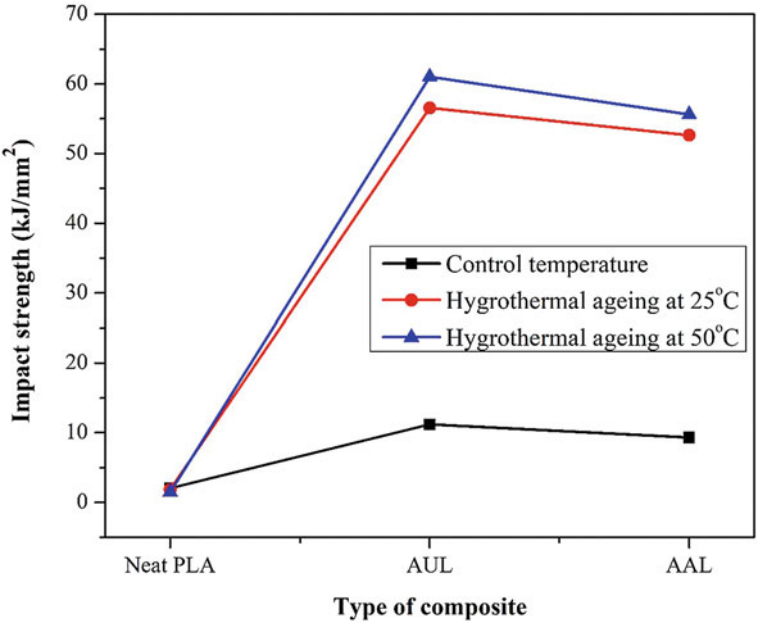


Fig. 9 Influence of hygrothermal parameters on the impact strength of PLA and hemp fibre/PLA composites (Islam and Pickering 2010)

enhancing the frictional work of fibre pull-out from PLA matrix which increased the impact strength. Similarly, due to the extent of swelling at higher temperatures, larger frictional work is needed resulting in the observed impact strengths. Furthermore, carbon fibre reinforced bio-epoxy composites revealed a decrease in the absorbed impact energy as the hygrothermal ageing period was increased (Liu et al. 2018). Additionally, the ballistic projectile was seen to rebound more in composites that were aged for a longer period of time (>1500 h) but absorbed the least energy once it is perforated.

8 Conclusions

In this chapter, a detailed and thorough description of hygrothermal ageing and its effect on the mechanical properties of biocomposites is presented. It may be noticed that biocomposites are severely affected by the variation in the hygrothermal ageing parameters. The variation in the properties of biocomposites stems from the absorption of water by the composites which is governed by the ageing temperature, RH, and ageing period. In addition to these parameters, the extent of moisture absorption is dependent on the internal material properties, the chemistry of the constituent

materials, surface properties and other related parameters. Nevertheless, the moisture absorption in composites can be restricted by several methods. Surface treatment methods are one of the most applied methods that produce significantly better results. This can be further complemented by the application of different coatings that prevent the percolation of water into the matrix of the composites. Furthermore, the use of high-performance additives and matrix materials can yield better interfacial bonding and subsequent increment in the properties even when aged for longer periods. Therefore, it may be concluded that hygrothermal ageing is a major contributor towards the variation of the properties of biocomposites and demands careful assessment to promote and assure optimum functionality of biocomposites for the intended application.

References

Ahmad MR, Chen B (2020) Influence of type of binder and size of plant aggregate on the hygrothermal properties of bio-concrete. Constr Build Mater 251. https://doi.org/10.1016/j.conbuildmat.2020.118981

Ahmad MR, Chen B, Haque MA, Ali Shah SF (2019) Development of a sustainable and innovant hygrothermal bio-composite featuring the enhanced mechanical properties. J Clean Prod 229:128–143. https://doi.org/10.1016/j.jclepro.2019.05.002

Andrade UR, Meyers MA, Chokshi AH (1994) Pergamon scripta metallurgica. Scr Metall Mater 30:933–938

Antov P, Savov V, Neykov N (2020) Sustainable bio-based adhesives for eco-friendly wood composites a review. Wood Res 65:51–62

Aouat T, Kaci M, Lopez-Cuesta JM, Devaux E (2019) Investigation on the durability of PLA bionanocomposite fibers under hygrothermal conditions. Front Mater 6:1–15

Athijayamani A, Thiruchitrambalam M, Natarajan U, Pazhanivel B (2009) Effect of moisture absorption on the mechanical properties of randomly oriented natural fibers/polyester hybrid composite. Mater Sci Eng A 517:344–353

Attaran SA, Hassan A, Wahit MU (2017) Materials for food packaging applications based on bio-based polymer nanocomposites. J Thermoplast Compos Mater 30:143–173

Avella M, Buzarovska A, Errico ME, Gentile G, Grozdanov A (2009) Co-challenges of bio-based polymer composites. Mater (Basel). 2:911–925

Azwa ZN, Yousif BF (2017) Physical and mechanical properties of bamboo fibre/polyester composites subjected to moisture and hygrothermal conditions. Proc Inst Mech. Eng Part L J Mater Des Appl 233:1065–1079

Babu RP, O'Connor K, Seeram R (2013) Current progress on bio-based polymers and their future trends. Prog Biomater 2:1–16

Bambach MR (2020) Durability of natural fibre epoxy composite structural columns: high cycle compression fatigue and moisture ingress. Compos Part C Open Access 2:100013

Bedian L, Villalba-Rodríguez AM, Hernández-Vargas G, Parra-Saldivar R, Iqbal HMN (2017) Bio-based materials with novel characteristics for tissue engineering applications: a review. Int J Biol Macromol 98:837–846. https://doi.org/10.1016/j.ijbiomac.2017.02.048

Beg MDH, Pickering KL (2008a) Mechanical performance of Kraft fibre reinforced polypropylene composites: Influence of fibre length, fibre beating and hygrothermal ageing. Compos Part A Appl Sci Manuf 39:1748–1755. https://doi.org/10.1016/j.compositesa.2008.08.003

Beg MDH, Pickering KL (2008b) Reprocessing of wood fibre reinforced polypropylene composites. Part I: hygrothermal ageing and its effects. Compos Part A Appl Sci Manuf 39:1565–1571

Benmahiddine F, Bennai F, Cherif R, Belarbi R, Tahakourt A, Abahri K (2020a) Experimental investigation on the influence of immersion/drying cycles on the hygrothermal and mechanical properties of hemp concrete. J Build Eng 32. https://doi.org/10.1016/j.jobe.2020.101758

Benmahiddine F, Cherif R, Bennai F, Belarbi R, Tahakourt A, Abahri K (2020b) Effect of flax shives content and size on the hygrothermal and mechanical properties of flax concrete. Constr Build Mater 262. https://doi.org/10.1016/j.conbuildmat.2020.120077

Benzarti K, Chlela R, Zombré W, Quiertant M, Curtil L (2018) Durability of flax/bio-based epoxy composites intended for structural strengthening. In: MATEC web conference ICCRRR 2018, p 07014

Cadu T, Van Schoors L, Sicot O, Moscardelli S, Divet L, Fontaine S (2019) Cyclic hygrothermal ageing of flax fibers' bundles and unidirectional flax/epoxy composite. Are bio-based reinforced composites so sensitive? Ind Crop Prod 141:111730

Cadu T, Berges M, Sicot O, Person V, Piezel B, Van Schoors L, Placet V, Corn S, Léger R, Divet L, Ienny P, Fontaine S (2018) What are the key parameters to produce a high-grade bio-based composite? application to flax/epoxy ud laminates produced by thermocompression. Compos, Part B. https://doi.org/10.1016/j.compositesb.2018.04.059

César dos Santos J, Ávila de Oliveira L, Panzera TH, Remillat CDL, Farrow I, Placet V, Scarpa F (2020) Ageing of autoclaved epoxy/flax composites: effects on water absorption, porosity and flexural behaviour. Compos Part B Eng 202

Chandrasekar M, Ishak MR, Jawaid M, Leman Z, Sapuan SM (2017) An experimental review on the mechanical properties and hygrothermal behaviour of fibre metal laminates. J Reinf Plast Compos 36:72–82

Chunhong W, Shengkai L, Zhanglong Y (2016) Mechanical, hygrothermal ageing and moisture absorption properties of bamboo fibers reinforced with polypropylene composites. J Reinf Plast Compos 35:1062–1074

Cuinat-Guerraz N, Dumont MJ, Hubert P (2016) Environmental resistance of flax/bio-based epoxy and flax/polyurethane composites manufactured by resin transfer moulding. Compos Part A Appl Sci Manuf 88:140–147. https://doi.org/10.1016/j.compositesa.2016.05.018

Deo C, Acharya SK (2010) Effect of moisture absorption on mechanical properties of chopped natural fiber reinforced epoxy composite. J Reinf Plast Compos 29:2513–2521

Doshi B, Sillanpää M, Kalliola S (2018) A review of bio-based materials for oil spill treatment. Water Res 135:262–277

Dwivedi G, Viswanathan V, Sampath S, Shyam A, Lara-Curzio E (2014) Fracture toughness of plasma-sprayed thermal barrier ceramics: Influence of processing, microstructure, and thermal aging. J Am Ceram Soc 97:2736–2744

Ferdosian F, Pan Z, Gao G, Zhao B (2017) Bio-based adhesives and evaluation for wood composites application. Polymers (Basel) 9

Fiore V, Scalici T, Badagliacco D, Enea D, Alaimo G, Valenza A (2017) Aging resistance of bio-epoxy jute-basalt hybrid composites as novel multilayer structures for cladding. Compos Struct 160:1319–1328. https://doi.org/10.1016/j.compstruct.2016.11.025

Fiore V, Sanfilippo C, Calabrese L (2020) Dynamic mechanical behavior analysis of flax/jute fiber-reinforced composites under salt-fog spray environment. Polymers (Basel). 12:1–18

Firdosh S, Narasimha Murthy HN, Pal R, Angadi G, Raghavendra N, Krishna M (2015) Durability of GFRP nanocomposites subjected to hygrothermal ageing. Compos Part B Eng 69:443–451. https://doi.org/10.1016/j.compositesb.2014.09.028

Foulc MP, Bergeret A, Ferry L, Ienny P, Crespy A (2005) Study of hygrothermal ageing of glass fibre reinforced PET composites. Polym Degrad Stab 89:461–470

Galvez P, Abenojar J, Martinez MA (2019) Effect of moisture and temperature on the thermal and mechanical properties of a ductile epoxy adhesive for use in steel structures reinforced with CFRP. Compos Part B Eng 176. https://doi.org/10.1016/j.compositesb.2019.107194

Garrison TF, Murawski A, Quirino RL (2016) Bio-based polymers with potential for biodegradability. Polymers (Basel) 8:1–22

Graupner N, Herrmann AS, Müssig J (2009) Natural and man-made cellulose fibre-reinforced poly(lactic acid) (PLA) composites: An overview about mechanical characteristics and application areas. Compos Part A Appl Sci Manuf 40:810–821. https://doi.org/10.1016/j.compositesa.2009.04.003

Helanto K, Matikainen L, Talj R, Rojas OJ (2019) Bio-based polymers for sustainable packaging and biobarriers: a critical review. BioResources 14:4902–4951

Hu Y, Li H, Fu X, Zhang X, Tao J, Xu J (2018) Hygrothermal characterization of polyimide–titanium-based fibre metal laminate. Polym Compos 39:2819–2825

Islam MS, Pickering KL, N.J. (2010) Foreman, influence of hygrothermal ageing on the physico-mechanical properties of alkali treated industrial hemp fibre reinforced polylactic acid composites. J Polym Environ 18:696–704

Jeannin T, Berges M, Gabrion X, Léger R, Person V, Corn S, Piezel B, Ienny P, Fontaine S, Placet V (2019) Influence of hydrothermal ageing on the fatigue behaviour of a unidirectional flax-epoxy laminate. Compos Part B Eng 174

Johansson C, Bras J, Mondragon I, Nechita P, Plackett D, Šimon P, Svetec DG, Virtanen S, Baschetti MG, Breen C, Clegg F, Aucejo S (2012) Renewable fibers and bio-based materials for packaging applications: a review of recent developments. Bio BioResources 7:2506–2552

Julian F, Méndez JA, Espinach FX, Verdaguer N, Mutje P, Vilaseca F (2012) Bio-based composites from stone groundwood applied to new product development. BioResources 7:5829–5842

Kakanuru P, Pochiraju K (2020) Moisture ingress and degradation of additively manufactured PLA, ABS and PLA/SiC composite parts. Addit Manuf 36. https://doi.org/10.1016/j.addma.2020.101529

Kaur M, Jayakumari LS (2017) Novel bio-based epoxidized cardanol/cenosphere syntactic foams, High Perform. Polym 29:785–796

Kim JT, Netravali AN (2012) Non-food application of Camelina meal: development of sustainable and green biodegradable paper-Camelina composite sheets and fibers Jun. Polym Polym Compos 33:1969–1976

Klimek P, Wimmer R (2017) Alternative raw materials for bio-based composites. Pro Ligno. 13:27–41

Kollia E, Saridaki X, Karagiannis D, Kostopoulos V (2020) Effect of water aging on the mechanical properties of flax fiber/bio-based resin composites. J Appl Polym Sci 137

Liu L, Zhao Z, Chen W, Shuang C, Luo G (2018) An experimental investigation on high velocity impact behavior of hygrothermal aged CFRP composites. Compos Struct 204:645–657

Majerski K, Surowska B, Bienias J (2018) The comparison of effects of hygrothermal conditioning on mechanical properties of fibre metal laminates and fibre reinforced polymers. Compos Part B Eng 142:108–116. https://doi.org/10.1016/j.compositesb.2018.01.002

Malmstein M, Chambers AR, Blake JIR (2013) Hygrothermal ageing of plant oil based marine composites. Compos Struct 101:138–143. https://doi.org/10.1016/j.compstruct.2013.02.003

Martin R (2008) Ageing of composites

Mather GC, Poulidi D, Thursfield A, Pascual MJ, Jurado JR, Metcalfe IS (2010) Hydrogen-permeation characteristics of a SrCeO3-based ceramic separation membrane: thermal, ageing and surface-modification effects. Solid State Ionics 181:230–235

Moudood A, Rahman A, Khanlou HM, Hall W, Öchsner A, Francucci G (2019) Environmental effects on the durability and the mechanical performance of flax fiber/bio-epoxy composites. Compos Part B Eng 171:284–293

Mustapha RB (2019) Properties of montmorillonite filled epoxy/acrylated epoxidized palm oil hybrid kenaf/glass fiber composites

Muthukumar C (2019) Mechanical properties of fibre metal laminates reinforced with carbon, flax and sugar palm fibre-based composites

Ouyang FY, Chang CH, You BC, Yeh TK, Kai JJ (2013) Effect of moisture on corrosion of Ni-based alloys in molten alkali fluoride FLiNaK salt environments. J Nucl Mater 437:201–207. https://doi.org/10.1016/j.jnucmat.2013.02.021

Pinto RJB, Carlos LD, Marques PAAP, Silvestre AJD, Freire CSR (2014) An overview of luminescent bio-based composites. J Appl Polym Sci 131

Rabii H, Van Schoors L, Gueguen M, Davies P (2015) Impact of hygrothermal ageing of low-density polyethylene/short flax fibre composites on the multi-scale properties. In: First international conference on bio-based building material AJCE, pp 220–226

Ramon E, Sguazzo C, Moreira PMGP (2018) A review of recent research on bio-based epoxy systems for engineering applications and potentialities in the aviation sector. Aerospace 5

Retegi A, Arbelaiz A, Alvarez P, Llano-Ponte R, Labidi J, Mondragon I (2006) Effects of hygrothermal ageing on mechanical properties of flax pulps and their polypropylene matrix composites. J Appl Polym Sci 102:3438–3445

Rocha RA, Muccillo ENS, Dessemond L, Djurado E (2010) Thermal ageing of nanostructured tetragonal zirconia ceramics: characterization of interfaces. J Eur Ceram Soc 30:227–231

Rocha IBCM, Raijmaekers S, Nijssen RPL, van der Meer FP, Sluys LJ (2017) Hygrothermal ageing behaviour of a glass/epoxy composite used in wind turbine blades. Compos Struct 174:110–122

Sallesh MBM (2017) Hygrothermal effects on the mechanical behaviour of all-cellulose composites

Schrefler BA, Pesavento F, Santagiuliana R, Sciumè G (2018) Mechanics of ageing-from building to biological materials. Ageing Mater Struct Towar Sci Solut Ageing Our Assets 39–55

Scida D, Assarar M, Poilâne C, Ayad R (2013) Composites: Part B Influence of hygrothermal ageing on the damage mechanisms of flax-fibre reinforced epoxy composite. Compos Part B 48:51–58. https://doi.org/10.1016/j.compositesb.2012.12.010

Selzer R, Friedrich K (1997) Mechanical properties and failure behaviour of carbon fibre-reinforced polymer composites under the influence of moisture. Compos Part A Appl Sci Manuf 28:595–604

Silva FAGS, Dourado F, Gama M, Poças F (2020) Nanocellulose bio-based composites for food packaging. Nanomaterials 10:1–29

Smeacetto F, Chrysanthou A, Salvo M, Moskalewicz T, D'Herin Bytner F, Ajitdoss LC, Ferraris M (2011) Thermal cycling and ageing of a glass-ceramic sealant for planar SOFCs. Int J Hydrogen Energy 36:11895–11903. https://doi.org/10.1016/j.ijhydene.2011.04.083

Smitthipong W, Chollakup R, Nardin M (2014) Bio-based composites for high-performance materials: from strategy to industrial application. https://books.google.com/books?id=UoPSBQAAQBAJ&pgis=1

Sombatsompop N, Chaochanchaikul K (2004) Effect of moisture content on mechanical properties, thermal and structural stability and extrudate texture of poly(vinyl chloride)/wood sawdust composites. Polym Int 53:1210–1218

Tserpes K, Tzatzadakis V, Katsiropoulos C (2019) Effect of hygrothermal ageing on the interlaminar shear strength of carbon fiber-reinforced rosin-based epoxy bio-composites. Compos Struct 226. https://doi.org/10.1016/j.compstruct.2019.111211

Tzatzadakis V, Tserpes K (2020) Experimental characterization of the hygrothermal ageing effects on the bulk mechanical properties and lap-shear strength of the novel bio-based epichlorohydrin / cardanol adhesive. J Adhes 00:1–19. https://doi.org/10.1080/00218464.2020.1817742

Väisänen T, Das O, Tomppo L (2017) A review on new bio-based constituents for natural fiber-polymer composites. J Clean Prod 149:582–596. https://doi.org/10.1016/j.jclepro.2017.02.132

Valgma M (2014) Hygrothermal ageing and its effects on the flexural properties and failure modes of plant oil based composites for maritime applications

Van Den Oever MJA, Beck B, Müssig J (2010) Agrofibre reinforced poly(lactic acid) composites: effect of moisture on degradation and mechanical properties. Compos Part A Appl Sci Manuf 41:1628–1635. https://doi.org/10.1016/j.compositesa.2010.07.011

Van Schoors L, Cadu T, Moscardelli S, Divet L, Fontaine S, Sicot O (2021) Why cyclic hygrothermal ageing modifies the transverse mechanical properties of a unidirectional epoxy-flax fibres composite ? To cite this version: HAL Id : hal-03161203. Ind Crop Prod 164:1–26

Wang M, Xu X, Ji J, Yang Y, Shen J, Ye M (2016) The hygrothermal aging process and mechanism of the novolac epoxy resin. Compos Part B 107:1–8. https://doi.org/10.1016/j.compositesb.2016.09.067

Wang Y, Zhu W, Wan B, Meng Z, Han B (2020) Hygrothermal ageing behavior and mechanism of carbon nanofibers modified flax fiber-reinforced epoxy laminates. Compos Part A 140. https://doi.org/10.1016/j.compositesa.2020.106142

Winandy JE, Morrell JJ (2017) Improving the utility, performance, and durability of wood- and bio-based composites. Ann For Sci 74:1–11

Yamada T, Fusayama T (1981) Effect of moisture contamination on high-copper amalgam. J Dent Res 60:716–723

Yang Z, Peng H, Wang W, Liu T (2010) Crystallization behavior of poly(ε-caprolactone)/layered double hydroxide nanocomposites. J Appl Polym Sci 116:2658–2667

Yang C, Zhu D, Yang F, Liu Q, Sun C, Lei K, Zheng Z, Wang X (2020) Quantitative analysis based on atomic force microscopy characterization of interfacial properties between carbon fibers and epoxy resin subjected to hygrothermal and thermal treatments. Compos Sci Technol 198. https://doi.org/10.1016/j.compscitech.2020.108278

Yorseng K, Rangappa SM, Pulikkalparambil H, Siengchin S, Parameswaranpillai J (2020) Accelerated weathering studies of kenaf/sisal fiber fabric reinforced fully biobased hybrid bioepoxy composites for semi-structural applications: Morphology, thermo-mechanical, water absorption behavior and surface hydrophobicity. Constr Build Mater 235. https://doi.org/10.1016/j.conbuildmat.2019.117464

Zheng G, He Z, Wang K, Liu X, Luo Q, Li Q, Sun G (2021) On failure mechanisms in CFRP/Al adhesive joints after hygrothermal aging degradation following by mechanical tests. Thin-Walled Struct 158. https://doi.org/10.1016/j.tws.2020.107184

Degradation Effects of Completely Biodegradable Composites to Moisture Absorption and Water Aging

Emel Kuram

Abstract Employing of biodegradable polymers and reinforcements for the development of composites is important for the reduction of environmental problems of non-biodegradable and petro-based polymers. Completely biodegradable composites (biocomposites, ecocomposites or green composites) are composed of natural fibers and natural matrices or synthetic biodegradable matrices. Completely biodegradable composites can replace synthetic fiber based composites due to excellent mechanical properties, low cost and low density. However, biodegradable composites have hydrophilic nature thus, tend to absorb a significant amount of moisture. Mechanical properties of biodegradable composites immersed in water degrade over time limiting the potential applications of these materials. Not only mechanical properties of biodegradable composites but also dimensions of biodegradable composites are affected by water content. Therefore, in this chapter, the works about processing, applications and water aging of completely biodegradable polymer composites were presented. Also, the results derived from literature studies after water aging of completely biodegradable polymer composites were stated.

Keywords Biodegradable composite · Degradation · Moisture absorption · Water aging

1 Introduction

Polymer matrices such as epoxy, polyester, vinyl ester are used for various structural applications due to good mechanical properties in comparison the biodegradable polymers. However, these polymers are non-biodegradable, non-recyclable and cause environmental problems. Therefore, using of biodegradable polymers for the development of composites is important for the reduction of environmental problems of non-biodegradable and petro-based polymers.

E. Kuram (✉)
Department of Mechanical Engineering, Gebze Technical University, 41400 Gebze, Kocaeli, Turkey
e-mail: kuram@gtu.edu.tr

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_6

Polymer composites are employed widely due to their corrosion resistance, ease of manufacturing, lightweight, low cost and wear property (Ali et al. 2018). Automobile and composite industries seek alternative low cost lignocellulosic materials, decreasing overall manufacturing cost and improving the properties of composites (Syed et al. 2010). Natural fiber based composites replace synthetic fiber based composites due to excellent mechanical properties, low cost and low density (Sature and Mache 2017). Moreover, natural fibers are abundant, biodegradable, environment friendly, non-abrasive and non-hazardous to human health (Sature and Mache 2017; Mercy et al. 2020). However, natural fiber has hydrophilic nature thus, tends to absorb a significant amount of moisture (Sature and Mache 2017) owing to its chemical composition and porous structure (Hill et al. 2009). The existence of hydroxyl and other polar groups in natural fiber is the reason for poor moisture resistance of biocomposites (Singh et al. 2014). Natural fibers have been employed in building components, interior panels in vehicles and packaging material (Syed et al. 2010). Mechanical properties of natural fiber based composites degrade over a period of time limiting the potential applications of these materials (Sature and Mache 2017). Natural fiber based composites can be molded into boards, frames, gratings, pallets, sheets, structural sections and some other shapes (Nair et al. 2014). Natural fiber based composites can be utilized as a substitute for masonry, metal, timber or wood for awnings, barricades, cubicles, facades, false ceiling, fences, flooring, kiosks, prefabricated housing, roofing, sheds/shelters and wall tiles (Nair et al. 2014). It is important to understand the characteristic and structure of fibers because fibers are the main load-bearing constituent of biocomposites (Singh et al. 2014). Natural fibers can be classified in accordance with the origin from where they are derived; these are: animal, mineral and plant fibers (Singh et al. 2014). Plant fibers can be subdivided into bast, leaf, seed and stalk fibers (Singh et al. 2014). The usage of mineral fibers is very limited due to their carcinogenic effects (Singh et al. 2014). Classification of natural fibers is given in Fig. 6.1.

Lignocellulosic fibers are employed as reinforcements in composite materials, especially in the automotive, building and construction sectors (Shahzad and Isaac 2014). They possess some pros in comparison to synthetic fibers such as biodegradability, environmentally friendly and low cost (Shahzad and Isaac 2014). Lignocellulosic polymer composites are employed in decks, roofs, siding and windows where they are subjected to weathering, which can result in the changes of chemical compositions and microstructure of these composites (Shahzad and Isaac 2014). These changes can influence the service life of these composites negatively by altering fatigue behaviour, impact resistance, modulus and strength (Shahzad and Isaac 2014). Lignocellulosic fibers employed as reinforcements in composites are presented in Table 6.1.

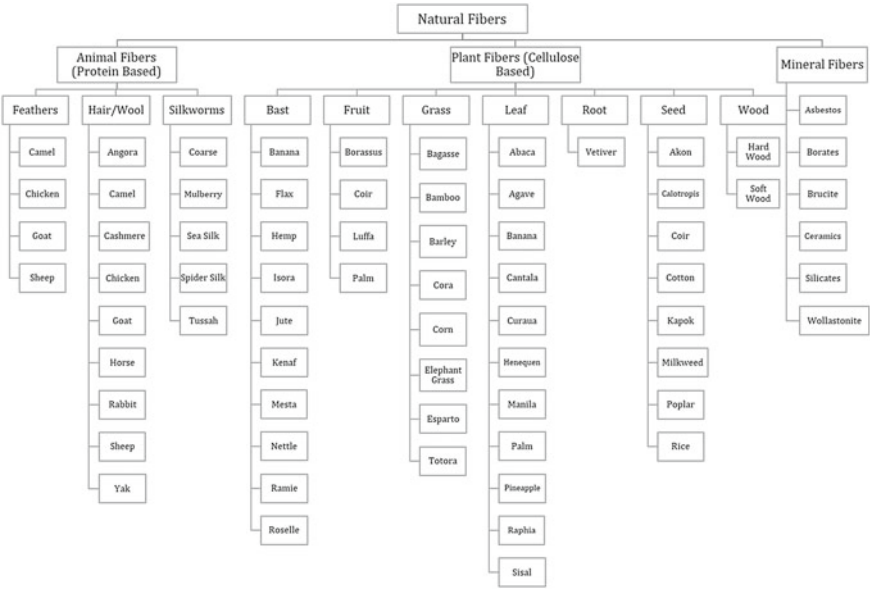


Fig. 6.1 Classification of natural fibers

Table 6.1 Lignocellulosic fibers employed as reinforcements in composites

Bast (stem) fibers	Leaf fibers	Seed (hairs) fibers	Stalk fibers	Fruit fibers	Wood fibers	Grasses and reeds
Cordia Flax Hemp Indian mallow Jute Kenaf Mesta Nettle Papyrus Ramie Roselle Sunhemp Urena	Abaca (Manila hemp) African palm Agaves Banana Cabuja Curaua Date-palm Henequen Isora New Zealand flax Pine Pineapple Raffia Sisal	Baobab Coir Cotton Kapok Milkweed	Bagasse Bamboo Banana stalk Cork stalk	Coconut Oil palm	Hardwood Softwood	Alpha Bagasse Bamboo Barley Canary grass Corn Elephant grass Esparto Oat Palm Rape Reed Rice Rye Seaweeds Wheat

2 Biodegradable Polymers and Composites

Biodegradable polymers can be classified by four categories depending on the origin (Avérous 2004):

- Agro-polymers from agro-resources such as cellulose and starch
- Polymers achieved by microbial production such as polyhydroxyalkanoates
- Chemically synthesized polymers from monomers obtained from agro-resources such as poly(lactic acid)
- Chemically synthesized polymers from monomers.

Based on the kind of polymers, biocomposites can be divided into two categories: partially (non-biodegradable polymers + natural fibers) and completely (biodegradable polymers + natural fibers) biodegradable composites. Partially biodegradable composites are developed from mixing of traditional petro-based non-biodegradable polymers such as epoxy, polyester, polyethylene (PE), polypropylene (PP) and polystyrene (PS) with natural fibers. Completely biodegradable composites (biocomposites, ecocomposites or green composites) are composed of natural fibers and natural matrices or synthetic biodegradable matrices such as poly(lactic acid) (PLA). They are completely degradable, eco-friendly, sustainable (Nair et al. 2014), more environmentally friendly and they possess lower carbon dioxide (CO_2) footprint (Farag 2017). They come directly from the earth and they can go back into the earth and composted in organic soil with no waste when they are disposed after being employed (Nair et al. 2014). Completely biodegradable composites can be developed by employing the traditional fabricating methods including compounding, compression molding, extrusion, filament winding, hand layup, injection molding and mixing, that have been used for composites made from synthetic fibers and synthetic polymers (Farag 2017).

Green composites can be employed for furniture (i.e. cubicles, desks and tables), housing panels (i.e. floors and walls), packaging applications, sport equipments (i.e. skateboards and tennis racquets), transportation panels (i.e. airplanes and car parts) and in mass-produced consumer products for short time usage before disposal (Nair et al. 2014). Completely biodegradable polyhydroxyalkanoate (PHA) based wood plastic composites are employed in applications from decking to furniture (Chan et al. 2020).

2.1 Biodegradable Matrices

Completely biodegradable matrices such as poly(ε-caprolactone) (PCL), polyglycolic acid, PHA, polyhydroxybutyrate (PHB), PLA, polyvinyl alcohol (PVA) and polyvinyl acetate, which are synthetic as well as cellulose, chitin, collagen/gelatin, lignin, polysaccharides and starch, which are natural, have been used.

The most abundant natural polymer is cellulose. Cellulose is found in plants in the form of microfibrils, building up the strong framework in the cell walls (Gáspár et al. 2005). Cellulose is utilized as either matrix or reinforcement. Moisture sensitivity of cellulose based materials limits the use of these materials for packaging applications (Gabr et al. 2013). But cellulose is less hydrophilic than starch (Farag 2017).

Poly(butylene succinate) (PBS) presents more advantages than that of PLA, such as better thermal stability and higher impact resistance (Kim et al. 2005; Petchwattana et al. 2016). PBS is an aliphatic thermoplastic polyester having biodegradability, good mechanical properties and low processing temperature (Liu et al. 2009). It is synthesized by the reaction of the glycol 1,4-butanediol and the aliphatic succinic acid (Kim et al. 2005). The degradation of PBS occurs by hydrolysis (Wang et al. 2009; Thirmizir et al. 2011). PBS can be used in disposable cups and plates, landfill covers, low stress bearing applications and packaging films (Lee et al. 2013).

PCL is a chemically synthesized polymer and it is not found in nature (Gáspár et al. 2005). However, PCL is a completely biocompatible, biodegradable and nontoxic to living organisms and possesses good resistance to oil, solvent and water (Malik et al. 2018). PCL based completely biodegradable materials have been utilized in different applications such as automobiles, biomedical area, drug delivery and food packaging (Malik et al. 2018).

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is biocompatible and biodegradable polymer obtained naturally by bacteria (Mazur and Kuciel 2019). Complexity, high cost of fabrication in comparison to petroleum based composites, low impact toughness and slow crystallization of PHBV limit its usage (Mazur and Kuciel 2019). It was reported that density, tensile strength, Young's modulus and strain at break of PHBV biopolymer were 1.25 g/cm^3, 23 MPa, 0.5 GPa and 35%, respectively (Hossain et al. 2011).

PLA is a transparent thermoplastic made from agricultural resources and has easy processing, high strength and stiffness (Adesina et al. 2019). It was reported that its tensile strength, Young's modulus and strain at break were 65 ± 1 MPa, 3.8 ± 0.1 GPa and $4.2 \pm 0.6\%$, respectively (Regazzi et al. 2016a). PLA is the most extensively employed biodegradable polymer (Wu 2015; Adesina et al. 2019) in the various industries such as automotive, biomedical, packaging, pharmaceutical, textile and tissue engineering (Adesina et al. 2019). PLA is derived from cornstarch, potato and sugarcane (Betancourt and Cree 2017). Notwithstanding these advantages of PLA, major drawback is water barrier properties (Adesina et al. 2019). To overcome this limitation, researchers adopt to blend PLA with natural filler.

Starch is a natural carbohydrate (Farag 2017), is one of the most abundant renewable polymers (biopolymer) of D-glucose and occurs as water-insoluble granules in the nature (Roy et al. 2011). Corn, potato, rice, tapioca and wheat are the most important sources of starch (Alvarez and Vázquez 2004; Roy et al. 2011). The availability of starch is second after cellulose in the nature (Roy et al. 2011). Starch consists of highly branched amylopectin and linear amylose molecules, with some minor components such as lipid and protein (Roy et al. 2011). In general, corn starch composes of 20–30% amylose and 70–80% amylopectin (Gáspár et al. 2005). Starch

is completely biodegradable and allows the development of completely biodegradable composites, reducing global warming (Roy et al. 2011) and has low cost (Farag 2017; Saleh et al. 2017). However, it has some limitations such as poor mechanical properties and a strong hydrophilic nature (water sensitive) (Alvarez and Vázquez 2004; Nair et al. 2014; Saleh et al. 2017). Therefore, starch is usually mixed with other components (Nair et al. 2014; Saleh et al. 2017) and incorporation of fillers is an efficient way for reducing its moisture sensitivity thus enhancing mechanical properties (Wan et al. 2009). Starch has been widely employed in textile industry (Shi and Wang 2017). Thermoplastic starch can be processed either by film casting or melt compounding (Farag 2017). Melt compounding consists of extruding and/or hot pressing of plasticized starch, whereas film casting involves pouring a heated water solution of the plasticized starch into mold (Farag 2017).

2.2 Biodegradable Reinforcements

Bacterial cellulose fibers are employed as biodegradable reinforcement (Wan et al. 2009). Bacterial cellulose has been extensively employed in acoustic diaphragms for audio speakers or headphones, for strong paper and medical applications such as artificial blood vessel, artificial skin, tissue engineering scaffold and wound dressing (Fontana et al. 1997; Wan et al. 2006, 2007; Czaja et al. 2007).

Basalt fiber is an igneous rack which can be melted and drawn into continuous filaments (Mazur and Kuciel 2019). It has better mechanical properties than glass fiber (Mazur and Kuciel 2019). It can replace with carbon fiber because of its chemical resistance, high resistance and thermal strength (Mazur and Kuciel 2019). Therefore, it fills the gap between carbon fiber and glass fiber (Mazur and Kuciel 2019).

Eggshell is a source of calcium carbonate ($CaCO_3$) as it contains 96–97% of $CaCO_3$ and 3–4% of membrane (Cree and Rutter 2015).

Flax fiber has higher mechanical properties in comparison to most other natural fibers (Radkar et al. 2019). It was reported that its density, tensile strength, Young's modulus and strain at break were 1.4–1.5 g/cm^3, 750 ± 490 MPa, 36 ± 13 GPa and 3.0 ± 1.9%, respectively (Regazzi et al. 2016a). But, one of the disadvantages of flax fiber is its hydrophilicity nature, limiting the use of it in structural applications (Radkar et al. 2019), in marine industry and for outdoor construction (Živković et al. 2017).

Jute fiber was also employed to develop completely biodegradable composites. It was reported that density, tensile strength, Young's modulus, strain at break and moisture absorption of jute fiber were 1.4 g/cm^3, 450–550 MPa, 0.30–0.78 GPa, 0.8–2.0% and 13%, respectively (Hossain et al. 2011).

Kenaf fiber is cheap and encouraging material for addition in completely biodegradable composites however its hydrophilic nature causes higher moisture absorption of composites (Lee et al. 2013).

Zein is the major storage protein in the corn endosperm and it is extracted from corn gluten by physical means; therefore, it is completely natural (Gáspár et al. 2005).

2.3 Preparation of Biodegradable Composites

Biodegradable polymers have high cost; therefore, natural fibers are added to diminish the cost (Lee et al. 2013).

Bacterial cellulose fibers were added to wheat starch plasticised with glycerol via a solution impregnation method. Glycerin (30% w/w) and starch were blended before the incorporation of water. Glycerol and starch solution was stirred at the temperature of 80 °C for 30 min. pH of solution was hold at 3–4 and the concentration changed from 10 to 20 (w/v)% (Wan et al. 2009).

Completely biodegradable composites from cellulose and laponite clay (hydrophilic bentonite, $H_2Al_2O_6Si$) were developed (Gabr et al. 2013). Clays with various ratios of 2.5, 5, 7.5, 10, 30 and 50 wt% were dispersed in water by agitation (Gabr et al. 2013). Cellulose was diluted with water at fiber amount of 0.2% then mixed with the clay solution (Gabr et al. 2013). Mixture was homogenized employing homogenizer for 1 h then stirred for 2 days with magnetic stirrer at room temperature (Gabr et al. 2013). Vacuum pump was used to filter the mixture for 1 day (Gabr et al. 2013).

Completely biodegradable composites from commercial blend based on about 38 wt% of cellulose, 38 wt% of starch and 22 wt% of additives and sisal fiber (5, 10 and 15 wt%) with a diameter of 0.3 ± 0.05 mm and length of 7.2 ± 0.6 mm were prepared by injection molding machine without previous blending to preserve the diameter and length of fiber (Alvarez and Vázquez 2004).

Composites from PBS and kenaf fiber (30 vol%) were prepared employing a twin screw counter rotating extruder at the screw speed of 50 rpm and the temperatures of 110–130 °C (Lee et al. 2013). Kenaf fiber was fed with the side feeder (Lee et al. 2013).

Biodegradable PBS and Burma Padauk (*Pterocarpus macrocarpus*) sawdust from 0 to 30 wt% were blended by a twin screw extruder at a temperature range of 140 to 160 °C and at a screw speed of 80 rpm (Petchwattana et al. 2017).

PCL as a matrix and hemp fiber with varying aspect ratios (19, 26, 30 and 38) as reinforcement were used to prepare biodegradable composites employing twin screw extruder (Diameter (D) = 20 mm, Length (L) = 900 mm) (Dhakal et al. 2018).

PHBV reinforced with 7.5 or 15 wt% basalt or wood fiber biodegradable composites were manufactured by a co-rotating twin screw extruder (Mazur and Kuciel 2019).

PHBV biopolymer, jute fabric and clay were employed as matrix, reinforcement and filler, respectively (Hossain et al. 2011). PHBV granules were dissolved into chloroform at 1:8 ratio and magnetically stirred for 4 h (Hossain et al. 2011). Clay was infused into biopolymer employing solution intercalation technique (Hossain et al. 2011). PHBV granules were dissolved into chloroform with/without clay and stirred for 6 h (Hossain et al. 2011).

Unstabilised PHBV (a common copolymer of PHA) and 50 wt% *Pinus radiata* wood flour were blended with a twin screw extruder (Chan et al. 2020).

Maleic-anhydride-grafted PLA (PLA-g-MA) and spent coffee grounds with and without treated (cross-linked) were blended with a mixer at 170–180 °C for 15 min at the speed of 50 rpm (Wu 2015). Spent coffee grounds and treated spent coffee grounds contents in composites were 10, 20, 30 and 40 wt% (Wu 2015).

Flax (20 wt% or 16 vol%) and PLA were compounded in a single screw extruder at 175, 180, 185, 185 °C and at 20 rpm (Le Duigou et al. 2014).

100% biodegradable composites of flax/PLA were made with a corotative twin screw extruder (screw length = 900 mm) at the temperature of 180 °C and flax weight contents in composites were 10 and 30% (Regazzi et al. 2016a, b).

Flax or hydroxyapatite (HA) fiber reinforced PLA was compounded employing a mixer (Khalili et al. 2019). PLA and HA (20, 30 and 40 wt%) were mixed at the temperature of 190 °C, speed of 200 rpm for 20 min (Khalili et al. 2019).

A completely biodegradable composite was developed with hemp fiber and PLA (polymerized corn starch) (Smoca 2019).

PLA and jute fiber (10 wt%) were compounded with co-rotating twin screw extruder (screw diameter (D) = 27 mm, screw speed = 100 rpm and length to diameter ratio = 40) at the temperatures of 160, 165, 165, 170, 170, 165 and 160 °C from feed zone to exit die (Jiang et al. 2019).

PLA and limestone or white chicken eggshell powders with particle size of 32 and 63 μm in amount of 5, 10 and 20 wt% were mixed by melt blending in a twin screw extruder at a temperature of 175 °C (Betancourt and Cree 2017).

Composites from PLA and kenaf fiber (10, 20, 30 and 40 wt%) were compounded by a mixer at 190 °C for 15 min with a speed of 50 rpm (Taib et al. 2010). PLA was plasticized with 10 wt% of polyethylene glycol (PEG) and denoted as matrix (Taib et al. 2010).

70 g corn starch, 30 g glycerol and 10 g additive were mixed to develop completely biodegradable composite (Gáspár et al. 2005).

Ramírez et al. (2011) prepared biodegradable composites depended on thermoplastic cassava starch and various content (5, 10, 15, 20, 25 and 30 wt%) of green coconut fiber. Cassava starch was blended with 30 wt% glycerol, following by blending of coconut fiber with the blend of glycerol and starch in a mixer for 1 min (Ramírez et al. 2011).

Corn starch (with 76% amylopectin and 24% amylose and had particle size between 4.9 and 33 μm with a mean of 16 μm) and 20, 50 and 70 wt% date palm (with chemical composition of 57.06, 16.97, 13.09 and 12.88 wt% for cellulose, hemicellulose, lignin and dissolved materials (pectin and wax), respectively) composites were prepared (Saleh et al. 2017).

Starch films with nanocrystals were fabricated by suspending 0.18 g of eucalyptus, oat or rice nanocrystals in 50 mL of distilled water and stirring at 15,500 rpm for 5 min (Bruni et al. 2020). These solutions were mixed into the glycerol and starch solutions and stirred at 11,000 rpm for 2 min (Bruni et al. 2020). Then these solutions heated up to 90 °C, hold at 90 °C for 30 min and stirred at 11,000 rpm for 5 min (Bruni et al. 2020). Finally, biocomposite films were poured into acrylic plates and dried in an oven at 35 °C for 24 h (Bruni et al. 2020).

Biomimetic laminated board made of starch/maize stalk fiber could be employed as biodegradable material owing to biodegradability, easy processability, low cost and non-polluting (Zhang et al. 2009). Cross-linking starch/maize stalk fiber-single layer jute fiber reinforced maize stalk fiber board, dual layer jute fiber reinforced maize stalk fiber board, jute fiber reinforced maize stalk fiber board were achieved in accordance with formulation of cross-linking maize starch adhesive and fabrication process of composite material (Fu et al. 2015).

Starch was mixed with glycerol, oil-flax, sorbitol and urea via a single screw extruder to solve low mechanical properties and poor water resistance of starch (Shi and Wang 2017).

3 Moisture Absorption and Water Aging

To compute moisture absorption and thickness swelling of biodegradable composites following procedure is implemented: The initial weight or thickness of sample is measured then, sample is kept in water bath and is taken out after certain time of immersion. Water on the surface of sample is wiped off and weight or thickness after immersion is measured.

The percentage of moisture absorption is computed by Eq. (6.1).

$$W = 100 \times \left(\frac{W_t - W_0}{W_0} \right) \tag{6.1}$$

where W denotes the percentage of moisture absorption or relative weight change, W_t is the weight of the immersed specimen at the time of t, W_0 is the initial weight before water aging (unaged specimen) and t is the aging time.

The percentage of thickness swelling is computed by Eq. (6.2).

$$T = 100 \times \left(\frac{T_t - T_0}{T_0} \right) \tag{6.2}$$

where T is the percentage of thickness swelling, T_t is the thickness at the time of t and T_0 is the initial thickness before water aging.

Polymer composites absorb moisture when subjected to humid environment or when aged in water (Shahzad and Isaac 2014). Moisture absorption of composites is important when they are used for invasive, long-term medical applications (Onal et al. 2008). Moisture absorption of composites bases on exposure time, filler content, nature of filler/reinforcement, orientation of reinforcement, relative humidity (RH) and temperature (Shahzad and Isaac 2014; Chethana et al. 2015; Adesina et al. 2019) but is not dependent on the amount of water around the composites (Chethana et al. 2015). Chain scission, fiber and matrix swelling, fiber-resin debonding and matrix cracking are typical results of moisture absorption (Shahzad

and Isaac 2014). Three different mechanisms can explain the moisture uptake characteristic of polymer composites (Singh et al. 2014). The main mechanism for moisture penetration into composite materials is diffusion of water molecules inside the fiber and matrix (Shahzad and Isaac 2014). The other mechanisms are capillary transport of water molecules into the flaws and gaps along the fiber/matrix interface, occurring owing to the poor wettability and impregnation (Shahzad and Isaac 2014; Singh et al. 2014), followed by diffusion from the interface into the fiber and resin and transport by micro cracks (Shahzad and Isaac 2014). The rate at which a composite subjected to moisture uptake decreases with time until eventually the liquid amount reaches an equilibrium (saturation) level (Shahzad and Isaac 2014).

Based on the mechanisms, the moisture sorption of fiber reinforced polymers can be categorized into five different kinds (Singh et al. 2014).

- Linear Fickian (Moisture weight gains gradually then reach an equilibrium state)
- Pseudo-Fickian (Moisture weight gains never reach an equilibrium state)
- Two stage diffusion (Moisture weight gains jump abruptly)
- Rapid moisture weight gain owing to fiber/matrix debonding and matrix debonding
- Reducing trend of moisture weight gains after initial take off.

To determine diffusion mechanisms, the kinetics of water absorption can be carried out by fitting the experimental data by Eq. (6.3): (Petchwattana et al. 2017).

$$\frac{M_t}{M_\infty} = kt^n \tag{6.3}$$

Equation (6.3) can be rewritten in log form:

$$\log\frac{M_t}{M_\infty} = \log k + n\log t \tag{6.4}$$

where M_t and M_∞ are the moisture (water) amount at time t and at equilibrium, respectively. k and n are the kinetic constants, computing from the slope and intercept of the log plot of M_t/M_∞ versus time (Petchwattana et al. 2017). n value bases on absorption mechanism (Petchwattana et al. 2017). n value is 0.5 ($n = 0.5$) for Fickian diffusion, n is smaller than 0.5 ($n < 0.5$) for pseudo-Fickian, n is higher than 0.5 ($n > 0.5$) for relaxation controlled and n is between 0.5 and 1.0 ($0.5 < n < 1.0$) for anomalous transport (Petchwattana et al. 2017).

In Fickian diffusion, the absorbed water increases linearly with the square root of time, then slows and reaches an equilibrium plateau, i.e. saturation (Kuram 2019). Fickian law is generally employed for estimating the diffusion coefficient and it is assumed that temperature and moisture are uniform throughout the volume (Grammatikos et al. 2015). Fick's transient equation is written as follows: (Grammatikos et al. 2015).

$$\frac{\partial z}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \tag{6.5}$$

where z is the distance into the thickness (h) from an aged surface, C is the water concentration and D is the diffusivity or diffusion coefficient.

Theoretically, moisture absorption in polymer composites can be described by Fick's second law of diffusion, given by: (Crank 1975; Wan et al. 2009).

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{\frac{-D(2n+1)^2\pi^2 t}{h^2}\right\} \tag{6.6}$$

where M_t and M_∞ are the moisture amount at time t and at equilibrium, respectively. D is the diffusion coefficient, h is the thickness of specimen and n is the summation index.

At the initial sorption $\left(\left(\frac{M_t}{M_\infty}\right) \leq 0.6\right)$, Eq. (6.6) can be reduced to:

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}}\left(\frac{Dt}{h^2}\right)^{1/2} \tag{6.7}$$

For $\left(\frac{M_t}{M_\infty}\right) > 0.6$, Eq. (6.6) can be reduced to (Shen and Springer 1976):

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right] \tag{6.8}$$

Equation (6.7) can be rewritten as:

$$M_t = kt^{1/2} \tag{6.9}$$

where k is the slope of M_t versus $t^{1/2}$ curve and k can be written as:

$$k = \frac{4M_\infty}{h}\left(\frac{D}{\pi}\right)^{1/2} \tag{6.10}$$

D is computed with the following formula:

$$D = \pi\left(\frac{h}{4M_\infty}\right)^2\left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \tag{6.11}$$

Moisture may be available in lignocellulosic fibers in the cell voids or lumina (free water) and adsorbed to the cellulose and hemicellulose in the cell wall (bound water) (Shahzad and Isaac 2014). Free water is available when all areas for the adsorption of

bound water in the cell wall are filled (Shahzad and Isaac 2014). This point is named as fiber saturation point and all water added to fiber after fiber saturation point exists as free water (Shahzad and Isaac 2014). Therefore, total moisture amount is the sum of bound and free water (Shahzad and Isaac 2014).

Cellulose fiber is hygroscopic because polymers that consist of cellulose and hemicellulose are rich in hydroxyl groups that are responsible for moisture absorption through hydrogen bonding (Shahzad and Isaac 2014). Though cellulose and hemicellulose are hydrophilic, lignin is hydrophobic (Shahzad and Isaac 2014). This implies that cell walls have a large affinity for water, however the water absorption capability of walls is limited to some extent by the existence of lignin (Shahzad and Isaac 2014).

When cellulose fiber is subjected to moisture, hydrogen bonds form between the hydroxyl groups of cellulose molecules and water (Shahzad and Isaac 2014). The first molecules may be taken by the hydrophilic groups of fiber and form a strong hydrogen bond (Shahzad and Isaac 2014). Other water molecules are attracted either to other hydrophilic groups or they can form further layers on top of water molecules absorbed by weaker hydrogen bonding (Shahzad and Isaac 2014). Hence cellulose fiber absorbs and desorbs moisture from the atmosphere till they reach the equilibrium step (Shahzad and Isaac 2014).

Cellulose fiber swells when moisture is absorbed and shrinks when moisture is desorbed, but it is water presence in cell walls (bound water) that is responsible for dimensional change (Shahzad and Isaac 2014). When water is added to cell wall, the increment in fiber volume is about proportional to volume of added water (Shahzad and Isaac 2014). Swelling of fiber proceeds till cell walls reach fiber saturation point, however water absorption above fiber saturation point is free water in lumina, which does not contribute to further swelling (Shahzad and Isaac 2014). This process is reversible, fiber shrinks when it loses moisture below fiber saturation point (Shahzad and Isaac 2014). Amorphous regions of cellulose, where hydroxyl groups are more accessible to water, contribute more swelling than the crystalline regions, where only crystallite surfaces are present for water uptake (Shahzad and Isaac 2014). Therefore, increment in crystallinity of fiber decreases its swelling capacity (Shahzad and Isaac 2014). Reduction in the amount of hydrophilic hemicellulose decreases swelling capacity of fiber (Shahzad and Isaac 2014). In lignocellulosic fibers, swelling of fibers as a result of moisture uptake influences dimensional stability and weakens fiber/matrix interface bonding, causing negative effects on the mechanical properties (Shahzad and Isaac 2014).

The most important kind of chemical degradation mechanism in the polymer matrix is hydrolysis, in which ions (H^+, H_3O^+ or OH^-) or water attack chemical groups in the matrix (Shahzad and Isaac 2014). The other kind of chemical degradation mechanism in the polymer matrix is oxidation with acids such as nitric and sulfuric or oxidizing agents such as hypochlorites and peroxides (Shahzad and Isaac 2014).

Another important effect of moisture sorption on the polymer matrix is plasticization (Shahzad and Isaac 2014). Small solute molecules cause a disruption of intermolecular bond between polymer chains, allowing easier chain movement, resulting

a drop in the glass transition temperature (T_g) of the polymer (Shahzad and Isaac 2014). Plasticization can result in a reduction in stiffness, increment in creep rate and increment in diffusion coefficient (Shahzad and Isaac 2014).

Natural fibers are sensitive to moisture and their long-term performance (Ali et al. 2018; Radkar et al. 2019) and mechanical properties (Radkar et al. 2019) are affected by water content, reacting as a plasticizer (Radkar et al. 2019). Also, this nature of natural fibers causes dimensional change and warping (Farag 2017).

In general, the moisture absorption curves achieved for composites can be divided into three zones. The initial zone represents the bound water, including hydrogen bonded water and monolayer water that is absorbed by the hydrophilic and polar groups of polymers (Chethana et al. 2015). In the second zone, water molecules present in small capillaries (Chethana et al. 2015). In the third zone, relative humidity is very high (Chethana et al. 2015).

Hydrolysis, plasticizing and swelling may occur during hygrothermal aging (combination of heat and moisture) (Spiridon et al. 2015). There are three paths for water absorption in plant fiber reinforced composites (Robert et al. 2010):

- Transportation by lumens in the plant fiber
- Capillary transport along the interface between matrix and fiber
- Diffusion of water molecules through matrix.

Moisture can break the bond between fiber and matrix, causing a poor interface, and moisture uptake can result in different swelling, developing stress that can lead matrix fracture (Almgren et al. 2009).

Moisture sorption of bacterial cellulose fiber reinforced starch biocomposites under 75% RH at 25 °C was determined (Wan et al. 2009). Moisture absorption mechanism of bacterial cellulose fiber reinforced starch biocomposites was found to follow a Fickian diffusion mode (Wan et al. 2009). The moisture absorption of the composites increased linearly with $t^{1/2}$ in the initial step, then increasing rate slowed down and finally led to a plateau (Wan et al. 2009). M_∞ decreased with increasing bacterial cellulose content and water absorption of 12.23 wt% was found for bacterial cellulose/starch composite containing 22% of bacterial cellulose (Wan et al. 2009). D and k values decreased with increasing bacterial cellulose fiber loading and D value decreased from 0.96 to 0.56×10^{-4} $mm^2\ s^{-1}$ with an increment of bacterial cellulose in the starch matrix from 7.8 to 22.0 wt% (Wan et al. 2009).

Completely biodegradable composites from cellulose and clay were hold at 95% RH for 48 h (Gabr et al. 2013). A decrement in hydrophilicity was found for cellulose after blending with clay, irrespective of the clay content (Gabr et al. 2013).

Completely biodegradable composites from cellulose, starch, additives and sisal fiber were immersed in distilled water at the temperature of 5, 25 and 60 °C (Alvarez and Vázquez 2004). Samples were removed from water bath at various times and dried with an absorbent paper (Alvarez and Vázquez 2004). Thickness of the samples with different fiber content and temperature is presented in Table 6.2. At temperatures of 5 and 25 °C, weight increased with aging time (Table 6.3) (Alvarez and Vázquez 2004). At temperature of 60 °C, weight increased and after a maximum weight was achieved, a loss of mass occurred (Table 6.3) owing to the extraction of additives

Table 6.2 Thickness of the samples with different fiber content and temperature (Alvarez and Vázquez 2004)

Temperature (°C)	Cellulose, starch, additives blends		Composites of cellulose, starch, additives blends and 5 wt% sisal fiber		Composites of cellulose, starch, additives blends and 10 wt% sisal fiber		Composites of cellulose, starch, additives blends and 15 wt% sisal fiber	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
5	3.2	3.48	3.12	3.38	3.12	3.37	3.12	3.35
25	3.2	3.66	3.12	3.54	3.12	3.53	3.12	3.51
60	3.2	3.39	3.12	3.28	3.12	3.29	3.12	3.32

Table 6.3 Effective diffusion coefficients (D_{eff}) for short times and longer times and maximum relative water uptake (M_{max}) (Alvarez and Vázquez 2004)

Sisal fiber (wt%)	Temperature (°C)	D_{eff} for short times (mm^2/s)	D_{eff} for longer times (mm^2/s)	M_{max} (%)
0	5	$1.4 \times 10^{-6} \pm 1 \times 10^{-7}$	$1.6 \times 10^{-6} \pm 1 \times 10^{-7}$	23.2 ± 0.3
5		$2.2 \times 10^{-6} \pm 4 \times 10^{-7}$	$2.9 \times 10^{-6} \pm 4 \times 10^{-7}$	18.8 ± 0.6
10		$2.6 \times 10^{-6} \pm 3 \times 10^{-7}$	$3.3 \times 10^{-6} \pm 4 \times 10^{-7}$	18.0 ± 1.2
15		$3.0 \times 10^{-6} \pm 1 \times 10^{-7}$	$4.4 \times 10^{-6} \pm 3 \times 10^{-7}$	18.2 ± 0.1
0	25	$3.4 \times 10^{-6} \pm 3 \times 10^{-7}$	$4.1 \times 10^{-6} \pm 5 \times 10^{-7}$	26.1 ± 0.8
5		$5.2 \times 10^{-6} \pm 1 \times 10^{-6}$	$8.8 \times 10^{-6} \pm 2 \times 10^{-6}$	19.1 ± 1.9
10		$5.8 \times 10^{-6} \pm 2 \times 10^{-6}$	$7.3 \times 10^{-6} \pm 3 \times 10^{-6}$	21.5 ± 3.8
15		$5 \times 10^{-6} \pm 9 \times 10^{-7}$	$7.0 \times 10^{-6} \pm 2 \times 10^{-6}$	21.6 ± 3.0
0	60	$1.7 \times 10^{-5} \pm 8 \times 10^{-7}$	$1.5 \times 10^{-5} \pm 2 \times 10^{-6}$	71.6 ± 1.0
5		$1.9 \times 10^{-5} \pm 2 \times 10^{-6}$	$2.0 \times 10^{-5} \pm 2 \times 10^{-5}$	63.8 ± 1.5
10		$2.2 \times 10^{-5} \pm 2 \times 10^{-6}$	$3.6 \times 10^{-5} \pm 3 \times 10^{-6}$	46.1 ± 2.5
15		$2.2 \times 10^{-5} \pm 5 \times 10^{-6}$	$4.2 \times 10^{-5} \pm 4 \times 10^{-6}$	39.3 ± 2.5

or soluble materials facilitated by plasticized matrix (Alvarez and Vázquez 2004). Diffusion coefficients increased with temperature indicating that it was activated by temperature, because matrix showed more flexibility and water acted as a plasticizer (Alvarez and Vázquez 2004). As soluble material was extracted, water absorption started to drop (Alvarez and Vázquez 2004).

Composites from PBS and kenaf fiber were immersed in distilled water for 60 days (Lee et al. 2013). The moisture uptake increased with the square root of time (Lee et al. 2013). Water absorption took place in the first 100 h (Lee et al. 2013). When the specimens reached saturation, the rate of absorption slowed down and finally reached equilibrium, showing that absorption curve followed Fick's second law (Lee et al. 2013). Higher water diffusion was seen in the composite owing to the water absorption tendency of kenaf fiber (Lee et al. 2013).

PBS and Padauk sawdust from 0 to 30 wt% composites were immersed in distilled water for 90 days (Petchwattana et al. 2017). Water sorption increased based on Padauk wood fiber loading (Petchwattana et al. 2017). Water absorption of PBS with 10 and 20 wt% wood gave single step and reached a plateau at about 400–450 h (Petchwattana et al. 2017). Maximum water absorption values of PBS with 10 and 20 wt% wood were 1.4 and 2.2%, respectively (Petchwattana et al. 2017). Incorporation of 30 wt% wood into PBS caused double steps of absorption (Petchwattana et al. 2017). The first one formed from 0 to 500 h which was same behaviour in PBS with 10 and 20 wt% sawdust (Petchwattana et al. 2017). After this point, it reached the first plateau from 500 to 900 h (Petchwattana et al. 2017). It absorbed water at much slower rate from 900 to 1,800 h prior to reaching the second plateau at about 4.5% absorption (Petchwattana et al. 2017). PBS/Padauk sawdust composites followed Fick's law of diffusion, whereas diffusion coefficient increased with wood amount (Petchwattana et al. 2017). This indicated that higher amount of water molecules could diffuse to the composites with higher amount of hydrophilic wood flour (Petchwattana et al. 2017). Maximum water sorption of about 4.5% was found at sawdust of 30 wt% (Petchwattana et al. 2017).

Hemp fiber/PCL biocomposites were immersed in a de-ionised water bath at 25 °C until near saturation of samples (Dhakal et al. 2018). All samples showed three distinct zones (Dhakal et al. 2018). At zone 1, ($t < 15.5\ h^{1/2}$), kinetic of moisture absorption was very fast (Dhakal et al. 2018). At zone 2, ($t > 15.5–21.9\ h^{1/2}$), kinetic of moisture absorption was slow, while at zone 3, ($t > 21.9\ h^{1/2}$), kinetic of moisture absorption was slow, reaching to a plateau (equilibrium moisture uptake) (Dhakal et al. 2018). It was found that the quantity and rate of moisture uptake of hemp fiber/PCL biocomposites increased with aspect ratios of hemp fiber, following Fickian behaviour (Dhakal et al. 2018). The hydrophobic and hydrophilic natures of PCL and hemp fiber caused the difference in the molecular interphase (Dhakal et al. 2018). Thus, the adhesion between polymer matrix and fiber became weaker, resulting increment in water ingression (Dhakal et al. 2018).

PHBV reinforced with 7.5 or 15 wt% basalt or wood fiber biodegradable composites were immersed in saline solution (2% by weight salt) at 40 °C for 1, 7, 21 and 28 days to simulate human body environment (Mazur and Kuciel 2019). Remaining water on the surface of samples was wiped with a tissue paper and specimens weighed

(Mazur and Kuciel 2019). The incorporation of basalt and wood fiber caused an increment in water uptake (Mazur and Kuciel 2019). Composites with wood fiber had a higher water absorption tendency (Mazur and Kuciel 2019). The highest water absorption rate (4.68×10^{-18} m^2/s) was observed for 15 wt% wood fiber reinforced PHBV composite (Mazur and Kuciel 2019). Though basalt fiber does not absorb water, it causes empty spaces between fiber and matrix, which creates microchannels accelerating water absorption (Mazur and Kuciel 2019). PHBV reinforced with 15 wt% basalt fiber biodegradable composite gave higher water absorption than PHBV reinforced with 7.5 wt% basalt fiber biodegradable composite owing to increasing cracks and microchannels (Mazur and Kuciel 2019).

Jute fiber reinforced PHBV composites were placed in distilled water (Hossain et al. 2011). When aging time increased, moisture absorption amount increased (Hossain et al. 2011). After 20 days of aging, there was no important change in moisture absorption and specimens almost saturated (Hossain et al. 2011). Moisture absorption results are given in Table 6.4 (Hossain et al. 2011). Moisture absorption amount of untreated jute fiber PHBV composites was found to be higher in comparison to treated jute fiber PHBV composites (Hossain et al. 2011). Clay infused specimens gave lower moisture absorption since nanoparticle behaved as a moisture barrier

Table 6.4 Moisture absorption results of jute fiber reinforced PHBV composites (Hossain et al. 2011)

Composites	Moisture gain (%)				
	After 7 days	After 14 days	After 20 days	After 30 days	After 60 days
Untreated jute fiber reinforced PHBV	3.987 ± 0.23	5.816 ± 0.16	6.148 ± 0.34	6.189 ± 0.18	6.279 ± 0.13
Treated jute fiber reinforced PHBV	3.836 ± 0.62	5.026 ± 0.53	5.835 ± 0.27	5.949 ± 0.44	5.938 ± 0.40
2% clay treated jute fiber reinforced PHBV	3.651 ± 0.44	4.572 ± 0.30	5.669 ± 0.29	5.824 ± 0.29	5.882 ± 0.25
3% clay treated jute fiber reinforced PHBV	3.639 ± 0.35	4.554 ± 0.36	5.475 ± 0.47	5.744 ± 0.37	5.8023 ± 0.10
4% clay treated jute fiber reinforced PHBV	3.602 ± 0.24	4.5792 ± 0.17	5.337 ± 0.35	5.643 ± 0.26	5.775 ± 0.21

Table 6.5 Flexural properties of jute fiber reinforced PHBV composites before and after moisture absorption for 60 days (Hossain et al. 2011)

Composites	Before moisture absorption		After moisture absorption	
	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
Untreated jute fiber reinforced PHBV	30.25 ± 1.38	1.91 ± 0.53	24.5 ± 1.29	1.50 ± 0.37
Treated jute fiber reinforced PHBV	33.88 ± 1.62	2.16 ± 0.48	26.0 ± 1.27	1.7 ± 0.21
2% clay treated jute fiber reinforced PHBV	38.17 ± 1.46	2.17 ± 0.49	28.0 ± 1.52	2.01 ± 0.28
3% clay treated jute fiber reinforced PHBV	39.43 ± 0.95	3.20 ± 0.51	30.8 ± 1.31	3.0 ± 0.65
4% clay treated jute fiber reinforced PHBV	40.87 ± 1.43	3.20 ± 0.36	34.4 ± 1.24	3.0 ± 0.19

(Hossain et al. 2011). Flexural properties of jute fiber reinforced PHBV composites before and after moisture absorption for 60 days are presented in Table 6.5 (Hossain et al. 2011).

PHBV and 50 wt% *Pinus radiata* wood flour composite was placed in RH 50% at the temperature of 20 °C (Chan et al. 2020).

Flax/PLA biocomposite aged in seawater at depth of 5 m for 2 years in Kernevel harbour, Lorient-France where temperature of water changed yearly from 8 to 19 °C (Le Duigou et al. 2014). Flax/PLA biocomposite suffered from high moisture sorption controlled by flax fiber (Le Duigou et al. 2014). The addition of flax fiber into PLA matrix led to an increment in water uptake and diffusion coefficient; they reached plateau values after 2 months (Le Duigou et al. 2014).

Composites of flax/PLA were immersed in distilled water (Regazzi et al. 2016a). During hygrothermal aging, elastic modulus of all composites reduced and this reduction was more significant when flax amount increased (Regazzi et al. 2016a). However, temperature was the most important responsible factor for the decrease in elastic modulus of all composites (Regazzi et al. 2016a). At the temperature of 50 °C, rigidity was negligible after only a few hours therefore, it was decided that 50 °C was not suitable for hygrothermal aging of flax/PLA composites and they were useless at this temperature for any structural application (Regazzi et al. 2016a).

In another study, PLA reinforced with 10 and 30% flax fiber composites were immersed at the temperatures of 20, 35 and 50 °C till 51 days (Regazzi et al. 2016b). Except for 30% flax fiber reinforced PLA aging at 50 °C, other absorption curves gave a gradual increment at long times, showing pseudo-Fick diffusion (Regazzi et al. 2016b). 30% flax fiber reinforced PLA aging at 50 °C demonstrated a weight loss beyond 144 h (Regazzi et al. 2016b).

Flax or HA (20, 30 and 40 wt%) fiber reinforced PLA composites were soaked in distilled water at temperatures of 25 and 60 °C (Khalili et al. 2019). Weight of moisture uptake was measured per 24 h for 14 days (Khalili et al. 2019). For flax fiber reinforced PLA composite, weight gain increased up to 12 days causing a higher

saturation value of 8.9% (Khalili et al. 2019). This was attributed to hydrophilic nature of flax fiber owing to polar groups (Khalili et al. 2019). Moisture absorption increased with both the existence of flax fiber and increasing of HA (Khalili et al. 2019). This was due to increasing amount of fillers reduced the content of PLA in composite (Khalili et al. 2019). As a consequence, less matrix was present to adhere natural fiber, thus subjecting fibers to environment (Khalili et al. 2019). Therefore, natural fiber absorbed more water owing to lack of adhesion to PLA/HA (Khalili et al. 2019). Moreover, HA is a hydrophilic (polar) filler, increasing water sorption tendency (Khalili et al. 2019). For 20 and 30 wt% HA fiber reinforced PLA composites, weight gain increased for 10 days and reached 16.3 and 16.7%, respectively (Khalili et al. 2019). 40 wt% HA fiber reinforced PLA composite reached a saturation with weight gain of 19.8% after 6 days (Khalili et al. 2019).

PLA/hemp fiber composites were immersed in a distilled water bath at 23 °C (Smoca 2019). After a week of sorption, the specimens increased in size, the sorption dynamics were slow and colour change occurred (Smoca 2019).

Hygrothermal aging of PLA/jute fiber composites was performed in deionized water that was kept constant at 50 °C (Jiang et al. 2019). In the first 7 days, water uptake increased rapidly (Jiang et al. 2019). It was declared that PLA/jute fiber composites presented Fickian behaviour (Jiang et al. 2019). Between 7 and 28 days, deviation from Fickian behaviour due to the weak interface between fiber and matrix was observed and water absorption increased more slowly without saturation (Jiang et al. 2019). This was owing to the capacity for water uptake and swelling of natural fiber and PLA (Almgren et al. 2009). Between 28 and 56 days, the rate of water uptake increased (Jiang et al. 2019).

PLA and limestone or white chicken eggshell with particle size of 32 and 63 μm in amount of 5, 10 and 20 wt% composites were aged in distilled water at room temperature for 8 weeks (56 days) (Betancourt and Cree 2017). It was concluded that both fillers tended to increase the water intake of composites owing to hydrophilic nature of fillers and water absorption was higher for smaller particle size owing to its larger surface area (Betancourt and Cree 2017). PLA/white chicken eggshell composites absorbed more water than PLA/limestone composites for all filler amount and particle sizes (Betancourt and Cree 2017). The higher water intake by PLA/white chicken eggshell composites was owing to the more porous surface of white chicken eggshell (Betancourt and Cree 2017).

Composites from PLA and kenaf fiber (varying between 0 and 40 wt%) were soaked in distilled water at room temperature for 60 days (Taib et al. 2010). Composites from PLA and kenaf fiber did not reach saturation after long time showing non-Fickian behaviour (Taib et al. 2010). Presence of microcracks that accelerate continuous movement of water molecules via capillary action and voids caused impossible for composites to reach saturation after 60 days of water aging (Taib et al. 2010). Water absorption increased with increasing kenaf fiber loading (Taib et al. 2010).

PLA-g-MA/spent coffee grounds and PLA-g-MA/treated spent coffee grounds composites were aged in distilled water and kept at 30 ± 2 °C for 60 days, during which they were taken from the water at interval of 10 days (Wu 2015). Water resistance of PLA-g-MA/treated spent coffee grounds composite was found to be greater

than that of PLA-g-MA/spent coffee grounds composite since the hydrophobicity of treated spent coffee grounds was improved owing to interactions with PLA-g-MA (Wu 2015). For both PLA-g-MA/treated spent coffee grounds and PLA-g-MA/spent coffee grounds composites, the percent mass gain during 60 days increased with spent coffee grounds or treated spent coffee grounds content owing to decreased chain mobility at high spent coffee grounds contents and hydrophilicity of spent coffee grounds, adhering weakly to the more hydrophobic PLA (Wu 2015).

Thermoplastic starch specimens were conditioned with saturated solutions of distilled water, potassium carbonate (K_2CO_3), potassium nitrate (KNO_3), sodium chloride (NaCl) and magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$) at RH of 43, 54, 75, 91 and 100% until constant weight at room temperature (Gáspár et al. 2005). Water resistance of cellulose filled thermoplastic starch was the worst whereas hemicellulose, polycaprolactone and zein based composites had better water resistance (Gáspár et al. 2005). Water sorption was rapid in the first 6 days, then the curves reached saturation (Gáspár et al. 2005). After 14 days of aging, zein filled thermoplastic starch gave the lowest water uptake (Gáspár et al. 2005).

Biodegradable composites depended on thermoplastic cassava starch and various content (5, 10, 15, 20, 25 and 30 wt%) of green coconut fiber immersed in water at 23 °C for 2 and 24 h (Ramírez et al. 2011). After 2 h, thermoplastic cassava starch gave 59.83% water intake, whereas 30 wt% coconut fiber reinforced thermoplastic cassava starch composite gave only 37.99% (Ramírez et al. 2011). The influence of adding coconut fiber into starch matrix on water intake was more pronounced after 24 h (Ramírez et al. 2011). When fiber amount increased, water intake, moisture absorption and swelling decreased (Ramírez et al. 2011). Thermoplastic cassava starch matrix gave the highest swelling, whereas it reduced with increasing coconut fiber amount in the composite (Ramírez et al. 2011). Also, samples were aged by holding them in a desiccator at 22–25 °C and relative humidity of 75 ± 2%, maintained employing a saturated solution of NaCl (Ramírez et al. 2011). It was found that the absorption rate of coconut fiber reinforced cassava starch composites was higher in the first six days and then it increased at a slow rate, tending to saturation (Ramírez et al. 2011).

Corn starch/date palm composites were placed in a humidity at 25 °C and 100% RH (Saleh et al. 2017). Two regions of moisture absorption kinetics were observed (Saleh et al. 2017). At the beginning, a rapid rise in moisture absorption rate was seen during the first 3 days, followed by a more gradual rise in moisture absorption rate until a saturation point, where the moisture amount was nearly the same (Saleh et al. 2017). Starch/20 wt% date palm and starch/50 wt% date palm composites reached the same saturation point of 37.5% moisture amount (Saleh et al. 2017). Diffusion coefficient reduced with fiber content to 1.5×10^{-9} for composites with 70 wt% date palm fiber (Saleh et al. 2017). Composites containing 70 wt% date palm fiber gave highest increment in thickness indicating highest fiber swelling (Saleh et al. 2017). Incorporation of cellulose fiber to starch matrix can decrease moisture absorption since hydrophilic cellulose fiber form fibrous network structure around starch, hindering the penetration of moisture (Saleh et al. 2017).

Starch films with eucalyptus, oat or rice nanocrystals were aged in magnesium nitrate solution for RH of 55 ± 3% at the temperature of 25 ± 3 °C for 7 days (Bruni et al. 2020). The incorporation of cellulose nanocrystals from three different sources, eucalyptus, oat and rice husks into native starch reduced moisture content however they did not influence moisture content in films from phosphorylated starch (Bruni et al. 2020).

Cross-linking starch/maize stalk fiber-single layer jute fiber reinforced maize stalk fiber board, dual layer jute fiber reinforced maize stalk fiber board, jute fiber reinforced maize stalk fiber board were immersed in five different RH conditions at saturated salt solutions of lithium chloride (11% RH), magnesium chloride (33% RH), potassium nitrate (95% RH), sodium bromide (59% RH) and sodium chloride (75% RH) (Fu et al. 2015). Dual layer jute fiber reinforced maize stalk fiber board was found to be better composite for water resistance at RH of 11% (Fu et al. 2015). Single layer jute fiber reinforced maize stalk fiber board was a better composite for water resistance at RH of 33, 59, 75 and 95% (Fu et al. 2015).

Starch with glycerol, oil-flax, sorbitol and urea composite gave moisture absorption of 17.67%, while it was 24.98% for starch (Shi and Wang 2017).

4 Degradation

Moisture uptake degrades polymer composites (Wan et al. 2009). Degradation bases on the amount of moisture absorption which determines the degradation of matrix and reinforcement, degree of interface failure and plasticizing effect (Wan et al. 2009).

Water uptake results in fiber/matrix interface failure and then matrix embrittlement, which are detrimental to ductility, stiffness and tensile strength (Jiang et al. 2019).

Water can establish hydrogen bonding (intermolecular interaction) with fiber surface decreasing adhesion among fiber and matrix (Le Duigou et al. 2013). Water absorption may incite swelling of fiber especially as free volume is present (Le Duigou et al. 2014). Different swelling among fiber and matrix causes high swelling stress resulting in cracking and delaminating (Dhakal et al. 2007; Azwa et al. 2013).

Chen et al. (2009) claimed that enzymatic degradation occurred for long-term immersion.

Two types of degradation occurred during immersion in aqueous media: Physical degradation with plasticizing effect and swelling, interfacial debonding and delamination and chemical degradation caused by fiber degradation and matrix hydrolysis (Gautier et al. 1999; Davies and Choqueuse 2008).

Biodegradable polymers suffer hydrolytic degradation as they are immersed in water and as a result of their structure, additive extraction from the sample takes place (Alvarez and Vázquez 2004). The first stage is water sorption, the second stage is extraction of soluble materials and the third stage is hydrolytic degradation (Alvarez and Vázquez 2004).

Degradation period can be summarized in three phases (Onal et al. 2008):

- Moisture ingress via diffusion, indicated by weight gain.
- Chemical interaction between chains of degradable polymers and water.
- Leaching of ions after chain scission, indicated by weight loss.

For biodegradable PBS and Burma Padauk sawdust composites, swelling began from the break of hydrogen bond (from cellulose, hemicellulose and lignin) then followed by liquid formation with hydrogen bonded via hydroxyl groups in wood particles (Petchwattana et al. 2017). Liquid molecules then adjoined with hydrogen bond to wood (Petchwattana et al. 2017). Thus, water with strong hydrogen bond swelled wood particle (Bledzki et al. 1998; Petchwattana et al. 2017).

For composites from PLA and kenaf fiber, absorption of water molecules by kenaf fiber caused swelling (Taib et al. 2010). Fiber swelling can result in internal stress in matrix causing microcracks along fiber length (Taib et al. 2010). Other effect of water uptake was fiber-matrix debonding (Taib et al. 2010).

It was declared that coconut fiber reinforced cassava starch composites did not disintegrate after swelling (Ramírez et al. 2011).

4.1 Mechanical Properties

Though below fiber saturation point the moisture amount has a great effect on the mechanical properties of fiber, increment in water amount above fiber saturation point results in very little change in the mechanical properties (Shahzad and Isaac 2014). The most important effect of absorption of bound water molecules in cell wall polymers is to plasticize or loosen cell wall microstructure (Shahzad and Isaac 2014). Reduction in cohesive forces in cell wall decreases stiffness, hence increasing deformation under stress (Shahzad and Isaac 2014). Most mechanical properties drop with increment in moisture content up to fiber saturation point since increased amount of bound water interferes with and reduces hydrogen bonding between organic polymers of cell wall (Shahzad and Isaac 2014).

Moisture sorption of bacterial cellulose fiber reinforced starch biocomposites under 75% RH at 25 °C was determined (Wan et al. 2009). Tensile strength of bacterial cellulose/starch biocomposites deteriorated after moisture sorption (Wan et al. 2009). The different retention of tensile strength between bacterial cellulose/starch biocomposites and starch indicated that the presence of bacterial cellulose decreased moisture attack, i.e., adding bacterial cellulose into starch improved in tensile strength retention (Wan et al. 2009).

Flexural modulus of completely biodegradable composites from cellulose, starch, additives and sisal fiber decreased with immersion time and the effect was more abrupt at high temperature (Alvarez and Vázquez 2004). It was declared that the reduction in flexural modulus by water absorption was more important than the reinforcing effect of fiber content (Alvarez and Vázquez 2004). The loss of modulus increased with temperature as a result of the reduction of T_g value (Table 6.6) (Alvarez

Table 6.6 Flexural modulus (GPa) of completely biodegradable composites from cellulose, starch, additives and sisal fiber before and after immersion (Alvarez and Vázquez 2004)

Sisal fiber (wt%)	5 °C		25 °C		60 °C	
	Initial	Final	Initial	Final	Initial	Final
0	1.94	1.30	1.93	1.21	1.94	1.03
5	2.06	1.31	2.06	1.27	2.08	1.08
10	2.17	1.32	2.14	1.28	2.16	1.09
15	2.23	1.32	2.22	1.32	2.19	1.09

and Vázquez 2004). As soluble material was extracted, modulus started to increase (Alvarez and Vázquez 2004).

For PBS and Padauk sawdust with 10, 20 and 30 wt% composites, tensile strength decreased by about 27, 34 and 32%, respectively after immersion in water (Petchwattana et al. 2017). Also, flexural strength reduced with immersion time (Petchwattana et al. 2017). These decrements in flexural and tensile strength were owing to plasticization effect, hydrolysis of ester linkages along PBS chains, leaching of wood particles and swelling of wood particles (Petchwattana et al. 2017).

Flexural (strength and structural rigidity) and tensile (modulus and strength) properties of hemp fiber/PCL biocomposites immersed in water decreased with aspect ratios of hemp fiber owing to the relative increment of moisture ingress in the fiber/matrix interface region, causing a weak fiber/matrix interface (Dhakal et al. 2018). For hemp fiber/PCL biocomposites immersed in water, a drop in the flexural and tensile modulus was found for the aspect ratio of 26 by 62% and 90%, respectively than those of unaged hemp fiber/PCL biocomposites, indicating the loss of the stiffness for the samples (Dhakal et al. 2018). Moisture absorption caused more energy required to break the specimens (Dhakal et al. 2018). Immersed samples absorbed more energy than unaged samples due to the weak fiber/matrix interfaces of aged samples allowing dissipation of more energy within the interfaces (Table 6.7) (Dhakal et al. 2018).

PHBV and 50 wt% *Pinus radiata* wood flour composite was mechanically stable when it was subjected to moisture (Chan et al. 2020).

Unaged flax/PLA biocomposite showed an initial brittle behaviour which became more ductile with immersion time (Le Duigou et al. 2014). The elastic-linear zone, where the damage is irreversible, reduced as a function of water aging (Le Duigou et al. 2014). The dissipated energy till the breakage, achieved from the area under loading curve, increased with water uptake (Le Duigou et al. 2014). Approximately 200 days of immersion caused a drastic drop in strength at break and Young's modulus (Le Duigou et al. 2014). PLA/flax composites immersed in seawater for 18 months gave a similar stiffness but lower tensile strength (Le Duigou et al. 2014). Drying of PLA/flax composites made the aging reversible; therefore, for aging times lower than 60 days, the degradation of stiffness was reversible (Le Duigou et al. 2014). Strength at break was more sensitive to irreversible degradation seeing that from 15 days, the degradation was no longer reversible (Le Duigou et al. 2014).

Table 6.7 Flexural and tensile properties of water aged and unaged hemp fiber/PCL biocomposites (Dhakal et al. 2018)

Composites	Aging conditions	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (mm)	Flexural strength (MPa)	Flexural modulus (GPa)	Deformation at peak load (mm)
PCL/hemp fiber with aspect ratio (AR) 19	Unaged	10.02 ± 0.42	0.27 ± 0.012	5.52 ± 0.26	14.9 ± 0.24	0.317 ± 0.006	16.19 ± 0.22
AR 26		12.25 ± 0.52	0.40 ± 0.021	4.643 ± 0.35	25.68 ± 0.26	0.605 ± 0.006	14.16 ± 0.18
AR 30		11.97 ± 0.21	0.36 ± 0.017	4.898 ± 0.19	23.72 ± 0.39	0.325 ± 0.009	15.09 ± 0.73
AR 38		11.77 ± 0.18	0.27 ± 0.007	6.555 ± 0.14	16.94 ± 0.22	0.364 ± 0.006	15.73 ± 0.27
AR 19	Aged in Water	8.63 ± 0.02	0.17 ± 0.012	7.834 ± 0.54	11.11 ± 0.46	0.220 ± 0.006	17.144 ± 0.23
AR 26		12.21 ± 0.49	0.21 ± 0.01	8.696 ± 0.84	18.29 ± 0.81	0.374 ± 0.028	17.912 ± 0.62
AR 30		9.60 ± 0.42	0.164 ± 0.014	8.741 ± 0.86	13.67 ± 0.28	0.274 ± 0.008	16.692 ± 0.29
AR 38		9.78 ± 0.32	0.17 ± 0.016	8.520 ± 0.89	14.35 ± 0.11	0.281 ± 0.005	17.424 ± 0.60

During immersion at the temperatures of 20, 35 and 50 °C, dynamic elastic modulus and ultimate tensile strength of PLA reinforced with 10 and 30% flax fiber composites reduced with aging time (Regazzi et al. 2016b). The amount of reduction increased with fiber content and temperature (Regazzi et al. 2016b). However, ductility was enhanced during aging (Regazzi et al. 2016b).

Mechanical properties decreased with both the existence of flax fiber and increasing of HA (Khalili et al. 2019).

In the first 7 days for hygrothermal aging of PLA/jute fiber composites, a small reduction in tensile strength was found (Jiang et al. 2019). Elastic modulus decreased and strain at failure increased (Jiang et al. 2019). This was owing to plasticizing effect of water molecules (Jiang et al. 2019) and it was declared that such change in mechanical properties was reversible (Regazzi et al. 2016b). Between 7 and 28 days, damage at the interface caused a drop in elastic modulus and tensile strength (Jiang et al. 2019). Between 28 and 56 days, cracking of PLA matrix reduced ductility, elastic modulus and tensile strength of composites (Jiang et al. 2019).

Moisture exposure of corn starch/date palm composites caused a reduction in mechanical properties (Saleh et al. 2017). After reaching moisture saturation, the retained tensile strength was approximately one-third of the beginning value and the retained impact strength was approximately two-thirds of the beginning value (Saleh et al. 2017).

4.2 Damage Characteristics

Damage characteristics of hemp fiber/PCL biocomposites changed between the unaged and aged in the water (Dhakal et al. 2018). For unaged hemp fiber/PCL biocomposites, the fracture was cut through the material and specimens had a more brittle behaviour (Dhakal et al. 2018). However, the fracture of aged hemp fiber/PCL biocomposites had a rougher edge with greater amount of fiber pull-out and immersed specimens showed more ductile tendency (Dhakal et al. 2018). From the observation of impacted samples, it was seen that delamination of interface and fiber pull-out were common for immersed specimens (Dhakal et al. 2018).

For flax/PLA biocomposite, the damage criterion increased more with the deformation and immersion time (Le Duigou et al. 2014). An increment of damage criterion from deformation of 0.3% for 60 days aged flax/PLA biocomposite in comparison to 0.6% for unaged flax/PLA biocomposite was found (Le Duigou et al. 2014). After aged for 2 years, the failure behaviour of matrix changed (Le Duigou et al. 2014). In addition to fiber plasticizing, PLA breakage became ductile (Le Duigou et al. 2014). After aging, some fiber breakages were present with long debonding length in comparison to unaged flax/PLA (Le Duigou et al. 2014). The existence of water caused a fiber bundles division, causing a decrement of stress transfer and then early damage of biocomposite (Le Duigou et al. 2014).

At 7 days for hygrothermal aging of PLA/jute fiber composites, there was no difference from unaged microstructure (Jiang et al. 2019). Between 7 and 28 days

damage at the interface was observed owing to different swelling and weakening of interface and at 21 days porosity increased (Jiang et al. 2019). Between 28 and 56 days cracking of PLA matrix was found due to the hydrolysis of matrix and first cracking at the interface between jute fiber and PLA occurred after 21 days of aging (Jiang et al. 2019).

4.3 Surface

Composites containing 20, 50 and 70 wt% date palm fiber gave minor cracks on the surface before moisture absorption while more and wider cracks on the surface were observed at the end of moisture absorption test (Saleh et al. 2017). When the moisture penetrates the surface of composite, the fiber swells and develops internal stress that form micro crack in the matrix, transports water through the fiber/matrix interface causing debonding of the fiber from the matrix (Saleh et al. 2017).

5 Conclusion

Using of completely biodegradable composites based on natural fibers and natural matrices or synthetic biodegradable matrices is important for the elimination of environmental problems of non-biodegradable and petro-based polymers. Completely biodegradable composites can replace synthetic fiber based composites due to excellent mechanical properties, low cost and low density. However, biodegradable composites possess hydrophilic nature thus, absorb a higher amount of moisture. Mechanical properties of biodegradable composites aged in water degrade over time limiting the potential applications of these materials. Not only mechanical properties of biodegradable composites but also dimensions of biodegradable composites are affected by water content. Therefore, in this chapter, the studies about processing, applications and water aging of completely biodegradable polymer composites were summarized.

Growth of completely biodegradable polymer composites continues at a rapid rate but, further study is still required to explore their water aging behaviour in order to employ at outdoor applications.

Following results were obtained from the literature studies:

1. The absorption rate of the most biodegradable composites was higher in the first days and then it increased at a slow rate, tending to saturation. Composites from PLA and kenaf fiber did not reach saturation after long time showing non-Fickian behaviour.

2. Moisture uptake degraded polymer composites. Water uptake caused fiber/matrix interface failure and then matrix embrittlement, which were detrimental to ductility, stiffness and tensile strength.

3. Enzymatic degradation occurred for long-term immersion.

4. Two types of degradation occurred during immersion in aqueous media: Physical degradation with plasticizing effect and swelling, interfacial debonding and delamination and chemical degradation caused by fiber degradation and matrix hydrolysis.

5. Biodegradable polymers suffered hydrolytic degradation as they were immersed in water.

6. Most mechanical properties reduced with increment in moisture content up to fiber saturation point.

Acknowledgements Words cannot describe how grateful I am to my doctor interventional neurologist Assoc. Prof. Hasan Huseyin Karadeli for giving me a second chance in life after my brain operation. Without his operation and treatment, I would be unable to do all the things I am able do now. I am forever grateful to him for saving my life in August 2019. I also dedicate this chapter to my family and Assoc. Prof. Hasan Huseyin Karadeli.

References

Adesina OT, Jamiru T, Sadiku ER et al (2019) Water absorption and thermal degradation behavior of graphene reinforced poly(lactic) acid nanocomposite. IOP Conf Ser: Mater Sci Eng 627:012015

Ali SZ, Nahian MK, Islam MA (2018) Effect of fiber content and post stress on moisture absorption of jute polyester composite. IOP Conf Ser: Mater Sci Eng 438:012024

Almgren KM, Gamstedt EK, Berthold F et al (2009) Moisture uptake and hygroexpansion of wood fiber composite materials with polylactide and polypropylene matrix materials. Polym Compos 30:1809–1816

Alvarez VA, Vázquez A (2004) Effect of water sorption on the flexural properties of a fully biodegradable composite. J Compos Mater 38:1165–1181

Avérous L (2004) Biodegradable multiphase systems based on plasticized starch: a review. J Macromol Sci C Polym Reviews 44:231–274

Azwa ZN, Yousif BF, Manalo AC et al (2013) A review on the degradability of polymeric composites based on natural fibres. Mater Des 47:424–442

Betancourt NG, Cree DE (2017) Mechanical properties of poly (lactic acid) composites reinforced with $CaCO_3$ eggshell based fillers. MRS Adv 2545–2550

Bledzki AK, Reihmane S, Gassan J (1998) Thermoplastics reinforced with wood fillers: a literature review. Polym-Plast Technol Eng 37:451–468

Bruni GP, de Oliveira JP, Fonseca LM et al (2020) Biocomposite films based on phosphorylated wheat starch and cellulose nanocrystals from rice, oat, and eucalyptus husks. Starch 72:1900051

Chan CM, Vandi L-J, Pratt S et al (2020) Mechanical stability of polyhydroxyalkanoate (PHA)-based wood plastic composites (WPCs). J Polym Environ 28:1571–1577

Chen H, Miao M, Ding X (2009) Influence of moisture absorption on the interfacial strength of bamboo/vinylester composites. Compos Part A 40:2013–2019

Chethana M, Prashantha K, Siddaramaiah, (2015) Studies on thermal behavior, moisture absorption, and biodegradability of ginger spent incorporated polyurethane green composites. J Appl Polym Sci 132:41614

Crank J (1975) The mathematics of diffusion. Bristol, England

Cree D, Rutter A (2015) Sustainable bio-inspired limestone eggshell powder for potential industrialized applications. ACS Sustain Chem Eng 3:941–949

Czaja WK, Young DJ, Kawecki M et al (2007) The future prospects of microbial cellulose in biomedical applications. Biomacromol 8:1–12

Davies P, Choqueuse D (2008) Ageing of composite in marine vessels. In: Martin R (ed) Ageing of composites. Woodhead Publishing, Cambridge

Dhakal HN, Zhang ZY, Richardson MOW (2007) Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. Compos Sci Technol 67:1674–1683

Dhakal HN, Ismail SO, Zhang Z et al (2018) Development of sustainable biodegradable lignocellulosic hemp fiber/polycaprolactone biocomposites for light weight applications. Compos Part A 113:350–358

Farag MM (2017) Design and manufacture of biodegradable products from renewable resources. In: Thakur VK, Thakur MK, Kessler MR (eds) Handbook of composites from renewable materials, vol 2. Wiley, New York

Fontana JD, Joerke CG, Baron M et al (1997) Acetobacter cellulosic biofilms search for new modulators of cellulogenesis and native membrane treatments. Appl Biochem Biotechnol 63–65:327–338

Fu Z, Wei W, Jin T et al (2015) Moisture absorption properties of biomimetic laminated boards made from cross-linking starch/maize stalk fiber. Int J Agric Biol Eng 8:65–71

Gabr MH, Phong NT, Abdelkareem MA et al (2013) Mechanical, thermal, and moisture absorption properties of nano-clay reinforced nano-cellulose biocomposites. Cellulose 20:819–826

Gáspár M, Zs B, Dogossy G et al (2005) Reducing water absorption in compostable starch-based plastics. Polym Degrad Stabil 90:563–569

Gautier L, Mortaigne B, Bellenger V (1999) Interface damage study of hydro-thermally aged glass-fibre-reinforced polyester composites. Compos Sci Technol 59:2329–2337

Grammatikos SA, Zafari B, Evernden MC et al (2015) Moisture uptake characteristics of a pultruded fibre reinforced polymer flat sheet subjected to hot/wet aging. Polym Degrad Stab 121:407–419

Hill CAS, Norton A, Newman G (2009) The water vapor sorption behavior of natural fibers. J Appl Polym Sci 112:1524–1537

Hossain MK, Dewan MW, Hosur MV et al (2011) Physical, mechanical, and degradability properties of chemically treated jute fiber reinforced biodegradable nanocomposites. J Eng Mater Technol 133:041003

Jiang N, Yu T, Li Y et al (2019) Hygrothermal aging and structural damage of a jute/poly (lactic acid) (PLA) composite observed by X-ray tomography. Compos Sci Technol 173:15–23

Khalili P, Liu X, Zhao Z et al (2019) Fully biodegradable composites: thermal, flammability, moisture absorption and mechanical properties of natural fibre-reinforced composites. Materials 12:1145

Kim H-S, Yang H-S, Kim H-J (2005) Biodegradability and mechanical properties of agro-flour-filled polybutylene succinate biocomposites. J Appl Polym Sci 97:1513–1521

Kuram (2019) Thermal and water ageing effect on mechanical, rheological and morphological properties of glass-fibrereinforced poly(oxymethylene) composite. Proc IMechE Part E: J Process Mech Eng 233:211–224

Le Duigou A, Davies P, Baley C (2013) Exploring durability of interfaces in flax fibre/epoxy micro-composites. Compos Part A 48:121–128

Le Duigou A, Bourmaud A, Davies P et al (2014) Long term immersion in natural seawater of Flax/PLA biocomposite. Ocean Eng 90:140–148

Lee JM, Ishak ZAM, Taib RM et al (2013) Mechanical, thermal and water absorption properties of kenaf-fiber-based polypropylene and poly(butylene succinate) composites. J Polym Environ 21:293–302

Liu L, Yu J, Cheng L et al (2009) Biodegradability of poly(butylene succinate) (PBS) composite reinforced with jute fibre. Polym Degrad Stabil 94:90–94

Malik N, Shrivastava S, Ghosh S B (2018) Moisture absorption behaviour of biopolymer polycapralactone (PCL)/organo modified montmorillonite clay (OMMT) biocomposite films. IOP Conf Ser: Mater Sci Eng 346:012027

Mazur K, Kuciel S (2019) Mechanical and hydrothermal aging behaviour of polyhydroxybutyrate-co-valerate (PHBV) composites reinforced by natural fibres. Molecules 24:3538

Mercy JL, Velmurugan R, Sasipraba T et al (2020) Neurofuzzy modelling of moisture absorption kinetics and its effect on the mechanical properties of pineapple fibre-reinforced polypropylene composite. J Compos Mater 54:899–912

Nair AB, Sivasubramanian P, Balakrishnan P et al (2014) Environmental effects, biodegradation, and life cycle analysis of fully biodegradable "green" composites. In: Thomas S, Joseph K, Malhotra SK et al (eds) Polymer composite, vol 3. Wiley, New York

Onal L, Cozien-Cazuc S, Jones IA et al (2008) Water absorption properties of phosphate glass fiber-reinforced poly-ε-caprolactone composites for craniofacial bone repair. J Appl Polym Sci 107:3750–3755

Petchwattana N, Covavisaruch S, Wibooranawong S et al (2016) Antimicrobial food packaging prepared from poly (butylene succinate) and zinc oxide. Measurement 93:442–448

Petchwattana N, Sanetuntikul J, Sriromreun P et al (2017) Wood plastic composites prepared from biodegradable poly(butylene succinate) and Burma padauk sawdust (*pterocarpus macrocarpus*): water absorption kinetics and sunlight exposure investigations. J Bionic Eng 14:781–790

Radkar SS, Amiri A, Ulven CA (2019) Tensile behavior and diffusion of moisture through flax fibers by desorption method. Sustainability 11:3558

Ramírez MGL, Satyanarayana KG, Iwakiri S et al (2011) Study of the properties of biocomposites. Part I. Cassava starch-green coir fibers from Brazil. Carbohyd Polym 86:1712–1722

Regazzi A, Corn S, Ienny P et al (2016a) Coupled hydro-mechanical aging of short flax fiber reinforced composites. Polym Degrad Stab 130:300–306

Regazzi A, Corn S, Ienny P et al (2016b) Reversible and irreversible changes in physical and mechanical properties of biocomposites during hydrothermal aging. Ind Crop Prod 84:358–365

Robert M, Roy R, Benmokrane B (2010) Environmental effects on glass fiber reinforced polypropylene thermoplastic composite laminate for structural applications. Polym Compos 31:604–611

Roy SB, Ramaraj B, Shit SC (2011) Polypropylene and potato starch biocomposites: physicomechanical and thermal properties. J Appl Polym Sci 120:3078–3086

Saleh AA, Saleh MA, Al Haron MH et al (2017) Insights into the effect of moisture absorption and fiber content on the mechanical behavior of starch-date-palm fiber composites. Starch 69:1600254

Sature P, Mache A (2017) Experimental and numerical study on moisture diffusion phenomenon of natural fiber based composites. Mater Today: Proc 4:10293–10297

Shahzad A, Isaac DH (2014) Weathering of lignocellulosic polymer composites. In: Thakur VK (ed) Lignocellulosic polymer composites: processing, characterization, and properties. Wiley, New York

Shen C-H, Springer GS (1976) Moisture absorption and desorption of composite materials. J Compos Mater 10:2–20

Shi D, Wang R (2017) The test of tensile properties and water resistance of a novel cross-linked starch prepared by adding oil-flax. IOP Conf Ser: Mater Sci Eng 274:012047

Singh I, Debnath K, Dvivedi A (2014) Mechanical behavior of biocomposites under different operating environments. In: Thakur V K (ed) Lignocellulosic polymer composites: processing, characterization, and properties. Wiley, New York

Smoca A (2019) Water absorption properties of hemp fibres reinforced PLA bio-composites. Eng Rural Develop 1079–1083

Spiridon I, Leluk K, Resmerita AM et al (2015) Evaluation of PLA-lignin bioplastics properties before and after accelerated weathering. Compos B Eng 69:342–349

Syed MA, Siddaramaiah SRT et al (2010) Investigation on physico-mechanical properties, water, thermal and chemical ageing of unsaturated polyester/turmeric spent composites. Polym-Plast Technol Eng 49:555–559

Taib RM, Ramarad S, Ishak ZAM et al (2010) Properties of kenaf fiber/polylactic acid biocomposites plasticized with polyethylene glycol. Polym Compos 31:1213–1222

Thirmizir MZA, Ishak ZAM, Taib RM et al (2011) Kenaf-bast-fiber-filled biodegradable poly(butylene succinate) composites: effects of fiber loading, fiber length, and maleated poly(butylene succinate) on the flexural and impact properties. J Appl Polym Sci 122:3055–3063

Wan YZ, Hong L, Jia SR et al (2006) Synthesis and characterization of hydroxyapatite-bacterial cellulose nanocomposites. Compos Sci Technol 66:1825–1832
Wan YZ, Huang Y, Yuan CD et al (2007) Biomimetic synthesis of hydroxyapatite/bacterial cellulose nanocomposites for biomedical applications. Mater Sci Eng C 27:855–864
Wan YZ, Luo H, He F et al (2009) Mechanical, moisture absorption, and biodegradation behaviours of bacterial cellulose fibre-reinforced starch biocomposites. Compos Sci Technol 69:1212–1217
Wang H, Ji J, Zhang W et al (2009) Biocompatibility and bioactivity of plasma-treated biodegradable poly(butylene succinate). Acta Biomater 5:279–287
Wu C-S (2015) Renewable resource-based green composites of surface-treated spent coffee grounds and polylactide: Characterisation and biodegradability. Polym Degrad Stabil 121:51–59
Zhang F, Wu N, Tong J et al (2009) Preparation and flexural properties of biomimetic laminated boards made from starch and maize stalk fiber. Int J Agric Biol Eng 2:24–31
Živković I, Fragassa C, Pavlović et al (2017) Influence of moisture absorption on the impact properties of flax, basalt and hybrid flax/basalt fiber reinforced green composites. Compos Part B 111:148–164

Hygrothermal Aging and Their Influence on Mechanical Properties of the Bio-composites

Hossein Ebrahimnezhad-Khaljiri

Abstract In the last decade, the environmental issues and cost productions were the effective factors, which increased the rate of replacing the bio-composites with the conventional composites like glass fibers/epoxy composites in the various applications especially secondary or tertiary applications. The bio-composites should be proper capability for maintaining their initial mechanical properties under the various work environments. One of the harsh work conditions is the environment with the high humidity and temperature, which is introduced as hygrothermal environment. Being in this environment under the various dynamic and static loading can age the bio-composites. The hygrothermal aging can influence on the mechanical performance of bio-composites, which can increase or reduce the mechanical properties of those. Characterizing and recognizing the effective factors under the hygrothermal aging can help to the producer or researchers to fabricate the proper bio-composites for using in the hygrothermal conditions. The aim of this chapter is to introduce some of the recognized mechanisms under hygrothermal aging and the effect of them on the mechanical properties of various bio-composites.

Keywords Bio-composites · Hygrothermal aging · Mechanical properties · Natural fibers · Bio-polymers

1 Introduction

The term of biocomposites refers to materials, which have been comprised at least one biological phase. The biological phase can be reinforcements, matrices or both of them (Akampumuza et al. 2017). The bio-based natural reinforcements can be extracted from plant, animal, and mineral sources (Sanjay et al. 2018; Mosiewicki and Aranguren 2013). Among these natural reinforcements, the bio-fibers have extremely growth for using instead of synthetic fibers in the composite industries. In other words, the researchers and engineers by developing the extraction methods and modifying

H. Ebrahimnezhad-Khaljiri (✉)
Faculty of Materials Science and Engineering, K. N. Toosi University of Technology, Tehran, Iran
e-mail: ebrahimnezhad-k@email.kntu.ac.ir

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_7

them created the proper situation for using these fibers. Cotton, hemp, flax, jute, sisal, and wood, as well as nano-cellulose fibers are the examples of plant natural fibers. Although, the variety sources of bio-fibers is so great, but, some of them have proper features for using in the various environmental conditions (Mokhothu and John 2015).

One of the environmental conditions for biocomposites is the hygrothermal environment. Aging in this environment can influence on the mechanical properties of those. In the hygrothermal conditions, the heat and water ingress influence on the degradation of reinforcement and matrix into the composites. Generally, the temperature ranges for testing the hygrothermal aging are considered between ambient temperatures up to 60 ˚C, but in some cases, the higher temperature like 80 ˚C can be selected for creating the hygrothermal aging conditions. In general view, the glass transition temperature (T_g) of used matrix has important role, so that, the aging temperatures for doing the hygrothermal tests are lower than T_g (Alam et al. 2018). Given up researches, the hygrothermal aging can influence on the mechanical properties of biocomposites by changing the mechanical behavior of matrix, bio-fibers and the matrix/bio-fibers interfaces. Therefore, investigating these changes is very important and should be considered in the designing the biocomposite parts. Some of the effects mechanisms have been listed in Table 1. These influence's parameters restrict using the bio-fibers into the composites for hygrothermal conditions. So, in the last decade, the scientist groups have tried to develop the possibility of using the bio-fibers into the bio-composites by characterizing the related mechanisms. Based on these efforts, it can be said that the flax, hemp and wood as well as bamboo fibers are some of the bio-fibers, which have proper features for using under hygrothermal conditions.

Table 1 The effect of hygrothermal aging on the various areas into the bio-composites (Jin et al. 2012)

Area	Effects
Bio-fibers	Promoting crack growth by diffusing in defects Plasticizing effect on the bio-fibers
Matrix	Expansion of matrix Plasticizing effect on the matrix Promoting the crack growth and matrix fracture Hydrolysis of matrix Changing the glass transition temperature
Fibers/matrix interface	Debonding the chemical bonds Promoting the crack growing by penetrating into the interface defects Creating the shear stress into the interfaces by matrix expansion phenomenon

2 Flax Fibers Reinforced Bio-composites

One of the bio-fibers for using as reinforcement into the polymeric materials is the flax fibers. Up to now, many researches was done about the effect of hygrothermal aging on the flax fibers reinforced bio-composites. For example, Retegi et al. (2006) investigated the flexural properties of flax/polypropylene (PP) composites after the immersing them into the water at the temperatures of 30, 50, 70 and 100 ˚C. They also added maleic anhydride polypropylene (MAPP) copolymer into the PP matrix. The obtained results showed that generally by increasing the temperature and immersion time, the flexural properties had the reducing trend. Adding the copolymer reduced this reduction trend. They mentioned that increasing the entanglement between fibers and PP matrix was the reason of this phenomenon. Although, the higher reduction in the mechanical properties at the immersion temperature of 100 ˚C was due to softening the desorbed zones of flax fibers.

Another common matrix for flax bio-composites is epoxy matrix. Therefore, investigating the hygrothermal aging of these composites is so necessary. Figure 1 shows the example of hygrothermal cyclic of these composites, which the aging was performed in the temperature of 55 ˚C at the relative humidity of 40 (as dry condition) and 90% (as wet condition) in the various cycling times. The tensile test of these samples showed, the elastic modulus was altered at the short time (until 4 weeks). But, the tensile strength and strain changed between 26 and 52 weeks, respectively (Fig. 2). It was confirmed that (Cadu et al. 2019), the reduction in the elastic modulus was due to the debonding fibers/fibers into the flax fibers, while creating more numbers of crack and degradation of flax fibers/epoxy interfaces were the reason of reduction in the tensile strength and strain.

Cuinat-Guerraz et al. (2016) compared the effect of hygrothermal aging on the mechanical behaviors of flax/bio-epoxy and flax/polyurethane (PU) composites. They subjected these composites at the temperature of 30 ˚C with the relative humidity of 90% and the immersion times of 0, 6, 23, 41, 336 and 720 h. Figure 3

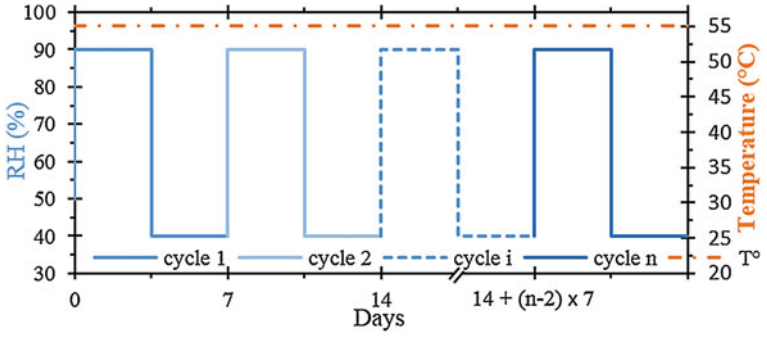


Fig. 1 The performed hygrothermal ageing cycles on the flax/epoxy bio-composites by Cadu et al. (2019). Reprinted with the permission from Elsevier

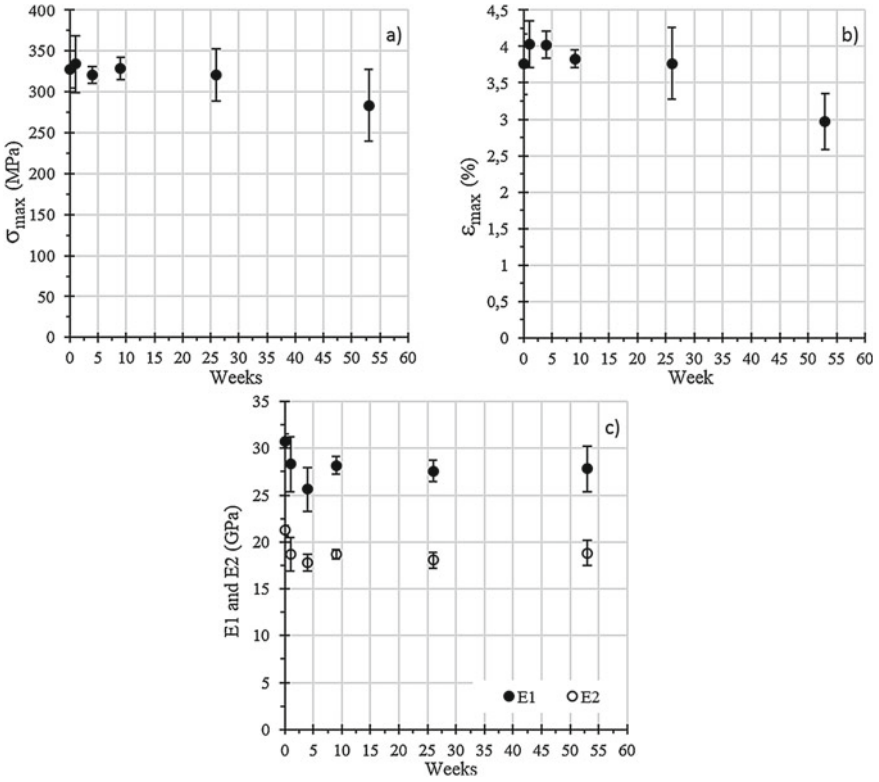


Fig. 2 Evolution of tensile mechanical properties of flax/epoxy unidirectional bio-composites depending on ageing duration. **a** Ultimate tensile stress, **b** Ultimate tensile strain and **c** E_1 and E_2 modulus. Reprinted from Cadu et al. (2019) with the permission from Elsevier

shows the effect of moisture absorption on the short beam strength of these two bio-composites. It can be found that the absorbed moisture due to hygrothermal aging increased the short beam strength of flax/PU composites, while the flax/epoxy bio-composites had reducing trend. This means that the interface strength of flax/PU improved. This can be attributed to the difference in the polarity of PU and epoxy matrices. PU is more polar than epoxy resin. Therefore, by absorbing the moisture at the low level, the stronger polar-polar interactions between water molecules, PU chains and cellulose of flax fibers can be happened, resulting to the creation of stronger interlaminar forces in the interfaces of flax/PU composites.

Figure 4 illustrates the effect of hygrothermal aging on the compressive strength of these bio-composites. The plasticization of bio-epoxy and flax fibers caused to reduce the compressive strength. The reduction trend in flax/PU is lower than that of flax/epoxy composite. This is due to the interaction between plasticization and polarization phenomena in PU polymer. This interaction can be confirmed by SEM observation. In Fig. 5a, b, it can be clearly seen the void defects in the interfaces of

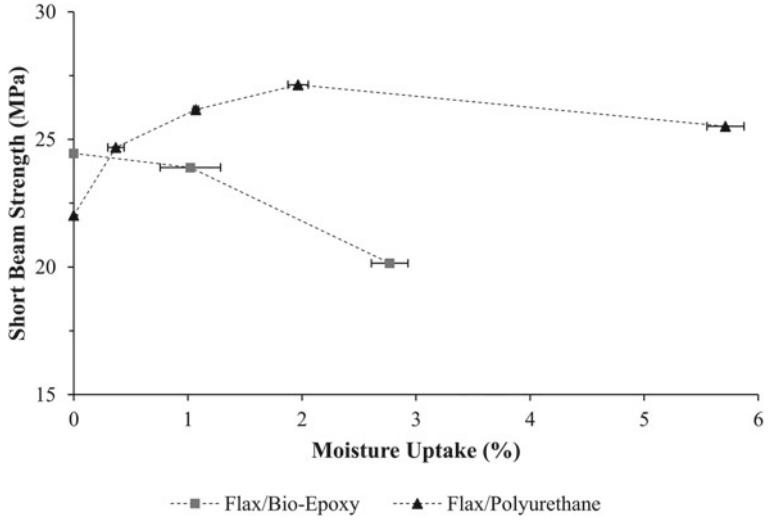


Fig. 3 Evolution of the short beam strength of bio-epoxy/flax and polyurethane/flax composites (90% RH and 30 °C). Reprinted from Cuinat-Guerraz et al. (2016) with the permission from Elsevier

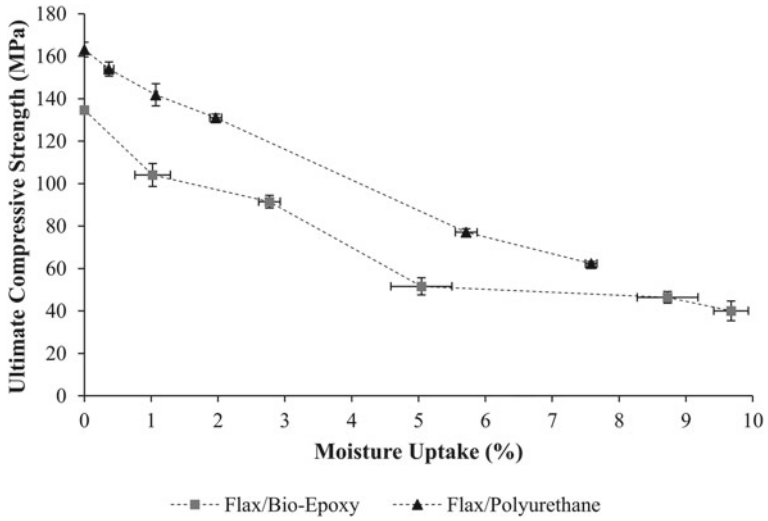


Fig. 4 Normalized compressive strength of bio-epoxy/flax and polyurethane/flax composites. Reprinted from Cuinat-Guerraz et al. (2016) with the permission from Elsevier

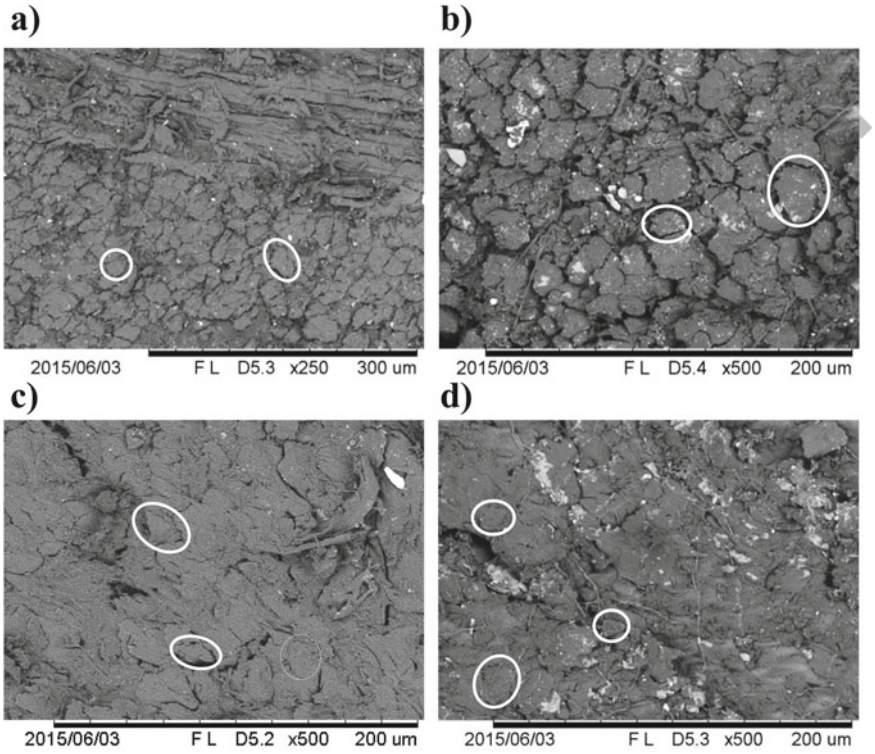


Fig. 5 SEM images—Fiber/matrix interface in an undamaged area before and after conditioning. Elementary fibres are circled in white. The bright white areas are charge accumulations. **a** bio-epoxy/flax, 0 h. **b** bio-epoxy/flax, 720 h. **c** polyurethane/flax, 0 h. **d** polyurethane/flax, 720 h. Reprinted from Cuinat-Guerraz et al. (2016) with the permission from Elsevier

the epoxy and flax fibers, where, these defects cannot be observed in the interface of flax/PU. This explains that why the flax/PU bio-composites has increasing trend in short beam strength after hygrothermal aging. Based on SEM images in Fig. 5c, d, it can be seen the matrix cracking defects into the PU matrix, which explains the reduction in mechanical properties of flax fibers/PU after 720 h aging (Cuinat-Guerraz et al. 2016).

Figure 6 shows the tensile strength of flax fibers/epoxy composites, which aged at the different temperatures of 23, 37.8 and 60 ˚C in the various immersion times. It can be seen that at the beginning stage of aging, the tensile strength had increasing trend and then stabilized for the samples being aged at 23 ˚C. In the aged sample at the temperature of 37.8 ˚C, the tensile strength slightly decreased, while by setting the aging temperature on the 60 ˚C, the tensile strength showed the seriously reduction. By this figure, it can be completely described the effect of hygrothermal aging and related mechanisms in the flax fibers/epoxy composites. At the first stages of aging, the water molecules can be permeated into the composites. The micro-fibrillar angle

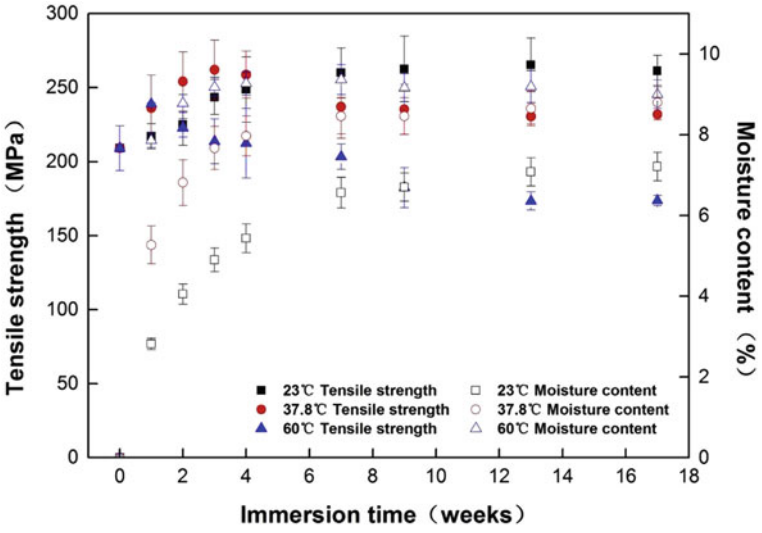


Fig. 6 Evolution of tensile strength and moisture content with immersion time of flax fabric/epoxy bio-composites at 23, 37.8 and 60 ˚C. Reprinted from Li and Xue (2016) with the permission from Elsevier

into the flax fibers can be modified by attaching free hydrophilic groups in S_2 layer on the water molecules, which resulting to the improving the tensile strength in this bio-composite. If absorbing the water molecules be continued by increasing the immersion times, the swelling each cell-wall layer of flax fibers can be occurred. This phenomenon caused that the transferred stresses by matrix cannot be loaded into the layers of flax fibers. In other words, the degradation of flax fibers can occur, resulting to reduce the tensile strength (Li and Xue 2016).

In the following two different behaviors can be observed into the flax fibers as natural fibers, which these behaviors are dependent to the aging temperature. In the lower aging temperature, the water absorption will be continued until the flax fibers be saturated. In this approach, the tensile strength can be stabilized and the reduction trend is stopped. In the higher aging temperatures (seen Fig. 6 in the temperature of 60 ˚C), the dissolution of pectins, hemi-celluloses and some poorly crystalized cellulose can be occurred in the primary wall of flax fibers. By occurring this phenomenon, the stress cannot efficiently transfer to the highly crystalline cellulose fibrils, consequently, the deterioration in the tensile strength of flax fibers reinforced bio-composites occurs (Li and Xue 2016).

Figure 7 shows the variation of tensile strength of aged and then dried samples. Based on this figure, it can be said that the tensile strength could be recovered for samples being aged up to 37.8 ˚C in the lower immersion times. This interesting phenomenon can be occurred, when the matrix neutralizes the degradation mechanisms. In other words, during the aging stages, the interaction between epoxy with viscoelastic behavior neutralized the plasticization and swelling mechanisms

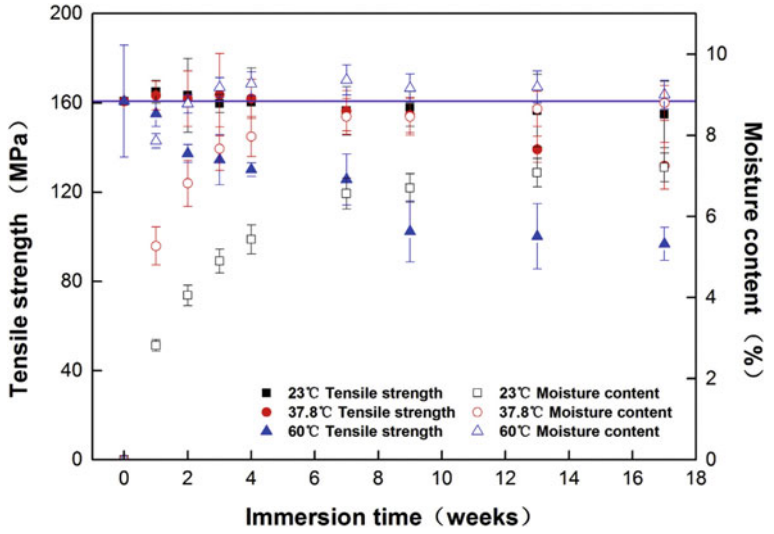


Fig. 7 Evolution of tensile strength of the specimens being aged and dried. The changes of moisture content with immersion time of flax fabric/epoxy bio-composites at 23, 37.8 and 60 ˚C were also shown. Reprinted from Li and Xue (2016) with the permission from Elsevier

in the flax fibers, resulted to recovery of tensile strength. Based on Fig. 7, it can be observed that this bio-composite could not completely recover its initial tensile strength, when the splitting and peeling occurred into the flax fibers. It seems that by using this recovery behavior and developing that via smart materials can improve the hygrothermal aging resistance into the bio-composites in the new future (Li and Xue 2016).

In the study of Scida et al. (2013), the flax fibers/epoxy composites were immersed into the environment with relative humidity of 90% and temperatures of 20 and 40 ˚C for 38 days. Figure 8 shows the fracture surface of these composites after hygrothermal aging. In unaged sample, the damage mechanism was the flax fibers fractures. Also, fibers pull out and debonding damage modes were seen. In the aged sample at 20 ˚C the micro-cavity of matrix was observed. By comparing Fig. 8a, d, it can be found that the aging flax fibers-epoxy bio-composites had similar damage mode, which was fibers fracture. Similar results in tensile strength was observed in the previous work (Li and Xue 2016) at the temperature of 37.8 ˚C. This means that this bio-composite up to 40 ˚C can resist against the hygrothermal aging in the low immersion times.

Due to the hygrothermal aging on the behavior of interfaces into the bio-composites, it can be predicted that the fatigue behaviors of these composites have reducing trend under these environments. Sodoke et al. (2016) investigated the fatigue behavior of the flax-epoxy composite under the hygrothermal aging in the temperature of 60 ˚C. By acoustic emission and SEM observation, they detected that the

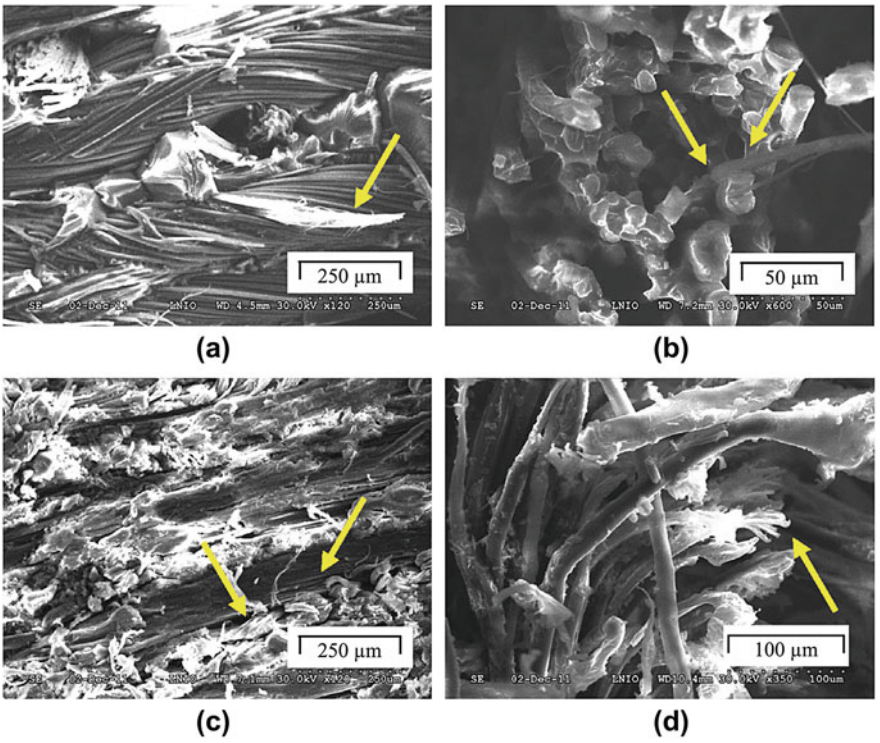


Fig. 8 SEM images taken from the fracture surfaces of flax fibers/epoxy bio-composites: unaged (**a**–**b**), after 38 days of ageing at 20 ˚C and 90% relative humidity (**c**) and after 38 days of ageing at 40 ˚C and 90% relative humidity (**d**) Reprinted from Scida et al. (2013) with the permission from Elsevier

flax/epoxy debonding and fibers pulling-out, were the main damage mechanisms during the fatigue of aged this bio-composite.

Surface modifying the natural fibers like flax fibers can improve the adhesion between fibers/matrices, which resulting to improve the mechanical properties. Wang et al. (2019a) modified the flax fibers with the alkalization, silanization and acetylation treatments. The obtained results showed that the diffusion coefficient of flax/epoxy bio-composites had the reducing trend under the hygrothermal conditions. Reducing this parameter especially by acetylation treatment improved the creep behavior of this aged bio-composite. In other work, this research group (Wang and Petru 2019) investigated the dynamic mechanical behavior of these aged bio-composites. Compared with the untreated bio-composite, the storage modulus increased after the surface treatments especially acetylation treatment. They mentioned that by the chemical treatment, the surface of flax fibers be more cleaner and rougher. Also, changing surface morphology led to large contact in their interfaces, resulted to the stringer interfaces and lower molecular mobility in the bio-composites.

3 Hemp Fibers Reinforced Bio-composites

One of the natural fibers with the high cellulose content is the hemp fibers, which have noteworthy mechanical properties, so that, they can be comparable with the glass or Kevlar fibers (Thygesen et al. 2007). Given up researches, it can be said that the most of the hygrothermal aging studies have been done about the hemp/concrete or hemp/ceramic based composites (Ahmad et al. 2020; Hussain et al. 2019). Whereas, the reported researches about the effect of hygrothermal aging on the mechanical properties of hemp/polymer composites is so limited. Some of the interesting research works are introduced in the following. One of the interesting research work is the hygrothermal aging the hemp/poly lactic acid (PLA) bio-composites, which was done by Islam et al. (2010). They added 30% aligned untreated long (AUL) and aligned alkali treated long (AAL) hemp fibers into the PLA matrix. For carrying out the hygrothermal aging, they subjected these composites into the water with the temperatures of 25 and 50 ˚C for 3 months. The effect of hygrothermal aging on the mechanical behaviors have been showed in Fig. 9.

As can be seen, the hygrothermal aging reduced all mechanical properties except the impact strength. These researchers mentioned that the plasticisation effect in the interface of hemp fibers/PLA was the reason of this increment. In other words, absorbing the moisture caused the swelling phenomenon on the surface of fibers, resulted to enhance the frictional work of fibers pull out from PLA matrix. Battegazzore et al. (2018) fabricated the hemp/cornstarch bio-composites as based board for building, automotive and in-door furniture. They aged this composite for 50 days. Figure 10 shows the effect of various relative humidity and temperature on the storage modulus of this bio-composite.

4 Wood Fibers Reinforced Bio-composites

Woods are one of the main sources for extracting the reinforcement for using in the bio-composites. Wood powders, short fibers, wood flour and Kraft fibers are the various wood ingredients, which can be used into the bio-composites (Beg and Pickering 2008a, b; Kamau-Devers et al. 2019; Mejri et al. 2018; Xu et al. 2015). For having the better view about the effect of hygrothermal aging on the wood based bio-composites, some of the interesting literatures are reviewed in the following. Beg and Pickering (2008a, b) fabricated the Kraft fibers/MAPP bio-composites. The percentage of used fibers into the MAPP was about the 40 wt%. Also, they aged this composite for 238 days and then investigated the effect of hygrothermal aging on the tensile strength, elastic modulus, failure strain, and impact strength of that. The outcome of these results are listed in the Table 2. Based on this table, the reduction of tensile strength and elastic modulus was due to degradation of fibers. The degradation in the interface was another reason, which was due to developing the shear stress at the interface through absorbing moisture, resulted to creating voids and pulling

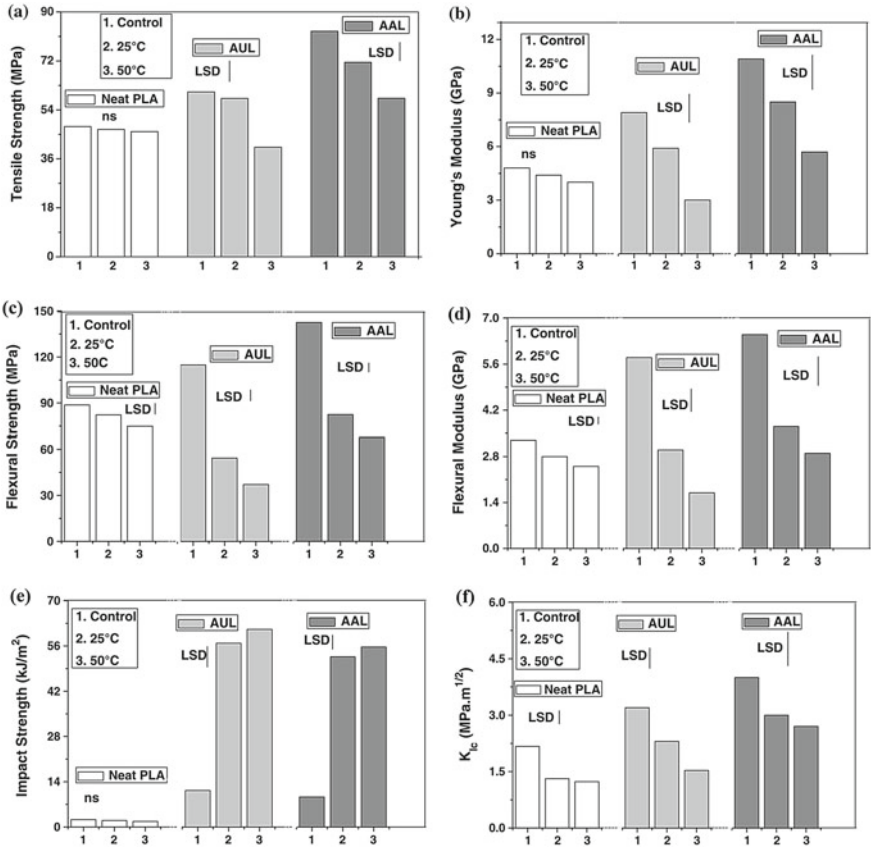


Fig. 9 Effect of hygrothermal ageing on mechanical properties of neat PLA, AUL and AAL composites at two different temperatures compared to control; **a** tensile strength, **b** Young's modulus, **c** flexural strength, **d** flexural modulus, **e** impact strength, **f** fracture toughness. LSD values are reported for significant ANOVA results. Reprinted from Islam et al. (2010) with the permission from Springer

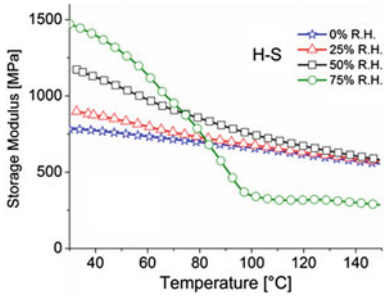


Fig. 10 Storage modulus as a function of temperature for hemp fibers/starch bio-composite. Reprinted from Battegazzore et al. (2018) with the permission from Springer

Table 2 The properties of composites with 40 wt% Kraft fibers before and after 238 days ageing. Reused from Beg and Pickering (2008a, b) with the permission from Elsevier

Properties	Composites	Hygrothermal ageing temperature (˚C)			
		Unaged	30	50	70
Diffusion coefficient (m^2/s)	With 4 wt% MAPP		–	2.4×10^{-13}	6.2×10^{-13}
	Without MAPP	–	2.9×10^{-13}	5.7×10^{-13}	8.8×10^{-13}
Thickness swelling (%)	With 4 wt% MAPP	–	2.3	3	3.2
	Without MAPP	–	3.7	4.2	4.7
Tensile strength (MPa)	With 4 wt% MAPP	41 ± 1.4	28	22.5	17
	Without MAPP	23 ± 1.5	19	17.5	16
Elastic modulus (MPa)	With 4 wt% MAPP	4553 ± 489	2282	2029	1578
	Without MAPP	3619 ± 436	1291	1226	1133
Failure strain (%)	With 4 wt% MAPP	1.99 ± 0.5	4	2.8	2.7
	Without MAPP	1.3 ± 0.37	5.6	5	4
Impact strength (KJ/m^2)	With 4 wt% MAPP	6.2 ± 0.5	11.5	9.2	6.3
	Without MAPP	5.5 ± 0.6	11.3	9.0	7.7

out the fibers in this composite. In this work, the failure strain and impact strength had the increasing trend after the hygrothermal aging, which was due to plasticizing effect in this composite. Wang et al. (2020a) aged the wood powder/PP composites by immersion those into the water with the temperature of 60 ˚C. The obtained results showed that absorbing water degraded the mechanical properties of these bio-composites, so that, the tensile strength and elastic modulus of composites with 15, 30 and 45 % wood powders reduced about 5.79, 17.2, 32.06, 25.3, 33.6 and 47.3%, respectively.

Del Saz-Orozco et al. (2015) added the lignin particles and wood flour to the phenolic foam and then investigated the effect of hygrothermal aging (38 ˚C, 97 ~ relative humidity for 2 weeks) on the mechanical properties and morphology of bio-composites. Like other bio-composites, the hygrothermal aging reduced the mechanical properties of these composites. Based on Fig. 11, these researchers mentioned, the cell size of these composite foams was not influenced by hygrothermal aging, whereas, they expected the increasing trend in the cell size. Because Desai et al. (2010) found that the cell sizes of phenolic, glass fibers/phenolic and aramid fibers/phenolic foams were increased, when they subjected under the 85% relative humidity at 40 ˚C for 6 weeks, this means that the lignin particles and wood flour prevented to change the cell size into these foams. As we know, changing the cell size of foam influences on the mechanical behavior of that, so that, increasing of that reduces the mechanical properties. To characterize the related mechanisms in these bio-composites under hygrothermal aging more investigations must be done in the future.

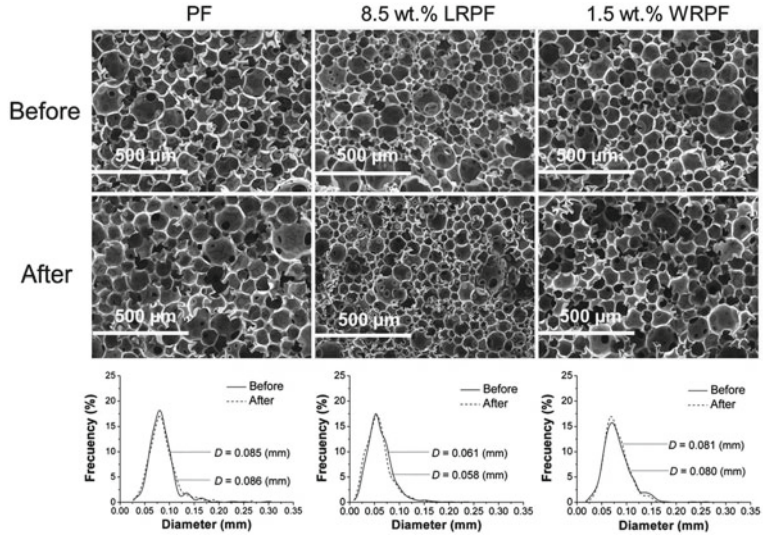


Fig. 11 SEM images and cell size distributions for unreinforced and reinforced phenolic foams before and after hygrothermal aging (LRPF: Lignin reinforced phenolic foams; WRPF: Wood reinforced phenolic foams). Reprinted from Del Saz-Orozco et al. (2015) with the permission from Elsevier

5 Bamboo Fibers Reinforced Bio-composites

Bamboo fibers are one of the natural fibers which slightly inferior to glass fibers in terms of mechanical properties, but they are approximately 10 times cheaper than glass fibers. Therefore, many studies with the comparing approach were done for using them instead of glass fibers (Sit and Ray 2019). To have the better view about the performance of bamboo fibers/polymeric bio-composites in the harsh conditions, it is better to compare the function of these bio-fibers into the various polymers in the hygrothermal situations, which has been listed in Table 3. Based on Table 3, it can be found that the bamboo fibers into the phenol formaldehyde matrix lost about the half of initial modulus, which the reason of that was the creating the crack and microcracks after subjecting this bio-composite into the hygrothermal condition (Zhou et al. 2019). In the study of Azwa and Yousif (2019), the bamboo fibers firstly were treated by NaOH solution as alkali surface modification method. Therefore, based on the reported results, it seems that the reduction trend in the tensile strength of bamboo/polyester bio-composites is negligible. The characterized mechanisms for this reduction were the eroding fibrils and shrinking the polyester under high temperature. The shear strength of bamboo fibers into the PP matrix showed the increasing trend after the aging under hygrothermal condition. This increment can be due to the rearranging the molecular chain of PP at the high temperature, which increased the crystalline structure of this polymer.

Table 3 Comparing the function of bamboo fibers into the various polymers after the hygrothermal aging

Composite	Properties	Variations	Mechanisms	Hygrothermal condition	References
Bamboo scrimber/phenol formaldehyde	Elastic modulus	44.33% reduction	Creation of cracks and microcracks	63 ˚C, 152 h	Zhou et al. (2019)
Bamboo bundle/phenol formaldehyde	Elastic modulus	53.89% reduction	Creation of cracks and microcracks	63 ˚C, 152 h	Zhou et al. (2019)
Bamboo laminated timber/ phenol formaldehyde	Elastic modulus	25.83% reduction	Creation of cracks and microcracks, Delamination	63 ˚C, 152 h	Zhou et al. (2019)
Bamboo/polyester	Tensile strength	13.6% reduction	Eroded fibrils Matrix shrinkage	80 ˚C, 48 h	Azwa and Yousif (2019)
Bamboo/polypropylene	Tensile strength	14.6% reduction	Damaging the matrix bonds	40 ˚C, 10 days, 93% relative humidity	Chunhong et al. (2016)
Bamboo/polypropylene	Shear strength	13.5% increment	Rearranging molecular chains	40 ˚C, 10 days, 93% relative humidity	Chunhong et al. (2016)
Bamboo/epoxy	Tensile strength	57% reduction	–	100 ˚C, 4 h, water	Huang and Bin (2019)

6 Other Natural Fibers Reinforced Bio-composites

Although in the last decade, the natural fibers composites had growing trend, but, the study about the effect of hygrothermal conditions on the mechanical properties of most of these composites is too limited. In this section, some of the famous natural fibers bio-composites, which subjected under the hygrothermal conditions are reviewing. Jiang et al. (2019) investigated the effect of hygrothermal aging on the structural damaging of jute/PLA bio-composites by X-ray tomography. These researchers aged the bio-composites at the temperature of 50 ˚C in different duration times. By using the 3D rendering, they characterized the formed voids (as reducing agent of mechanical properties into the bio-composites) around the jute fibers after 21 days immersion time (Fig. 12). Hu et al. (2010) subjected uncoated and coated jute fibers reinforced PLA under the hygrothermal aging. The main characterized defects during the aging process were pores, microcracks, delamination, and composite structure relaxation, which extremely reduced the tensile strength of these bio-composites, after 120 h immersing into the 70˚C water vapor environment.

Bhagavathi et al. (2021) added the micro-crystalline cellulose (MCC) into the PU for investigating the effect of hygrothermal aging on the lap shear strength of biocomposite adhesive. The performed aging cycle was heating the bio-composite

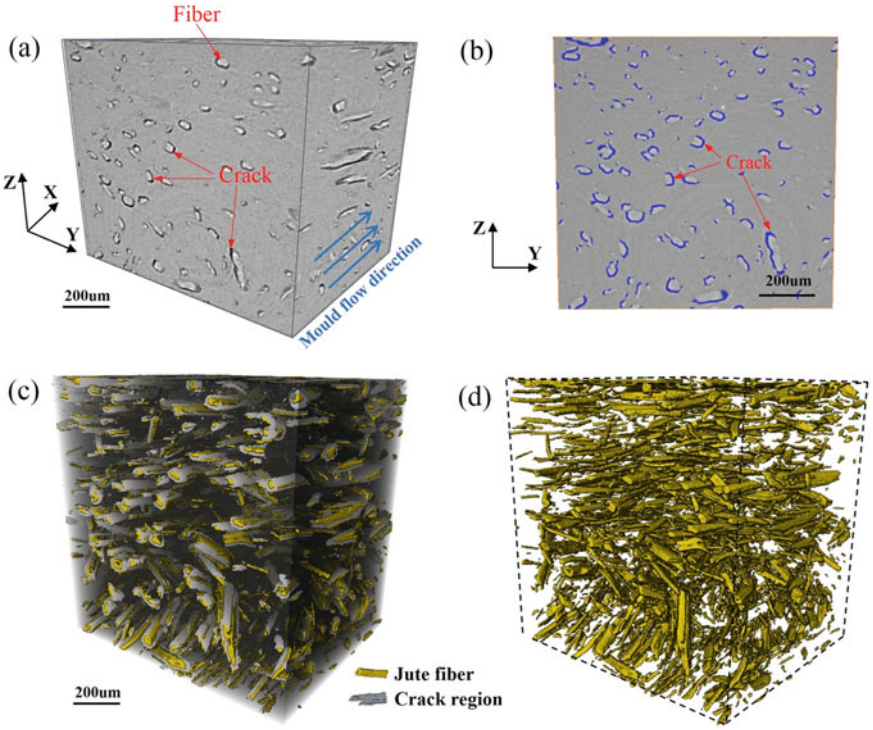


Fig. 12 Distribution of voids and jute fibers in the composite after aging 21 days; **a** 3D dimensional view (HR tomograph) with fibers and cracks labeled, **b** image segmentation by contrast threshold to identify voids (cracks), **c** 3D rendering of segmented fibers and cracks, **d** 3D rendering of fibers only. Reprinted from Jiang et al. (2019) with the permission from Elsevier

to 40 ˚C and holding that for 15 h with the relative humidity of more than 90%, in the following, cooling that down to −20 ˚C and holding it for 2 h, and in the final step, heating that up to 70˚C for holding 4 h in the relative humidity of 50%. The obtained results showed that after one week of hygrothermal aging, the strength was enhanced, which was possibly due to a post curing effect of PU, resulted to stronger interface between MCC and PU. The shear strength of this biocomposite reduced in the second week and after 4 weeks, the shear strength of that was lower than unaged sample. Aouat et al. (2019) added MCC and cellulose nano-whiskers (CNW) into the PLA. Then, the effect of hygrothermal aging (95% relative humidity in the temperatures of 45 and 60 ˚C for various durations) on the tensile properties of those bio-composites were investigated. After 25 days, the elastic modulus of exposed MCC to the 45 ˚C was reduced from 2.95 to 2.77 GPa. Also, the obtained modulus after 7 days in the exposure temperature of 60˚C reduced down to 1.3 GPa. The elastic modulus of CNW/PLA was about 3.38 GPa. After 25 days in the temperature of 45 ˚C and 7 days in the temperature of 60 ˚C, the elastic modulus was 3.02 and 1.1 GPa,

respectively. The molecular weight reduction due to chain scission and degradation of bio-composites were the mentioned mechanisms for these reduction trends.

In some cases, the extracted reinforcements from natural sources can be added in form of particles or short fibers into the polymers. For example, Mohd Ishak et al. (2001) added rice husk into the PP to investigate the effect of hygrothermal aging on this bio-composite. The aging environment was water with the temperatures of 35 and 90 ˚C, which this biocomposite was put into that for 35 h. The obtained tensile strength of sample at the temperature of 30 ˚C showed 3.7% reduction, while at the temperate of 90 ˚C, the tensile strength reduced about 14.7%. The deterioration interfacial bonding was reported as reason of this reduction trends. In other work, Yu et al. (2018) included the ramie short fibers into the PLA. The obtained results after hygrothermal aging (water bath with temperature of 60˚C for three weeks) showed reducing trend in tensile, flexural and impact strengths, which were about 91, 89 and 44%, respectively. The degradation of PLA and debonding were the effective mechanisms in this work.

7 Polymer Composite Bio-materials

Some of the polymers like PE, PEG, PLA, PCL and PEEK can be used in the bio-applications, because of having biocompatibility (Paxton et al. 2019). For improving the features of these polymers, they can be composed with the other materials. In this section, some admirable research works, which have investigated the effect of hygrothermal aging on the mechanical performance of these materials, are briefly reviewed. Salem et al. (2021) added MoS_2, cuttlebone (CB) and red coral (RC) to high density polyethylene (HDPE). Then, they immersed these composites into the water and Ringer's solution at the temperature of 80˚C for 21 days to investigate the effect of hygrothermal aging on the tribology behaviors. Figure 13 depicts the wear rate of unaged and aged these composites. Based on this figure, it can be found that HDPE-CB had the maximum wear rate, so that, after aging, the wear rate enhanced about 50%, which was due to degradation of fiber-matrix interface by water absorbing and swelling CB in this composite. The aged HDPE-MoS_2 composites in Ringer's solution and water showed about 15% increment in wear rate. Oxidizing MoS_2 and producing MoO_3 and H_2S from that were mentioned as increment mechanisms in this sample. The aged HDPE-RC composite in water environment had not noteworthy changes, but into the Ringer's solution showed 24% increment in the wear rate. The RC has Mg-calcite in its structure. So, Mg can react with chloride ions of Ringer's solution, which caused to dissolution of Mg-calcite, resulted to create debonding phenomenon in the interface of RC/HDPE. Belotti et al. (2019) added 0.5 wt% graphene oxide (GO), 1 wt% nano diamond, 10 wt% short carbon fibers and all of them into ultra-high molecular weight polyethylene (UHMWPE). The wear results of unaged and aged samples have been illustrated in Fig. 14. Based on these results, the authors said that the hygrothermal aging had not significantly effect on the wear performance of these composites. Tham et al. (2014) aged the halloysite nanoclay

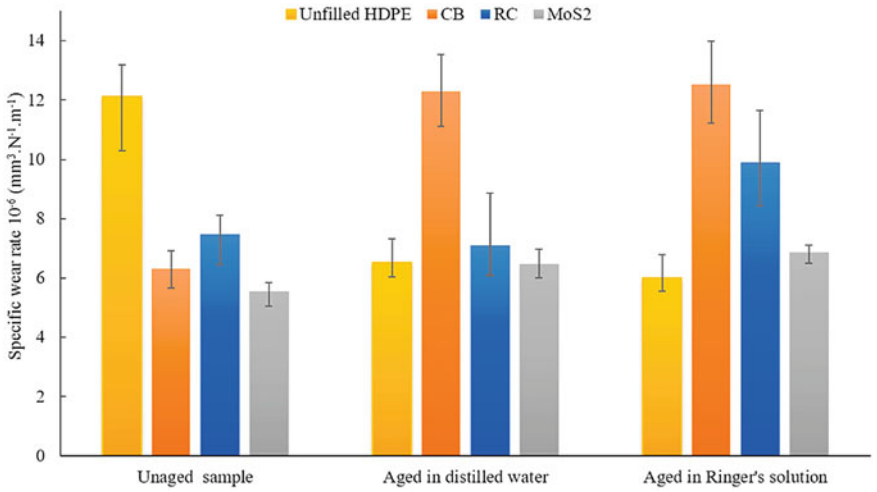


Fig. 13 Average specific wear rate of HDPE composites at the end of wear tests. Reprinted from Salem et al. (2021) with the permission from Elsevier

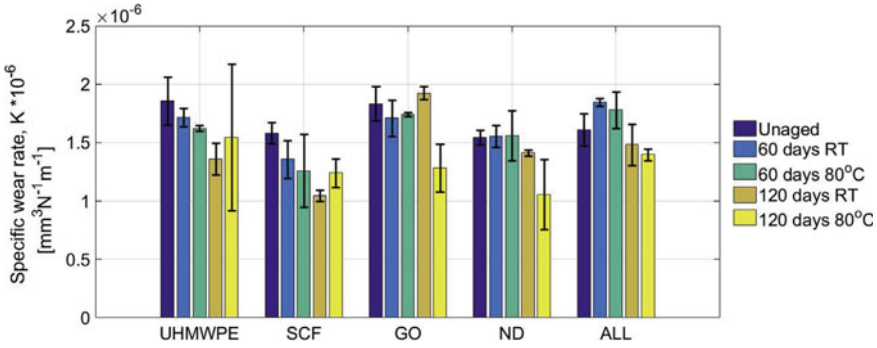


Fig. 14 Average specific wear rate of the composites (UHMWPE: Ultra high molecular weight polyethylene; SCF: Short carbon fibers; GO: Graphene oxide; ND: Nano diamonds). Reprinted from Belotti et al. (2019) with the permission from Elsevier

(HNC)/PLA bio-composite in the different temperatures of 30, 40 and 50 ˚C for investigating the effects of aging on the Charpy impact properties. They found that in the temperature of 50 ˚C, the PLA was hydrolyzed, so that, the aging environment became acidic (pH in range of 2.5–2.7). This finding introduces the new mechanism, which can reduce the mechanical properties of PLA bio-composites.

Malmstein et al. (2013) compared the flexural properties of aged glass fibers/linseed oil, glass fibers/castor oil and glass fibers/epoxy composites in the various aging duration times. Based on the obtained results from this literature, it

can be said that after the aging, the glass fibers/castor oil composite had lower reduction in the flexural properties, as compared with glass fibers/epoxy as conventional composite. Whereas, the glass fibers/linseed oil composite could not resist against the hygrothermal conditions, so that, after 20 weeks, it lost about 70% of initial flexural properties. In the study of Tserpes et al. (2019), the carbon fibers/rosin based epoxy resin as bio-composite was exposed to the temperature of 70 ˚C with relative humidity of 85% for 7 days. The reported results from interlaminar shear strength showed, this bio-composite had good resistance against this hygrothermal aging, so that, the only negligible reduction was seen in this mechanical property.

8 Partially/Fully Bio-reinforced Hybrid Composites

Several definitions are introduced by various researchers for hybrid composites. One of the common definitions is that the hybrid composites are the materials with the at least two different reinforcements into a common matrix. The hybrid composites can be categorized according to the used reinforcements, which can be two different fibers (Ebrahimnezhad-Khaljiri et al. 2020a) or nano/micro fillers (Bigdilou et al. 2020), fiber-metal (Ebrahimnezhad-Khaljiri et al. 2020b), and fiber-filler (Chavhan and Wankhade 2020). The aim of hybridization is to achieve the new features into the composite materials. Therefore, the second reinforcement can be added into the bio-composites to develop the new features into them. The aim of this section is to introduce some admirable researches about the interaction of hygrothermal aging and mechanical properties into the hybrid bio-composites. It can be introduced the new definition for these composites, which are partially bio-reinforced hybrid composites (PBRHC) or fully bio-reinforced hybrid composites (FBRHC). In the PBRHC, at least one of the reinforcements should be bio-based materials, whereas in the FBRHC, all of the reinforcements such as fibers and fillers are bio-based materials.

Cheng et al. (2020) fabricated carbon/flax hybrid composites with the various configurations for subjecting them into the water bath with the temperature of 60 ˚C for 300 h. The obtained results showed that the tensile and flexural strengths decreased after aging. In the hybrid composites, the carbon layer caused to alleviate the interfacial deterioration due to protecting effect of that against the water molecules diffusion. In the similar work, Wang et al. (2020b) aged these hybrid composites under relative humidity of 85% in the temperatures of 40 and 70 ˚C. Like previous work, they mentioned that the carbon fibers had isolating effect, especially when they are located on the surface of flax fibers, so that, the diffusion rate of water molecules extremely reduced, resulted to decrease the destructive effects of hygrothermal aging. The basal/jute-epoxy composite is one of the PBRHY, which can be used in many applications. Fiore et al. (2017) investigated the hygrothermal aging (87% relative humidity at the temperature of 35˚C for 115 min) resistance of that. The reported results showed that the sandwich structures had the better aging resistance especially when the basalt fibers are used as outer layers. By increasing the thickness of basalt layers on the surface, the aging resistance improved, which

was due to postponing the degradative effects of aging. Wang et al. (2019b) used the nanoclay in form of grafting method in the flax/epoxy bio-composites to improve the hygrothermal aging resistance. The grafting nanoclay on the flax fibers reduced the saturation moisture uptake and coefficient of diffusion by 38.4 and 13.2%, respectively. After immersing six weeks, the retention rate of tensile modulus in the composite containing nanoclay increased about 33.8%, as compared with neat flax/epoxy composite. The grafted nanoclay had not obvious effect on the tensile strength composites under hygrothermal aging, but increased the tensile strain.

9 Conclusion

In the last decade, many efforts have been done by various research groups to develop the bio-composites for using them instead of conventional composites, due to having lower production costs and environmental issues. Being into the harsh environments like hygrothermal situations can influence on the mechanical properties of these composites. If the relative humidity and temperature of this environment be moderate, some mechanical properties such as impact strength, failure strain and shear strength may be improved by plasticizing the matrix or changing the fibrils angels. But, if the temperature and relative humidity of hygrothermal environment be high, the bio-composites cannot resist against the aging in this environment, which resulting to the deterioration of mechanical properties. The effect of water molecules on the bio-fibers, matrices, and the fibers/matrix interfaces are the main reasons of these deteriorations. Controlling the diffusion of water molecules can reduce the hygrothermal aging effects, which can be done by surface treatments of bio-fibers.

10 Future Perspective

Although, the effect of hygrothermal aging in some of the bio-composites has been investigated by various research groups, but the only flax, hemp and wood based bio-composites had proper developing trend and the study on the other famous bio-composites like sisal and jute based bio-composite is too limited. Therefore, it can be predicted, these bio-composites will develop in the future. Reducing the destructive effects of hygrothermal aging is the subject, which can be developed by selecting the proper surface modification of bio-fibers or adding the proper nanoparticles for reducing the hydrophilicity of bio-fibers. Enhancing the strength in the fibers/matrix interfaces by nanomaterials especially nano callouses crystalline or whiskers is another way for improving the hygrothermal resistance in bio-composites. The other developing view point is creating the recovery capability of initial mechanical properties under hygrothermal aging, which can be done by creating self-healing ability or changing the fibril angels into the bio-composites.

References

Ahmad MR, Chen B, Haque MA, Shah SFA (2020) Utilization of industrial and hazardous waste materials to formulate energy-efficient hygrothermal bio-composites. J Clean Prod 250. https://doi.org/10.1016/j.jclepro.2019.119469

Akampumuza O, Wambua PM, Ahmed A et al (2017) Review of the applications of biocomposites in the automotive Industry. Polym Compos 38:2553–2569. https://doi.org/10.1002/pc.23847

Alam P, Robert C, Brádaigh Ó, CM, (2018) Tidal turbine blade composites—a review on the effects of hygrothermal aging on the properties of CFRP. Compos Part B Eng 149:248–259. https://doi.org/10.1016/j.compositesb.2018.05.003

Aouat T, Kaci M, Lopez-Cuesta JM, Devaux E (2019) Investigation on the durability of PLA bionanocomposite fibers under hygrothermal conditions. Front Mater 6:323. https://doi.org/10.3389/fmats.2019.00323

Azwa ZN, Yousif BF (2019) Physical and mechanical properties of bamboo fibre/polyester composites subjected to moisture and hygrothermal conditions. Proc Inst Mech Eng Part L J Mater Des Appl 233:1065–1079. https://doi.org/10.1177/1464420717704221

Bigdilou B, M, Eslami-Farsani R, Ebrahimnezhad-Khaljiri H, Mohammadi MA, (2020) Experimental assessment of adding carbon nanotubes on the impact properties of Kevlar-ultrahigh molecular weight polyethylene fibers hybrid composites. J Ind Text. https://doi.org/10.1177/1528083720921483

Battegazzore D, Alongi J, Duraccio D, Frache A (2018) All natural high-density fiber- and particleboards from hemp fibers or rice husk particles. J Polym Environ 26:1652–1660. https://doi.org/10.1007/s10924-017-1071-9

Beg MDH, Pickering KL (2008a) Reprocessing of wood fibre reinforced polypropylene composites. Part II: Hygrothermal ageing and its effects. Compos Part A Appl Sci Manuf 39:1565–1571. https://doi.org/10.1016/j.compositesa.2008.06.002

Beg MDH, Pickering KL (2008b) Mechanical performance of Kraft fibre reinforced polypropylene composites: Influence of fibre length, fibre beating and hygrothermal ageing. Compos Part A Appl Sci Manuf 39:1748–1755. https://doi.org/10.1016/j.compositesa.2008.08.003

Belotti LP, Vadivel HS, Emami N (2019) Tribological performance of hygrothermally aged UHMWPE hybrid composites. Tribol Int 138:150–156. https://doi.org/10.1016/j.triboint.2019.05.034

Bhagavathi LR, Deshpande AP, Janaki Ram GD, Panigrahi SK (2021) Hygrothermal aging, fatigue and dynamic mechanical behavior of cellulosic particles reinforced one-component moisture curable polyurethane adhesive joints. Int J Adhes Adhes 105. https://doi.org/10.1016/j.ijadhadh.2020.102771

Cadu T, Van Schoors L, Sicot O et al (2019) Cyclic hygrothermal ageing of flax fibers' bundles and unidirectional flax/epoxy composite. Are bio-based reinforced composites so sensitive? Ind Crops Prod 141:111730. https://doi.org/10.1016/j.indcrop.2019.111730

Chavhan GR, Wankhade LN (2020) Improvement of the mechanical properties of hybrid composites prepared by fibers, fiber-metals, and nano-filler particles—a review. Mater Today Proc 27:72–82. https://doi.org/10.1016/j.matpr.2019.08.240

Cheng M, Zhong Y, Kureemun U et al (2020) Environmental durability of carbon/flax fiber hybrid composites. Compos Struct 234. https://doi.org/10.1016/j.compstruct.2019.111719

Chunhong W, Shengkai L, Zhanglong Y (2016) Mechanical, hygrothermal ageing and moisture absorption properties of bamboo fibers reinforced with polypropylene composites. J Reinf Plast Compos 35:1062–1074. https://doi.org/10.1177/0731684416637681

Cuinat-Guerraz N, Dumont MJ, Hubert P (2016) Environmental resistance of flax/bio-based epoxy and flax/polyurethane composites manufactured by resin transfer moulding. Compos Part A Appl Sci Manuf 88:140–147. https://doi.org/10.1016/j.compositesa.2016.05.018

Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Lignin particle- and wood flour-reinforced phenolic foams: Friability, thermal stability and effect of hygrothermal aging on mechanical

properties and morphology. Compos Part B Eng 80:154–161. https://doi.org/10.1016/j.compositesb.2015.05.043
Desai AA, Basbagill J, Nutt SR, Alonso MV (2010) Diffusivity and climatic simulation of hybrid foams. J Cell Plast 46:461–478. https://doi.org/10.1177/0021955X10373641
Ebrahimnezhad-Khaljiri H, Eslami-Farsani R, Akbarzadeh E (2020a) Effect of interlayer hybridization of carbon, Kevlar, and glass fibers with oxidized polyacrylonitrile fibers on the mechanical behaviors of hybrid composites. Proc Inst Mech Eng Part C J Mech Eng Sci 234:1823–1835. https://doi.org/10.1177/0954406219897935
Ebrahimnezhad-Khaljiri H, Eslami-Farsani R, Talebi S (2020b) Investigating the high velocity impact behavior of the laminated composites of aluminum/jute fibers-epoxy containing nanoclay particles. Fibers Polym 21:2607–2613. https://doi.org/10.1007/s12221-020-1209-6
Fiore V, Scalici T, Badagliacco D et al (2017) Aging resistance of bio-epoxy jute-basalt hybrid composites as novel multilayer structures for cladding. Compos Struct 160:1319–1328. https://doi.org/10.1016/j.compstruct.2016.11.025
Hu RH, Sun M, young, Lim JK, (2010) Moisture absorption, tensile strength and microstructure evolution of short jute fiber/polylactide composite in hygrothermal environment. Mater Des 31:3167–3173. https://doi.org/10.1016/j.matdes.2010.02.030
Huang JK, Bin YW (2019) The mechanical, hygral, and interfacial strength of continuous bamboo fiber reinforced epoxy composites. Compos Part B Eng 166:272–283. https://doi.org/10.1016/j.compositesb.2018.12.013
Hussain A, Calabria-Holley J, Lawrence M, Jiang Y (2019) Hygrothermal and mechanical characterisation of novel hemp shiv based thermal insulation composites. Constr Build Mater 212:561–568. https://doi.org/10.1016/j.conbuildmat.2019.04.029
Islam MS, Pickering KL, Foreman NJ (2010) Influence of hygrothermal ageing on the physico-mechanical properties of alkali treated industrial hemp fibre reinforced polylactic acid composites. J Polym Environ 18:696–704. https://doi.org/10.1007/s10924-010-0225-9
Jiang N, Yu T, Li Y et al (2019) Hygrothermal aging and structural damage of a jute/poly (lactic acid) (PLA) composite observed by X-ray tomography. Compos Sci Technol 173:15–23. https://doi.org/10.1016/j.compscitech.2019.01.018
Jin P, Wang D, Tan X (2012) Review of hygrothermal effects on carbon fiber-reinforced composite materials. Adv Mater Res 490–495:3611–3615. https://doi.org/10.4028/www.scientific.net/AMR.490-495.3611
Kamau-Devers K, Kortum Z, Miller SA (2019) Hydrothermal aging of bio-based poly(lactic acid) (PLA) wood polymer composites: studies on sorption behavior, morphology, and heat conductance. Constr Build Mater 214:290–302. https://doi.org/10.1016/j.conbuildmat.2019.04.098
Li Y, Xue B (2016) Hydrothermal ageing mechanisms of unidirectional flax fabric reinforced epoxy composites. Polym Degrad Stab 126:144–158. https://doi.org/10.1016/j.polymdegradstab.2016.02.004
Malmstein M, Chambers AR, Blake JIR (2013) Hygrothermal ageing of plant oil based marine composites. Compos Struct 101:138–143. https://doi.org/10.1016/j.compstruct.2013.02.003
Mejri M, Toubal L, Cuillière JC, François V (2018) Hygrothermal aging effects on mechanical and fatigue behaviors of a short-natural-fiber-reinforced composite. Int J Fatigue 108:96–108. https://doi.org/10.1016/j.ijfatigue.2017.11.004
Mohd Ishak ZA, Yow BN, NG BL et al (2001) Hygrothermal aging and tensile behavior of injection-molded rice husk-filled polypropylene composites. J Appl Polym Sci 81:742–753. https://doi.org/10.1002/app.1491
Mokhothu TH, John MJ (2015) Review on hygroscopic aging of cellulose fibres and their biocomposites. Carbohydr Polym 131:337–354. https://doi.org/10.1016/j.carbpol.2015.06.027
Mosiewicki MA, Aranguren MI (2013) A short review on novel biocomposites based on plant oil precursors. Eur Polym J 49:1243–1256. https://doi.org/10.1016/j.eurpolymj.2013.02.034
Paxton NC, Allenby MC, Lewis PM, Woodruff MA (2019) Biomedical applications of polyethylene. Eur Polym J 118:412–428. https://doi.org/10.1016/j.eurpolymj.2019.05.037

Retegi A, Arbelaiz A, Alvarez P et al (2006) Effects of hygrothermal ageing on mechanical properties of flax pulps and their polypropylene matrix composites. J Appl Polym Sci 102:3438–3445. https://doi.org/10.1002/app.24331

Salem A, Bensalah W, Mezlini S (2021) Effect of hygrothermal aging on the tribological behavior of HDPE composites for bio-implant application. Polym Test 94. https://doi.org/10.1016/j.polymertesting.2020.107050

Sanjay MR, Madhu P, Jawaid M et al (2018) Characterization and properties of natural fiber polymer composites: A comprehensive review. J Cleaner Prod 172:566–581. https://doi.org/10.1016/j.jclepro.2017.10.101

Scida D, Assarar M, Poilâne C, Ayad R (2013) Influence of hygrothermal ageing on the damage mechanisms of flax-fibre reinforced epoxy composite. Compos Part B Eng 48:51–58. https://doi.org/10.1016/j.compositesb.2012.12.010

Sit M, Ray C (2019) Free vibration characteristics of glass and bamboo epoxy laminates under hygrothermal effect: a comparative approach. Compos Part B Eng 176. https://doi.org/10.1016/j.compositesb.2019.107333

Sodoke FK, Toubal L, Laperrière L (2016) Hygrothermal effects on fatigue behavior of quasi-isotropic flax/epoxy composites using principal component analysis. J Mater Sci 51:10793–10805. https://doi.org/10.1007/s10853-016-0291-z

Tham WL, Ishak ZAM, Chow WS (2014) Water absorption and hygrothermal aging behaviors of SEBS-g-MAH toughened poly(lactic acid)/halloysite nanocomposites. Polym Plast Technol Eng 53:472–480. https://doi.org/10.1080/03602559.2013.845208

Thygesen A, Thomsen AB, Daniel G, Lilholt H (2007) Comparison of composites made from fungal defibrated hemp with composites of traditional hemp yarn. Ind Crops Prod 25:147–159. https://doi.org/10.1016/j.indcrop.2006.08.002

Tserpes K, Tzatzadakis V, Katsiropoulos C (2019) Effect of hygrothermal ageing on the interlaminar shear strength of carbon fiber-reinforced rosin-based epoxy bio-composites. Compos Struct 226. https://doi.org/10.1016/j.compstruct.2019.111211

Wang X, Petrů M (2019) Effect of hygrothermal aging and surface treatment on the dynamic mechanical behavior of flax fiber reinforced composites. Materials (basel) 12:2376. https://doi.org/10.3390/ma12152376

Wang A, Xian G, Li H (2019a) Effects of fiber surface grafting with nano-clay on the hydrothermal ageing behaviors of flax fiber/epoxy composite plates. Polymers (basel) 11:1278. https://doi.org/10.3390/polym11081278

Wang X, Petrů M, Yu H (2019b) The effect of surface treatment on the creep behavior of flax fiber reinforced composites under hygrothermal aging conditions. Constr Build Mater 208:220–227. https://doi.org/10.1016/j.conbuildmat.2019.03.001

Wang A, Wang X, Xian G (2020a) Mechanical, low-velocity impact, and hydrothermal aging properties of flax/carbon hybrid composite plates. Polym Test 90. https://doi.org/10.1016/j.polymertesting.2020.106759

Wang W, Guo X, Zhao D et al (2020b) Water absorption and hygrothermal aging behavior of wood-polypropylene composites. Polymers (basel) 12:782. https://doi.org/10.3390/POLYM12040782

Xu C, Xing C, Pan Hl (2015) Hygrothermal aging properties of wood plastic composites made of recycled high density polypropylene as affected by Inorganic pigments. Polym Eng Sci 55:2127–2132. https://doi.org/10.1002/pen.24054

Yu T, Sun F, Lu M, Li Y (2018) Water absorption and hygrothermal aging behavior of short ramie fiber reinforced poly(lactic acid) composites. Polym Compos 39:1098–1104. https://doi.org/10.1002/pc.24038

Zhou H, Wang G, Chen L et al (2019) Hydrothermal aging properties of three typical bamboo engineering composites. Materials (basel) 12:1450. https://doi.org/10.3390/ma12091450

Effects of Natural Weathering on Aesthetics, Thermal and Mechanical Properties of the Bio-composites

Tarkan Akderya, Cemal Bilir, and Buket Okutan Baba

Abstract Bio-composite materials, which are a serious alternative to synthetic-based fibre and matrix materials due to their high characteristics and biodegradability, cause difficulties and uncertainties for usage conditions due to their high sensitivity to climatic conditions. Scientific studies have shown that climatic factors such as temperature, humidity, radiation, UV rays, and acid rain that act synergistically in natural weathering conditions, cause degradation and changes in the bio-composite material's characteristics. Examining the material's behaviour under natural weathering conditions provides the most realistic and reliable results in terms of determining the shelf life of the material and knowing its behaviour in the usage environment. In this study, changes in thermal, mechanical, and aesthetic properties of bio-composite materials exposed to natural ventilation conditions were investigated. It has been observed that natural weathering induces dramatic decreases in thermal and mechanical properties of bio-composite materials, especially with the effect of prolonged exposure times, and causes changes in colour, surface deterioration and changes in shape.

Keywords Natural weathering · Bio-composite · Mechanical properties · Thermal properties · Aesthetics

T. Akderya (✉)
Department of Biomedical Engineering, Faculty of Engineering and Architecture, University of Bakırçay, Menemen, Izmir 35660, Turkey
e-mail: tarkan.akderya@bakircay.edu.tr

C. Bilir
Department of Pediatric Surgery, Faculty of Medicine, University of Bakırçay, Menemen, Izmir 35660, Turkey

B. O. Baba
Department of Mechanical Engineering, Faculty of Engineering and Architecture, Izmir Katip Çelebi University, 35620 Çiğli, Izmir, Turkey

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_8

1 Introduction

Deterioration of the environment's natural equilibrium, increasing natural disasters, and environmental awareness on governmental and personal basis have led to increased sustainability awareness. Therefore, the search for environment-friendly products used in industrial and daily life has been launched. One of the areas where environment-friendly material applications are used is the field of composite material production. In this respect, it has begun to search for green composite materials that can be an alternative to synthetic fibre and synthetic matrix composite materials with a wide range of use and superior properties.

Within the scope of the search for sustainable materials, it is seen that the use of biobased plastics and their composites (bio-composites) is on a significant growth trend. Bio-composites produced from local and renewable sourced materials contribute to sustainability by increasing ecological efficiency, contributing to the establishment of green chemistry and green industry, and paving the way to produce new generation materials, processes and products (Bharath and Basavarajappa 2016). In reducing the carbon footprint caused by traditional composite materials, bio-composite materials can be an alternative, and these materials can also help reduce the strain on the environment (Chang et al. 2020).

Bio-composite materials can be evaluated in two main classes: green composites or partly eco-friendly composites, depending on the fibres and matrix's sustainability. While the matrix and fibres of green composites are entirely obtained from renewable resources, either the matrix or fibres of partly eco-friendly composites are obtained from environmentally friendly sustainable sources (Mohanty et al. 2005; Mitra 2014; Peças et al. 2018; Akderya et al. 2020).

Natural fibre-reinforced bio-composites are additives that are used as reinforcement elements, obtained from natural sources. When compared with synthetic fibres, they have superior characteristic properties such as renewability, abundance, biodegradability, affordability, flexibility during the production process, specific stiffness, low carbon footprint and low density (Nabi Saheb and Jog 1999; Akil et al. 2011; Mukherjee and Kao 2011; Faruk et al. 2012; and Hiremath 2020; Chaudhary et al. 2020). The classification of natural fibres is schematised in Fig. 1, and accordingly, natural fibres can be divided into two main classes, organic and non-organic. Organic natural fibres can be examined in two different groups, plant-based and animal-based. As an example of plant-based natural fibres as a reinforcement element; jute (Rahman et al. 2014), flax (Li et al. 2009), hemp (Popa et al. 2013), kenaf (Kamal et al. 2014), ramie (Krasowska et al. 2010), banana (Rodríguez et al. 2018), coir (Sanal 2016), kapok (Sellivam et al. 2016), bamboo (Astadini et al. 2020; del Pilar Fajardo Cabrera de Lima et al. 2020; Hung et al. 2012; Chaowana and Barbu 2017), rice (Wang et al. 2010; Chen et al. 2015), palm (Abu-Sharkh and Hamid 2004), straw (Yaacab et al. 2016), broom (Nouar et al. 2020) can be given. Human hair (Verma and Singh 2016), alpaca hair (Fortunati et al. 2015), sheep wool (Aluigi et al. 2014), chicken feather (Akderya et al. 2020) can be used as a reinforcement element

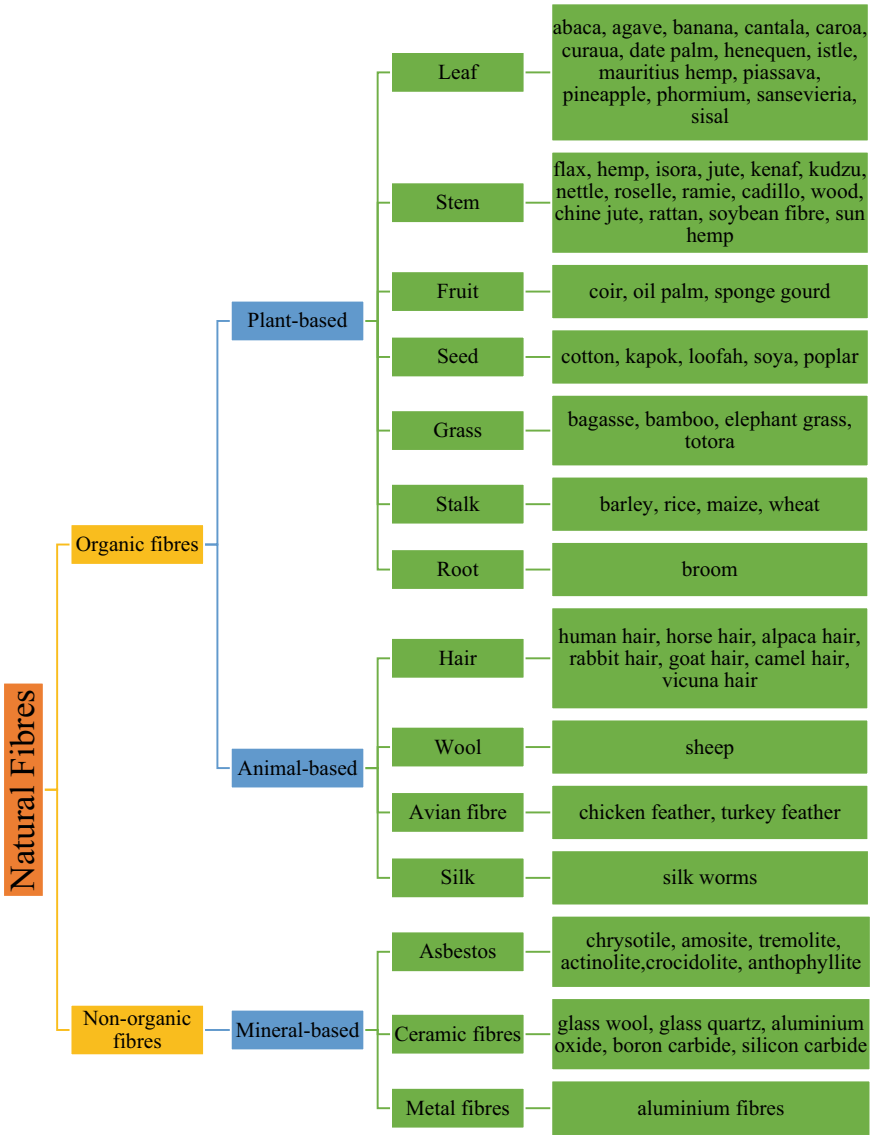


Fig. 1 Classification of natural fibres and their origins (Riedel and Nickel 2002; John and Thomas 2008; Tridico 2009; Chandramohan and Marimuthu 2011; Akil et al. 2011; Azwa et al. 2013; Pandey et al. 2015; Bharath and Basavarajappa 2016; Sapuan et al. 2017; Mayandi et al. 2018; and Hiremath 2020; Hiremath and Sridhar 2020)

from animal-based fibres. Non-organic mineral-based natural fibres can be evaluated in three groups: asbestos, ceramic fibres, and metal fibres. Chrysotile, amosite, tremolite, actinolite, crocidolite, and anthophyllite are examples of asbestos class (Lang et al. 1986; Rinaudo et al. 2005), glass wool, glass quartz, aluminium oxide, boron carbide, and silicon carbide are in the ceramic fibre class, and in addition to those, aluminium fibre can be given as an example of metal fibre class (Chandramohan and Marimuthu 2011; Sapuan et al. 2017).

There has been a noticeable increase in the trend of use of bio-composite materials in recent years. In this direction, scientific studies are carried out to detect the changes in bio-composites' properties in outdoor conditions to determine their shelf life. There are harsh environmental conditions that all materials can be exposed to in outdoor conditions. These conditions include acid rain, variable temperatures, high and low temperatures, wind, solar radiation, oxygen, biotic factors, and humidity. Natural weathering environment conditions are illustrated in Fig. 2. External conditions may cause degradation in the material and leakage of additives in its structure and entry of additives that are not in its structure. (Yew et al. 2009; Badji et al. 2018a; Liu et al. 2020; González-López et al. 2020).

Some researchers focused on the behaviour of natural fibre-reinforced bio-composite materials in different environmental conditions. Duigou et al. (2011) conducted a study to determine how to protect the external layers of flax/poly (l-lactic acid) (PLLA) bio-composite material from seawater ageing. Another study was carried out by Duigou et al. (2014) to obtain the effects of long-term seawater ageing on the flax/poly (lactic acid) (PLA) bio-composite. Ogunsona et al. (2017) investigated the behaviour of biocarbon reinforced nylon bio-composites under accelerated hydrothermal ageing conditions. Lila et al. (2019) conducted a study in which

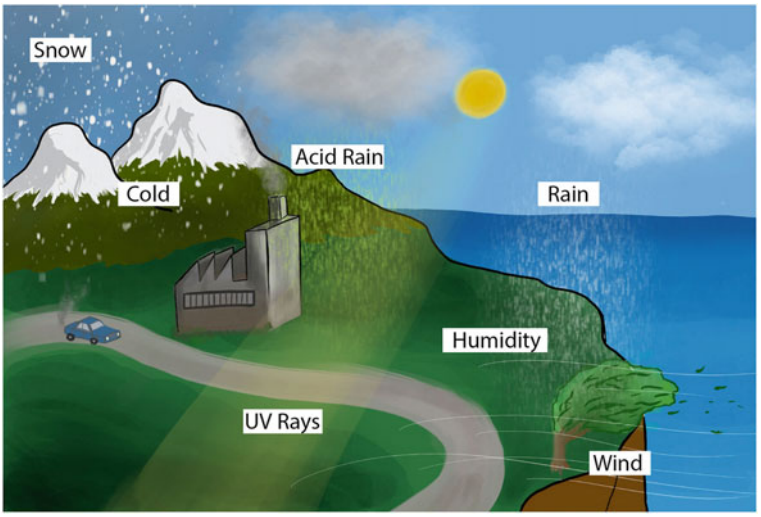


Fig. 2 Natural weathering conditions diagram

they examined the behaviour of bagasse fibre/PLA bio-composites under accelerated thermal ageing. The study on the differences between the bio-composite properties using pineapple leaf and palm fibre as reinforcement elements and polypropylene as a matrix was carried out by Chollakup et al. (2017). When the results of these studies were examined, it is seen that bio-composites degraded due to reasons such as matrix cracking, swelling, hydrolysis, debonding of fibre/matrix, and high-water uptake as a result of exposure to severe environmental conditions.

2 Natural Weathering Conditions

The high sensitivity of bio-composites to climatic conditions constitutes uncertainty and obstacle for their usage conditions. A limited number of scientific studies (Badji et al. 2018a, b, c; Abdullah et al. 2019) have been conducted to gain insight into bio-composites' durability and behaviour under natural weathering conditions with different climatic conditions (Badji et al. 2018d). With natural weathering, more than one external environmental factors synergistically affect the material at the same time. In the natural weathering environment, it cannot be precisely known what factor causes the dramatic changes in the material's properties (Badji et al. 2018d). The biggest reason for the application of natural weathering technique on materials is to obtain reliable and realistic results for the behaviour of the material in real-life conditions (Pospíšil et al. 2006; Lv et al. 2015; González-López et al. 2020).

The most influential factors that cause degradation of both polymer matrix and natural fibre in bio-composite materials exposed to natural weathering environment are high temperatures or oxidative processes caused by free radicals due to ultraviolet (UV) rays, and degradation phenomena bring about decrease in physicochemical properties of bio-composites (Stark and Matuana 2004; Fabiyi et al. 2008; Badji et al. 2018d). The polymer matrix undergoes Norrish type I and II reactions chain scissions (Parikh et al. 2006) during natural weathering exposure and transforms into lower molecular weight products (Stark and Matuana 2004; Fabiyi et al. 2008; Thirmizir et al. 2011; Badji et al. 2018d). In addition to Norrish type reactions, degradation phenomena cause effects in the matrix, such as absorption of UV rays by the lignin substance, photo-yellowing effect, and quinoid structure formation. Moreover, degradation phenomena cause chromophoric groups' formation in plant-based natural fibres (Beg and Pickering 2008; Azwa et al. 2013; and Hiremath 2020; Siakeng et al. 2020).

3 Results

3.1 Effects on Mechanical Properties

Having knowledge about the mechanical behaviour of materials gives a chance to intervene with a proactive approach to prevent malfunctions and errors that can potentially occur in engineering applications. Few scientific studies have been done to reveal the behavioural changes in bio-composites' mechanical properties in natural weathering environments.

Changes in some bio-composites' mechanical properties after exposure to natural weathering such as flexural strength, flexural modulus, tensile strength, tensile modulus, elongation at break, hardness and impact strength are given in Table 1. According to this table, most of the mechanical properties have decreased with natural weathering environments. The decrease in hardness values results from polymer chain scissions due to surface cracks and embrittlement occurring in natural weathering environment (Du et al. 2010). With the extension of the natural weathering duration, the number of chain scissions increase. Increasing the number of chain scissions results in the formation of shorter polymer chains and therefore, a decrease in overall mechanical properties (Fabiyi et al. 2008). Stark and Matuana (Stark et al. 2004; Stark and Matuana 2006) attributed the decrease in flexural strength values the fact that the crystallinity of composites increases at the beginning of the exposure period due to UV light and water exposure encountered in the natural weathering environment and decreases with the prolongation of this period. At the beginning of the exposure, the shorter and more mobile chains recrystallise. With the prolongation of the exposure, the chain scissions continue, and thus, the crystal regions are affected, and the crystallinity decreases.

The decrease in mechanical strength properties has been associated with the deterioration of the composite material's structure and properties. Natural weathering environment causes the composite materials to deteriorate, thus weakening the matrix-filler interfacial bonding. The swelling and shrinkage of natural fibres or particles with hydrophilic capability by absorbing and desorbing moisture cause the quality of the matrix-filler interface bonding to decrease (Beg and Pickering 2007, 2008). Stress concentration and chain scissions forming a brittle layer on the matrix surface, and the degradation of fillers led to an increase in composite materials' brittleness. Natural fibres deteriorating due to long-term natural weathering causes chromophoric groups to form in the composite material. These groups increased the photooxidation of composites. Moreover, thanks to photodegradation, additives with lignin in their structure have led to the formation of free radicals. Free radicals have had a detrimental effect on the structure of the matrix material by increasing chain scissions' speed (Beg and Pickering 2007; Naumann et al. 2012; Zhou et al. 2016).

The decrease in matrix-fibre interfacial bonding success of naturally weathered and therefore degraded composite materials may be caused by the inability to distribute the energy generated at the moment of impact through vibration and

Table 1 Mechanical properties of naturally weathered bio-composites

Study done by	Natural Weathering Site	Duration	Material	Mechanical Properties			
Homkhiew et al. (Homkhiew et al. 2014)	Hat Yai, Songkhla, Thailand	One year	Rubberwood flour reinforced polypropylene	**Maximum strain (%)**	**Hardness (Shore D)**	**Flexural strength (MPa)**	**Flexural modulus (GPa)**
			Neat polypropylene	6.95 to 2.26 76.25% ↓	75.6 to 65.9 12.82% ↓	50.1 to 28.6 42.85% ↓	1.67 to 0.97 23.22% ↓
			25% rubberwood flour reinforced polypropylene	3.99 to 3.53 11.29% ↓	76.4 to 72.3 5.32% ↓	44.3 to 42.5 4.09% ↓	1.93 to 1.73 10.26% ↓
			45% rubberwood flour reinforced polypropylene	2.36 to 2.04 13.39% ↓	78.3 to 74.8 4.47% ↓	43.4 to 39.5 8.95% ↓	2.66 to 2.23 16.30% ↓
Popa et al. (Popa et al. 2013)	Massa Martana, Perugia, Italy	600 hours	Hemp shives reinforced polypropylene	**Tensile strength (MPa)**	**Elongation at break (%)**	**Young modulus (GPa)**	**Charpy impact strength (kJ/m^2)**
			60% hemp shives reinforced polypropylene	28.9 to 25.3 %12.46 ↓	2.1 to 16.2 %671.43 ↑	1.99 to 2.3 %15.58 ↑	7.49 to 3.74 %50.01 ↓
Zhou et al. (Zhou et al. 2016)	Fuzhou, China	One year	Bamboo powder reinforced polypropylene foam	**Tensile strength (MPa)**	**Flexural modulus (GPa)**	**Flexural strength (MPa)**	**Notched impact strength (kJ/m^2)**
			33% bamboo powder reinforced polypropylene foam	22.23 to 20.08 %9.67 ↓	2.80 to 2.52 %10.00 ↓	41.75 to 40.50 %2.99 ↓	6.19 to 5.16 %16.64 ↓
Astadini et al. (Astadini et al. 2020)	Surakarta, Indonesia	Two months	Bamboo reinforced polyethylene	**Tensile strength (MPa)**	**Elongation at break (%)**	**Young modulus (MPa)**	**Charpy impact strength (kJ/m^2)**
			20% bamboo reinforced polyethylene	20.30 to 21.35 5.17% ↑	0.26 to 0.29 11.54% ↑	234.85 to 110.61 47.01% ↓	3.39 to 2.95 12.98% ↓
Badji et al. (Badji et al. 2018d)	Pau, Southwest of France	12 months	Hemp fibres reinforced polypropylene	**Elastic modulus (MPa)**	**Flexural strength (MPa)**	**Flexural strain (%)**	
			Neat polypropylene	1922 to 1750 8.95% ↓	71.61 to 46.61 34.91% ↓	5 to 3.5 30.00% ↓	

(continued)

Table 1 (continued)

Study done by	Natural Weathering Site	Duration	Material	Mechanical Properties			
			10wt% hemp fibres reinforced polypropylene	2702 to 2435 9.89% ↓	79.62 to 66.23 16.82% ↓	Same	
			30wt% hemp fibres reinforced polypropylene	4685 to 3734 20.30% ↓	88.57 to 72.45 18.20% ↓	Same	
del Pilar Fajardo Cabrera de Lima et al. (del Pilar Fajardo Cabrera de Lima et al. 2020)	Porto Alegre, Brasil	One year	Bamboo fibre reinforced polypropylene	**Tensile stress at break (MPa)**	**Elongation at break (%)**	**Elasticity Module (GPa)**	**Izod impact strength (kj/m²)**
			30% bamboo fibre reinforced polypropylene	12.45 to 7.80 37.35% ↓	0.99 to 0.80 19.20% ↓	1.40 to 0.85 39.29% ↓	11.00 to 7.80 29.01% ↓
Soccalingame et al. (Soccalingame et al. 2016)	Alès, Gard, France	One year	Wood flour reinforced polypropylene	**Tensile yield strength (MPa)**	**Tensile elongation at yield (%)**	**Charpy impact strength (kJ/m²)**	
			Neat polypropylene	39 to 16 58.97% ↓	7 to 1 85.71% ↓	No break to 1	
			10% wood flour reinforced polypropylene	39 to 32 17.95% ↓	4 to 3 25.00% ↓	17 to 2 88.24% ↓	
			30% wood flour reinforced polypropylene	43 to 37 13.95% ↓	Same	9 to 6 33.33% ↓	
Chan et al. (Chan et al. 2019)	Queensland, Australia	One year	Wood flour reinforced polyhydroxyalkanoate, wood flour reinforced poly(lactic acid), wood flour reinforced polyethylene	**Tensile strength (MPa)**	**Elongation at break (%)**	**Tensile modulus (GPa)**	
			Neat polyhydroxyalkanoate	31.98 to 33.32 4.19% ↑	8.81 to 5.37 39.05% ↓	2.57 to 3.18 23.74% ↑	
			20% wood flour reinforced polyhydroxyalkanoate	29.30 to 24.49 16.42% ↓	2.21 to 1.38 37.56% ↓	4.48 to 3.71 17.19% ↓	

(continued)

Table 1 (continued)

Study done by	Natural Weathering Site	Duration	Material	Mechanical Properties			
			50% wood flour reinforced polyhydroxyalkanoate	21.39 to 12.57 41.23% ↓	0.87 to 0.95 9.20% ↑	5.28 to 2.67 49.43% ↓	
			50% wood flour reinforced poly(lactic acid)	27.81 to 10.01 64.01% ↓	0.90 to 0.62 31.11% ↓	4.28 to 2.09 51.17% ↓	
			50% wood flour reinforced polyethylene	12.03 to 5.94 50.62% ↓	1.22 to 0.94 22.95% ↓	2.25 to 1.32 41.33% ↓	
Thirmizir et al. (Thirmizir et al. 2011)	Penang, Malaysia	Six months	Kenaf bast fibres reinforced poly(butylene)	**Flexural strength (MPa)**	**Flexural modulus (GPa)**		
			Neat poly(butylene)	36.69 to 20.00 %45.49 ↓	0.61 to 0.73 19.67% ↑		
			10wt% kenaf bast fibres reinforced poly(butylene)	36.90 to 27.11 %26.53 ↓	1.16 to 0.92 20.69% ↓		
			20wt% kenaf bast fibres reinforced poly(butylene)	37.46 to 21.33 %43.06 ↓	2.59 to 1.12 56.76% ↓		
			30wt% kenaf bast fibres reinforced poly(butylene)	41.13 to 17.32 %57.89 ↓	3.13 to 1.95 37.70% ↓		
			40wt% kenaf bast fibres reinforced poly(butylene)	39.65 to 14.30 %63.93 ↓	3.25 to 1.34 58.77% ↓		
Abu-Sharkh and Hamid (Abu-Sharkh and Hamid 2004)	Dhahran, Saudi Arabia	Nine months	Date palm fibre reinforced polypropylene	**Tensile strength (MPa)**	**Elongation at break (%)**		
			Neat polypropylene	33.40 to 17.13 48.71% ↓	11.18 to 3.32 29.70% ↓		
			29% date palm fibre reinforced polypropylene	27.73 to 24.67 11.03% ↓	4.42 to 4.50 1.81% ↑		
	Lappeenranta, Finland	One year	Wood fibre reinforced polypropylene	**Charpy impact strength (kJ/m^2)**			

(continued)

Table 1 (continued)

Study done by	Natural Weathering Site	Duration	Material	Mechanical Properties			
Butylina et al. (Butylina et al. 2012)			70% wood fibre reinforced polypropylene (control sample)	3.16 to 3.02 4.43% ⬇			
Rahman et al. (Rahman et al. 2011)	Johor, Malaysia	Four months	Rice husk reinforced polyethylene	**Impact strength (kJ/m^2)**			
			30% rice husk reinforced polyethylene	7.44 to 5.63 24.33% ⬇			

the inability to spread this energy in weak matrix-fibre regions (Oksman et al. 2009; Rahman et al. 2011).

3.2 Effects on the Thermal Properties

Exposure to natural weathering conditions has caused some changes in the thermal properties of composite materials. These changes are given in Table 2, as revealed by some scientific studies. The decrease in the first melting temperature of naturally weathered composites indicates the degradation of the matrix's lamellar fold surfaces, and the decrease in the second melting temperature indicates the effect of decaying molecules on crystal phase formation. The smaller and more defective molecules in the crystals formed during the recrystallisation process are the reason for the decrease in the second melting temperature (Rabello and White 1996, 1997; Butylina et al. 2012). Under natural weathering conditions, changes occurring on the matrix's lamellar structure due to cross-linking with UV rays' effect may affect the mechanical properties, while the melting temperatures may remain unchanged if they do not affect the bulk properties of the matrix. In case of exposure to high energy levels such as gamma-ray or electron irradiation, chain scissions and cross-linking in the amorphous phase cause changes in the bulk crystal structure of the composite material, and thus a decrease in the peak melting temperature is observed (Mitomo et al. 1994; Bergmann et al. 2007; Wei and McDonald 2016; Chan et al. 2019).

Photodegradation appears to be more predominant in the amorphous phase whose molecular chain is susceptible to further crystallisation; however, the crystallinity's overall decrease indicates that the crystalline phase is generally affected (Stark and Matuana 2006; Homkhiew et al. 2014; Badji et al. 2018a). One of the reasons for the decrease in crystallinity may be the impurities caused by factors such as dust and moisture accumulating in the composite material during exterior natural weathering exposure or the presence of smaller and more defective molecules in the material (Butylina et al. 2012; Soccalingame et al. 2016). The increase in the degree of crystallinity under natural weathering conditions may result from the change in molecular weight due to degradation of the polymer of the composite leading to chain breakage and subsequent secondary crystallisation (Fabiyi and McDonald 2014).

3.3 Effects on the Aesthetics

Some alterations in lightness and colours have been observed as a result of factors such as high temperature, UV rays and rain, with the exposure of composite materials to natural weathering conditions for specific periods. Total colour change is calculated by taking the lightness, redness and yellowness values of the composite into consideration. The changes in the visual properties of composites under natural weathering conditions are given in Table 3. When Rahman et al. (2011) exposed the

Table 2 Thermal properties of naturally weathered bio-composites

Study done by	Natural Weathering Site	Duration	Material	Thermal Properties			
Butylina et al. (Butylina et al. 2012)	Lappeenranta, Finland	One year	Wood fibre reinforced polypropylene	**First melting temperature (°C)**	**Second melting temperature (°C)**	**Crystallisation temperature (°C)**	**Crystallinity (%)**
			70% wood fibre reinforced polypropylene (control sample)	164 to 155 5.49% ⬇	164 to 144 12.20% ⬇	120 to 115 4.17% ⬇	65.15 to 54.55 16.27% ⬇
Badji et al. (Badji et al. 2018a)	Pau, Southwest of France	One year	Hemp fibres reinforced polypropylene	**Crystallinity rate from first heating step (%)**	**Crystallinity rate from the second heating step (%)**		
			Neat polypropylene	45.89 to 44.00 4.12% ⬇	50.85 to 46.65 8.26% ⬇		
			10wt% hemp fibres reinforced polypropylene	45.90 to 42.92 6.49% ⬇	50.80 to 47.92 5.67 ⬇		
			30wt% hemp fibres reinforced polypropylene	46.93 to 35.05 25.31% ⬇	52.55 to 41.89 20.29% ⬇		
Soccalingame et al. (Soccalingame et al. 2016)	Alès, Gard, France	One year	Wood flour reinforced polypropylene	**Crystallinity rate from first heating step (%)**	**Crystallinity rate from the second heating step (%)**		
			10% wood flour reinforced polypropylene	46.0 to 45.5 1.09% ⬇	50.7 to 43.6 14.00% ⬇		
			30% wood flour reinforced polypropylene	42.3 to 37.8 10.64% ⬇	46.9 to 43.4 7.46% ⬇		

(continued)

Table 2 (continued)

Study done by	Natural Weathering Site	Duration	Material	Thermal Properties			
Chan et al. (Chan et al. 2019)	Queensland, Australia	One year	Wood flour reinforced polyhydroxyalkanoate	**Peak melting temperature (°C)**	**Melt crystallisation temperature (°C)**		
			Neat polyhydroxyalkanoate	173.77 to 172.33 0.83% ↓	112.39 to 116.45 3.61% ↑		
			20% wood flour reinforced polyhydroxyalkanoate	172.14 to 172.21 0.04%	109.70 to 122.67 11.82% ↑		
			50% wood flour reinforced polyhydroxyalkanoate	169.29 to 170.09 0.47%	105.88 to 119.70 13.05% ↑		
Hung et al. (Hung et al. 2012)	Taichung City, Taiwan	Three years	Bamboo fibres reinforced high-density polyethylene	**Crystallinity (%)**			
			60% bamboo fibres reinforced high-density polyethylene	53.88 to 82.76 53.60% ↑			
Akderya et al. (Akderya et al. 2020)	Manisa, Turkey	Five years	Chicken feather fibre reinforced poly(lactic acid)	**Melting temperature (°C)**	**Crystallinity (%)**		
			Neat poly(lactic acid)	153.15 to 150.00 2.06% ↓	29.26 to 3.14 89.27% ↓		
			2% chicken feather fibre reinforced poly(lactic acid)	154.65 to 155.07 0.27%	4.50 to 6.79 50.89% ↑		
			5% chicken feather fibre reinforced poly(lactic acid)	155.75 to 155.49 0.17%	3.74 to 4.98 33.16% ↑		
			10% chicken feather fibre reinforced poly(lactic acid)	155.15 to 155.66 0.33%	2.52 to 6.11 142.46% ↑		
del Pilar Fajardo Cabrera de Lima	Porto Alegre, Brasil	One year	Bamboo fibre reinforced polypropylene	**Melting temperature**	**Crystallinity (%)**		

(continued)

Table 2 (continued)

Study done by	Natural Weathering Site	Duration	Material	Thermal Properties			
et al. (del Pilar Fajardo Cabrera de Lima et al. 2020)				**(°C)**			
			30% bamboo fibre reinforced polypropylene	165 to 166 0.61%	50.89 to 43.41 14.70% ⬇		
Abu-Sharkh and Hamid (Abu-Sharkh and Hamid 2004)	Dhahran, Saudi Arabia	Nine months	Date palm fibre reinforced polypropylene	**Melting temperature (°C)**			
			Neat polypropylene	163.46 to 155.52 4.86% ⬇			
			29% date palm fibre reinforced polypropylene	162.25 to 161.33 0.57%			
Fabiyi and McDonald (Fabiyi and McDonald 2014)	Moscow, Idaho, USA	Four months	Pine fibre reinforced polypropylene	**Crystallinity (%)**			
			60% pine fibre reinforced polypropylene	38.43 to 41.99 9.26% ⬆			

Table 3 Aesthetics of naturally weathered bio-composites

Study done by	Natural Weathering Site	Duration	Material	Colour measurements			
Zhou et al. (Zhou et al. 2016)	Fuzhou, China	One year	Bamboo powder reinforced polypropylene foam	**Lightness (L*)**	**Redness (a*)**	**Yellowness (b*)**	**The colour change (ΔE*)**
			33% bamboo powder reinforced polypropylene foam	27.82 to 50.39 ΔL: 22.57 ↑	1.11 to -2.40 Δa: -3.51 ↓	4.78 to 4.88 Δb: 0.10	22.80
Thirmizir et al. (Thirmizir et al. 2011)	Penang, Malaysia	Six months	Kenaf bast fibres reinforced poly(butylene)	**Lightness (L)**	**Redness (a*)**	**Yellowness (b*)**	**The colour change (ΔE*)**
			Neat poly(butylene)	70.25 to 74.12 ΔL: 3.87 ↑	-1.45 to -1.80 Δa: -0.35 ↓	3.47 to 5.33 Δb: 1.86 ↑	4.30
			10wt% kenaf bast fibres reinforced poly(butylene)	36.12 to 47.51 ΔL: 11.39 ↑	1.84 to 1.28 Δa: -0.56 ↓	7.30 to 6.18 Δb: -1.12 ↓	11.46
			20wt% kenaf bast fibres reinforced poly(butylene)	32.50 to 49.37 ΔL: 16.87 ↑	2.09 to 0.88 Δa: -1.21 ↓	6.76 to 5.75 Δb: -1.01 ↓	16.94
			30wt% kenaf bast fibres reinforced poly(butylene)	29.16 to 53.48 ΔL: 24.32 ↑	1.96 to 0.49 Δa: -1.47 ↓	6.21 to 5.30 Δb: -0.91 ↓	24.38
			40wt% kenaf bast fibres reinforced poly(butylene)	28.38 to 54.82 ΔL: 26.44 ↑	1.82 to -1.16 Δa: -2.98 ↓	5.69 to 4.72 Δb: -0.97 ↓	26.48
Wang et al. (Wang et al. 2010)	Harbin city, Heilongjiang Province, China	Two years	Rice-hull powder reinforced polyethylene	**Lightness (L*)**	**The colour change (ΔE*)**		
			50% rice-hull powder reinforced polyethylene (red lumber)	32.88 to 41.49 ΔL: 8.61 ↑	12.8		
			50% rice-hull powder reinforced polyethylene (yellow lumber)	49.24 to 60.91 ΔL: 11.67 ↑	9.2		
Study done by	**Natural Weathering Site**	**Duration**	**Material**	**Colour measurements**			
Rahman et al. (Rahman et al. 2011)	Johor, Malaysia	Four months	Rice husk reinforced polyethylene	**Lightness (L*)**	**The colour change (ΔE*)**		
			30% rice husk powder reinforced polyethylene	47.54 to 58.26 ΔL: 10.72 ↑	11.67		

polyethylene reinforced with 30% rice husk powder composite to natural weathering environment for four months, it caused a colour change in the composite as a result of photooxidation on the sample surfaces. Rain, which is one of the factors of natural weathering environment, accelerates the erosion process on the composite material's surface and is a source of moisture that can cause dimensional changes. Typical surface erosion spreads faster in materials such as wood-based materials with low density, and the surface of the material becomes rougher as a result of this spread. Surface erosion spread is a slowly progressing process and does not show itself in short periods (Rahman et al. 2011).

4 Future Perspective

Bio-composite materials are new trend materials that are being used as an alternative to traditional materials in a wide variety of industrial and engineering applications. Increased awareness and interest in long-term sustainability and environmental sensitivity, as well as superior properties such as high specific strength, high hardness values, higher fatigue strength, impact absorption, superior resistance to corrosion, recyclability, non-toxicity, and low-cost cause bio-composites to be evaluated in the class of engineering materials, and it is predicted that their frequency of use will increase in the future. Static and dynamic failures such as matrix cracking, fibre breakage and layer delamination, high sensitivity to climatic conditions and the inability to predict the mechanical behaviour of natural fibre reinforced composites present challenges in predicting the reliable performance of bio-composites. In order for the components of bio-composite materials to be selected correctly, long-term reliable performance must be determined. For this purpose, real-time experimental studies in natural weathering environment and accelerated weathering studies on bio-composites are mandatory to carry out. There is a need to develop new combined evaluation criteria in both macro and nano scale by demonstrating consistency between these studies.

5 Conclusion

Bio-composites encounter factors such as humidity, high and low temperatures, radiation and UV rays in natural environments. These factors cause deterioration in the mechanical, and thermal properties and aesthetics of bio-composite materials. Mechanical properties such as flexural strength, tensile strength, modulus of elasticity, elongation at break, impact resistance change with influences such as chain scissions and reduction of fibre-matrix interfacial bonding success. Thermal properties such as crystallinity and melting temperature deteriorate with recrystallisation,

resulting in the formation of smaller and more defective molecules. Aesthetic properties such as lightness, surface roughness and shape also change with effects such as photooxidation, moisture absorption and photodegradation.

References

Abdullah AH, Bakar AA, Ismail H et al (2019) The effects of accelerated weathering on the tensile properties of kenaf reinforced biocomposites. In: IOP conference series: materials science and engineering. Institute of Physics Publishing

Abu-Sharkh BF, Hamid H (2004) Degradation study of date palm fibre/polypropylene composites in natural and artificial weathering: mechanical and thermal analysis. In: Polymer degradation and stability. Elsevier Ltd, pp 967–973

Akderya T, Özmen U, Baba BO (2020) Investigation of long-term ageing effect on the thermal properties of chicken feather fibre/poly(lactic acid) biocomposites. J Polym Res 27. https://doi.org/10.1007/s10965-020-02132-2

Akil HM, Omar MF, Mazuki AAM et al (2011) Kenaf fiber reinforced composites: a review. Mater Des 32:4107–4121

Aluigi A, Tonetti C, Rombaldoni F et al (2014) Keratins extracted from Merino wool and Brown Alpaca fibres as potential fillers for PLLA-based biocomposites. J Mater Sci 49:6257–6269. https://doi.org/10.1007/s10853-014-8350-9

Astadini NA, Widiastuti I, Harjanto B et al (2020) Natural weathering effect on mechanical and physical properties of recycled high-density polyethylene composite with bamboo reinforcement. In: Lecture notes in mechanical engineering. Springer, pp 659–666

Azwa ZN, Yousif BF, Manalo AC, Karunasena W (2013) A review on the degradability of polymeric composites based on natural fibres. Mater Des 47:424–442

Badji C, Beigbeder J, Garay H et al (2018a) Correlation between artificial and natural weathering of hemp fibers reinforced polypropylene biocomposites. Polym Degrad Stab 148:117–131. https://doi.org/10.1016/j.polymdegradstab.2018.01.002

Badji C, Beigbeder J, Garay H et al (2018b) Natural weathering of hemp fibers reinforced polypropylene biocomposites: relationships between visual and surface aspects, mechanical properties and microstructure based on statistical approach. Compos Sci Technol 167:440–447. https://doi.org/10.1016/j.compscitech.2018.08.036

Badji C, Beigbeder J, Garay H et al (2018c) Under glass weathering of hemp fibers reinforced polypropylene biocomposites: impact of volatile organic compounds emissions on indoor air quality. Polym Degrad Stab 149:85–95. https://doi.org/10.1016/j.polymdegradstab.2018.01.020

Badji C, Beigbeder J, Garay H et al (2018d) Exterior and under glass natural weathering of hemp fibers reinforced polypropylene biocomposites: impact on mechanical, chemical, microstructural and visual aspect properties. Polym Degrad Stab 148:104–116. https://doi.org/10.1016/j.polymdegradstab.2017.12.015

Beg MDH, Pickering KL (2008) Accelerated weathering of unbleached and bleached Kraft wood fibre reinforced polypropylene composites. Polym Degrad Stab 93:1939–1946. https://doi.org/10.1016/j.polymdegradstab.2008.06.012

Beg MDH, Pickering KL (2007) The effects of residual lignin content on wood fibre reinforced polypropylene composites. In: Advanced materials research. Trans Tech Publications, pp 323–326

Bergmann A, Teßmar J, Owen A (2007) Influence of electron irradiation on the crystallisation, molecular weight and mechanical properties of poly-(R)-3-hydroxybutyrate. J Mater Sci 42:3732–3738. https://doi.org/10.1007/s10853-006-1411-y

Bharath KN, Basavarajappa S (2016) Applications of biocomposite materials based on natural fibers from renewable resources: a review. Sci Eng Compos Mater 23:123–133

Butylina S, Hyvärinen M, Kärki T (2012) A study of surface changes of wood-polypropylene composites as the result of exterior weathering. Polym Degrad Stab 97:337–345. https://doi.org/10.1016/j.polymdegradstab.2011.12.014

Chan CM, Pratt S, Halley P et al (2019) Mechanical and physical stability of polyhydroxyalkanoate (PHA)-based wood plastic composites (WPCs) under natural weathering. Polym Test 73:214–221. https://doi.org/10.1016/j.polymertesting.2018.11.028

Chandramohan D, Marimuthu, (2011) A review on natural fibers. Int J Res Rev Appl Sci 8:194–206

Chang BP, Mohanty AK, Misra M (2020) Studies on durability of sustainable biobased composites: a review. RSC Adv 10:17955–17999

Chaowana P, Barbu MC (2017) Bamboo: potential material for biocomposites. In: Lignocellulosic fibre and biomass-based composite materials: processing, properties and applications. Elsevier Inc., pp 259–289

Chaudhary V, Bajpai PK, Maheshwari S (2020) Effect of moisture absorption on the mechanical performance of natural fiber reinforced woven hybrid bio-composites. J Nat Fibers 17:84–100. https://doi.org/10.1080/15440478.2018.1469451

Chen RS, Ab Ghani MH, Ahmad S et al (2015) Rice husk flour biocomposites based on recycled high-density polyethylene/polyethylene terephthalate blend: effect of high filler loading on physical, mechanical and thermal properties. J Compos Mater 49:1241–1253. https://doi.org/10.1177/0021998314533361

Chollakup R, Askanian H, Delor-Jestin F (2017) Initial properties and ageing behaviour of pineapple leaf and palm fibre as reinforcement for polypropylene. J Thermoplast Compos Mater 30:174–195. https://doi.org/10.1177/0892705715598356

del Pilar Fajardo Cabrera de Lima L, Santana RMC, Rodríguez CDC (2020) Influence of coupling agent in mechanical, physical and thermal properties of polypropylene/bamboo fiber composites: under natural outdoor aging. Polymers (basel) 12. https://doi.org/10.3390/POLYM12040929

Du H, Wang W, Wang Q et al (2010) Effects of pigments on the uv degradation of wood-flour/HDPE composites. J Appl Polym Sci 118:1068–1076. https://doi.org/10.1002/app.32430

Fabiyi JS, McDonald AG (2014) Degradation of polypropylene in naturally and artificially weathered plastic matrix composites. Maderas Cienc y Tecnol 16:275–290. https://doi.org/10.4067/S0718-221X2014005000021

Fabiyi JS, McDonald AG, Wolcott MP, Griffiths PR (2008) Wood plastic composites weathering: visual appearance and chemical changes. Polym Degrad Stab 93:1405–1414. https://doi.org/10.1016/j.polymdegradstab.2008.05.024

Faruk O, Bledzki AK, Fink HP, Sain M (2012) Biocomposites reinforced with natural fibers: 2000–2010. Prog Polym Sci 37:1552–1596

Fortunati E, Aluigi A, Armentano I et al (2015) Keratins extracted from Merino wool and Brown Alpaca fibres: thermal, mechanical and biological properties of PLLA based biocomposites. Mater Sci Eng C 47:394–406. https://doi.org/10.1016/j.msec.2014.11.007

González-López ME, Martín del Campo AS, Robledo-Ortíz JR et al (2020) Accelerated weathering of poly(lactic acid) and its biocomposites: a review. Polym Degrad Stab 179

Hiremath SS (2020) Natural fiber reinforced composites in the context of biodegradability: a review. In: encyclopedia of renewable and sustainable materials. Elsevier, pp 160–178

Hiremath A, Sridhar T (2020) Use of bio-fibers in various practical applications. In: encyclopedia of renewable and sustainable materials. Elsevier, pp 931–935

Homkhiew C, Ratanawilai T, Thongruang W (2014) Effects of natural weathering on the properties of recycled polypropylene composites reinforced with rubberwood flour. Ind Crops Prod 56:52–59. https://doi.org/10.1016/j.indcrop.2014.02.034

Hung KC, Chen YL, Wu JH (2012) Natural weathering properties of acetylated bamboo plastic composites. Polym Degrad Stab 97:1680–1685. https://doi.org/10.1016/j.polymdegradstab.2012.06.016

John MJ, Thomas S (2008) Biofibres and biocomposites. Carbohydr Polym 71:343–364

Kamal I, Beyer G, Saad MJ et al (2014) Kenaf For biocomposite: an overview. J Sci Technol 6:41–66

Krasowska K, Brzeska J, Rutkowska M et al (2010) Environmental degradation of ramie fibre reinforced biocomposites. Polish J Environ Stud 19:937–945

Lang PL, Katon JE, O'Keefe JF, Schiering DW (1986) Identification of fibres by infrared and Raman microspectroscopy

Le Duigou A, Bourmaud A, Davies P, Baley C (2014) Long term immersion in natural seawater of Flax/PLA biocomposite. Ocean Eng 90:140–148. https://doi.org/10.1016/j.oceaneng.2014.07.021

Le Duigou A, Deux JM, Davies P, Baley C (2011) Protection of Flax/PLLA biocomposites from seawater ageing by external layers of PLLA. Int J Polym Sci 2011. https://doi.org/10.1155/2011/235805

Li X, Panigrahi S, Tabil LG (2009) A study on flax fiber-reinforced polyethylene biocomposites. Appl Eng Agric 25:525–531. https://doi.org/10.13031/2013.27454

Lila MK, Shukla K, Komal UK, Singh I (2019) Accelerated thermal ageing behaviour of bagasse fibers reinforced Poly (Lactic Acid) based biocomposites. Compos Part B Eng 156:121–127. https://doi.org/10.1016/j.compositesb.2018.08.068

Liu P, Zhan X, Wu X, et al (2020) Effect of weathering on environmental behavior of microplastics: properties, sorption and potential risks. Chemosphere 242

Lv Y, Huang Y, Yang J et al (2015) Outdoor and accelerated laboratory weathering of polypropylene: a comparison and correlation study. Polym Degrad Stab 112:145–159. https://doi.org/10.1016/j.polymdegradstab.2014.12.023

Mayandi K, Rajini N, Manojprabhakar M, et al (2018) Recent studies on durability of natural/synthetic fiber reinforced hybrid polymer composites. In: Durability and life prediction in biocomposites, fibre-reinforced composites and hybrid composites. Elsevier, pp 1–13

Mitomo H, Watanabe Y, Ishigaki I, Saito T (1994) Radiation-induced degradation of poly(3-hydroxybutyrate) and the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate). Polym Degrad Stab 45:11–17. https://doi.org/10.1016/0141-3910(94)90173-2

Mitra BC (2014) Environment friendly composite materials: biocomposites and green composites. Def Sci J 64:244–261. https://doi.org/10.14429/dsj.64.7323

Mohanty AK, Misra M, Drzal LT et al (2005) Natural fibers, biopolymers, and biocomposites: an introduction. In: Natural fibers, biopolymers, and biocomposites. CRC Press, pp 1–36

Mukherjee T, Kao N (2011) PLA based biopolymer reinforced with natural fibre: a review. J Polym Environ 19:714–725. https://doi.org/10.1007/s10924-011-0320-6

Nabi Saheb D, Jog JP (1999) Natural fiber polymer composites: a review. Adv Polym Technol 18:351–363. https://doi.org/10.1002/(SICI)1098-2329(199924)18:4%3c351::AID-ADV6%3e3.0.CO;2-X

Naumann A, Stephan I, Noll M (2012) Material resistance of weathered wood-plastic composites against fungal decay. Int Biodeterior Biodegrad 75:28–35. https://doi.org/10.1016/j.ibiod.2012.08.004

Nouar Y, Zouaoui F, Nekkaa S et al (2020) Effect of chemical treatment on thermophysical behavior of Spanish broom flour-reinforced polypropylene biocomposite. J Polym Eng. https://doi.org/10.1515/polyeng-2020-0073

Ogunsona EO, Misra M, Mohanty AK (2017) Accelerated hydrothermal aging of biocarbon reinforced nylon biocomposites. Polym Degrad Stab 139:76–88. https://doi.org/10.1016/j.polymdegradstab.2017.03.013

Oksman K, Mathew AP, Långström R et al (2009) The influence of fibre microstructure on fibre breakage and mechanical properties of natural fibre reinforced polypropylene. Compos Sci Technol 69:1847–1853. https://doi.org/10.1016/j.compscitech.2009.03.020

Pandey JK, Nagarajan V, Mohanty AK, Misra M (2015) Commercial potential and competitiveness of natural fiber composites. In: Biocomposites: design and mechanical performance. Elsevier Inc., pp 1–15

Parikh A, Parikh H, Parikh K (2006) Norrish Type I an II Reaction (Cleavage). Name reactions in organic synthesis. Foundation Books, Delhi, pp 325–329

Peças P, Carvalho H, Salman H, Leite M (2018) Natural fibre composites and their applications: a review. J Compos Sci 2:66. https://doi.org/10.3390/jcs2040066
Popa MI, Pernevan S, Sirghie C et al (2013) Mechanical properties and weathering behavior of polypropylene-hemp shives composites. J Chem. https://doi.org/10.1155/2013/343068
Pospíšil J, Pilař J, Billingham NC et al (2006) Factors affecting accelerated testing of polymer photostability. In: Polymer degradation and stability, pp 417–422
Rabello MS, White JR (1997) Crystallization and melting behaviour of photodegraded polypropylene-II. Re-Crystal Degrad Mol Polym (guildf) 38:6389–6399. https://doi.org/10.1016/S0032-3861(97)00214-0
Rabello MS, White JR (1996) Photodegradation of talc-filled polypropylene. Polym Compos 17:691–704. https://doi.org/10.1002/pc.10661
Rahman MM, Afrin S, Haque P (2014) Characterization of crystalline cellulose of jute reinforced poly (vinyl alcohol) (PVA) biocomposite film for potential biomedical applications. Prog Biomater 3. https://doi.org/10.1007/s40204-014-0023-x
Rahman WAWA, Sin LT, Rahmat AR et al (2011) Comparison of rice husk-filled polyethylene composite and natural wood under weathering effects. J Compos Mater 45:1403–1410. https://doi.org/10.1177/0021998310381545
Riedel U, Nickel J (2002) Applications of natural fiber composites for constructive parts in aerospace, automobiles, and other areas. In: Biopolymers online. Wiley
Rinaudo C, Gastaldi D, Belluso E, Capella S (2005) Application of Raman Spectroscopy on asbestos fibre identification. Neues Jahrb Fur Mineral Abhandlungen 182:31–36. https://doi.org/10.1127/0077-7757/2005/0030
Rodríguez LJ, Orrego CE, Ribeiro I, Peças P (2018) Life-cycle assessment and life-cycle cost study of banana (Musa sapientum) fiber biocomposite materials. In: Procedia CIRP. Elsevier B.V., pp 585–590
Sanal I (2016) Coir fiber-reinforced composites. In: Green approaches to biocomposite materials science and engineering. IGI Global, pp 247–275
Sapuan SM, Tamrin KF, Nukman Y et al (2017) Natural fiber-reinforced composites: types, development, manufacturing process, and measurement. In: Comprehensive materials finishing. Elsevier Inc., pp 203–230
Sellivam RKCP, Husseinsyah S, Leng TP et al (2016) Effect of Adipic acid content on properties of soy protein Isolate/Kapok Husk biocomposite films. Procedia Chem 19:891–896. https://doi.org/10.1016/j.proche.2016.03.131
Siakeng R, Jawaid M, Asim M (2020) Polymers accelerated weathering and soil burial effect on biodegradability, colour and textureof. Polymers (basel) 458:1–15
Soccalingame L, Perrin D, Bénézet JC, Bergeret A (2016) Reprocessing of UV-weathered wood flour reinforced polypropylene composites: study of a natural outdoor exposure. Polym Degrad Stab 133:389–398. https://doi.org/10.1016/j.polymdegradstab.2016.09.011
Stark NM, Matuana LM (2004) Surface chemistry changes of weathered HDPE/wood-flour composites studied by XPS and FTIR spectroscopy. Polym Degrad Stab 86:1–9. https://doi.org/10.1016/j.polymdegradstab.2003.11.002
Stark NM, Matuana LM (2006) Influence of photostabilizers on wood flour-HDPE composites exposed to xenon-arc radiation with and without water spray. Polym Degrad Stab 91:3048–3056. https://doi.org/10.1016/j.polymdegradstab.2006.08.003
Stark NM, Matuana LM, Clemons CM (2004) Effect of processing method on surface and weathering characteristics of wood-flour/HDPE composites. J Appl Polym Sci 93:1021–1030. https://doi.org/10.1002/app.20529
Thirmizir MZA, Ishak ZAM, Taib RM et al (2011) Natural weathering of Kenaf Bast fibre-filled poly(Butylene Succinate) composites: effect of fibre loading and compatibiliser addition. J Polym Environ 19:263–273. https://doi.org/10.1007/s10924-010-0272-2
Tridico SR (2009) Natural animal textile fibres: structure, characteristics and identification. In: Identification of textile fibers. Elsevier Ltd., pp 27–67

Verma A, Singh VK (2016) Human hair: a biodegradable composite fiber–a review. Int J Waste Resour 6. https://doi.org/10.4172/2252-5211.1000206

Wang W, hong, Bu F hua, Zhang Z ming, et al (2010) Performance of rice-hull-PE composite exposed to natural weathering. J for Res 21:219–224. https://doi.org/10.1007/s11676-010-0036-9

Wei L, McDonald AG (2016) Accelerated weathering studies on the bioplastic, poly(3-hydroxybutyrate-co-3-hydroxyvalerate). Polym Degrad Stab 126:93–100. https://doi.org/10.1016/j.polymdegradstab.2016.01.023

Yaacab ND, Ismail H, Ting SS (2016) Potential use of paddy straw as filler in poly lactic acid/paddy straw powder biocomposite: thermal and thermal properties. Procedia Chem 19:757–762. https://doi.org/10.1016/j.proche.2016.03.081

Yew GH, Chow WS, Mohd Ishak ZA, Mohd Yusof AM (2009) Natural weathering of poly (Lactic Acid): effects of rice starch and epoxidized natural rubber. J Elastomers Plast 41:369–382. https://doi.org/10.1177/0095244309103663

Zhou X, Huang S, Chen L (2016) Effect of antiaging agents on the outdoor natural weathering of bamboo powder/polypropylene foamed composites. J Vinyl Addit Technol 22:311–319. https://doi.org/10.1002/vnl.21433

Degradation Effects on the Mechanical and Thermal Properties of the Bio-Composites Due to Accelerated Weathering

Juliana Botelho Moreira, Suelen Goettems Kuntzler, Cleber Klasener da Silva, Jorge Alberto Vieira Costa, and Michele Greque de Morais

Abstract Bio-composites are promising materials to be used as an alternative to composites. Weathering studies can evaluate the effects of the degradation on bio-composites properties. By accelerated weathering testing, it is possible to predict the durability of materials in a short time. Exposure to UV radiation, moisture, and temperature can cause leading to loss of color and brightness, roughness, and aging of bio-composites. The chemical characteristics, crystallinity, and molecular weight of bio-composites are also affected, with the possibility of randomly break down the polymer chains. The reduction in tensile and flexural strength and thermal properties are also consequences of the degradation process. In this way, to solve this problem, the reinforcement of bio-composites has been investigated. Therefore, this chapter addresses the main environmental factors involved in accelerated weathering and the degradation effects on morphology, molecular characteristics, and thermal and mechanical properties of bio-composites caused by this testing. The influence of nanofillers on the degradation rate of composites are also mentioned.

Keywords Moisture · Nanofillers · Natural fibers · Polymers · Temperature · UV radiation

1 Introduction

The accelerated growth of the global economy seeks to develop products from innovative, sustainable, and quality materials. However, some products are often marketed without proper evaluation of the durability and resistance of these materials. Various composite materials may show wear in color and physical resistance after long periods of utilization by the user (Mohseni et al. 2011).

Weathering testing can be used to streamline the product quality validation process. Accelerated weathering testing makes it possible to predict the durability

J. B. Moreira (✉) · S. G. Kuntzler · C. K. da Silva · J. A. V. Costa · M. G. de Morais
College of Chemistry and Food Engineering, Federal University of Rio Grande (FURG), P.O. Box 474, Rio Grande, RS 96203-900, Brazil

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_9

of materials when subjected to adverse environmental conditions. These conditions simulate what would take years of natural weathering in a short time (Sun et al. 2020). The main weathering testing use UV radiation, extreme conditions of temperature and humidity. These parameters can act as a single factor or a combined application (Grossman 1977).

Coupled with population growth is the increased demand for consumer goods. With this, researchers have been carrying out studies to meet the needs of the population sustainably. Therefore, the use of bio-composites has shown potential for use in the material sciences, especially in the field of composite, as they are full or partial degradable, contributing to reduce environmental pollution (Lila et al. 2019). Moreover, bio-composites have been studied and applied in other areas, such as packaging production (Kiryukhin et al. 2018), paints (Gao et al. 2019; Lankone et al. 2020), coatings containing biopolymers (Aziz et al. 2016), and incorporation of natural pigments in polymeric fibers for application in food packaging (Kuntzler et al. 2018; Moreira et al. 2019; Silva et al. 2019).

Bio-composite material can be used as an alternative to conventional materials because it presents less risk to the environment. However, they must demonstrate similarity or superiority in properties and functions. The critical factor associated with the application and use of bio-composites is their behavior during maintenance conditions. Thus, weathering studies must be carried out (Lila et al. 2019). In this sense, research on accelerated weathering provides the effects of the degradation of composites during the stages of maintenance and use in a short time (González-López et al. 2020).

Reinforcement with natural fibers and nanofillers improves the thermal and mechanical properties of bio-composites. Besides, they enhance polymer blends' miscibility and contribute to minimizing the effects generated by degradation due to weathering (Rivera-Briso and Serrano-Aroca 2018). However, depending on the bio-composite composition and the conditions of exposure, nanofillers can accelerate or slow down the materials' degradation (Antunes et al. 2020a). In this context, this chapter addresses the main environmental factors involved in accelerated weathering and the effects of degradation, morphology, molecular characteristics, and thermal and mechanical properties of bio-composites caused by this technique. The influence of nanofiller on the degradation rate of composites are also mentioned.

2 Environmental Factors

In the accelerated weathering technique, environmental factors such as solar radiation, temperature, moisture, and microbiota are studied (Pickett 2018). The data generated in these tests can be related to the durability of materials such as coatings, adhesives, polymers, metals, wood, textiles, and construction materials (Xie et al. 2020). The main effects of weathering on materials are associated with appearance (color change, loss of shine, turbidity), mechanical properties (weakening, loss

of strength), morphology (scaling, cracking, bubble formation), and oxidation (Sun et al. 2020).

2.1 Solar Radiation

Solar radiation is composed of different wavelengths, from ultraviolet (UV) (up to 400 nm), visible (400–800 nm), and infrared (IR) (800–3000 nm). The radiation that falls on materials on the Earth's surface ranges from 295 to 3000 nm because the shorter wavelengths are absorbed by oxygen in the Earth's upper atmosphere and ozone in the stratosphere (Pickett 2018). The location also influences the intensity of the incidence of radiation (ASTM G177 2020).

A fraction corresponding to 5% of UV light from solar energy that strikes the Earth's surface is responsible for the degradation of polymeric compounds. The degradation can be of photochemical origin that happens directly in the polymeric chemical structure, or it can occur through the absorption of the wavelengths by impurities. Visible radiation causes the material to fade due to the degradation of pigmented compounds, while infrared radiation influences thermal properties, contributing to the elevation of the material's temperature (Grossman 1977; Nichols 2018).

In the accelerated weathering testing, it should be considered the type of lamp used to simulate the solar radiation since there are different wavelengths for each radiation source. Moreover, the irradiance provided must be uniform within a wavelength range similar to sunlight (González-López et al. 2020).

2.2 Moisture

The effects of moisture due to accelerated weathering can result in degradation, cracking, and depigmentation of materials (Michel and Billington 2012). In laboratory weathering testing, degradation can occur by humidifying the chamber air or by spraying water. Hydrolysis is more related to the immersion of materials, and photodegradation is accelerated by spraying and condensation (González-López et al. 2020). In condensation and spraying processes, sulfate ions are deposited on the material surface, increasing acidity, accelerating its degradation (Grossman 1977). According to ASTM G154 (2016), pure water must contain a maximum of 1 ppm of total solids and 0.2 ppm of silica.

Despite the chamber conditions simulating natural environmental conditions, rain and solar radiation are seasonal factors. Therefore, comparing natural weathering to accelerated weathering can generate results with significant variation (Grossman 1977). According to Pickett (2018), the material surface is opaquer after laboratory wear, while materials exposed to the open air appear much clearer. These statements can be related to the controlled conditions, where there is a soft and cloudy spray of

the water. On the other hand, in the natural environment, the rains tend to be more aggressive and combined with particulates and winds.

2.3 Temperature and Microbiota

Most polymers have a degradation above 100 °C. Thus, the temperature used in the weathering process does not directly affect the degradation of these materials. However, the accelerated weathering' effect on polymers occurs in a series of physicochemical reactions that depend on the temperature to occur, leading to final degradation (Nichols 2018). Elevated temperatures accelerate hydrolysis and photo-oxidation reactions due to the effects of radiation and moisture, in addition to increasing degradation rates (Gijsman 2018). In accelerated weathering tests, temperature cycles are applied, thus causing heating and cooling of the material. Therefore, mechanical properties, such as stretching and contraction of the material, are affected, resulting in the weakening of the polymeric structure and promoting fractures (González-López et al. 2020).

The ability of microorganisms to multiply in several environmental conditions makes them an important factor in degradability tests of bio-composites (Kavitha et al. 2016). The action of microorganisms may not occur directly on the degradation of the material. However, they may be responsible for producing compounds that can act on the materials. The release of acids, for example, can cause corrosion or weaken the material's structures (Ghanbarzadeh and Almasi 2013). Algae and fungi cannot generally metabolize high molecular weight polymers. Nonetheless, these microorganisms can grow on the surfaces when the polymer is broken down into smaller molecules or when the physical structure is damaged (Pickett 2018).

3 Accelerated Weathering

The use of laboratory techniques to evaluate the degradation of materials aims to reproduce in a short time the conditions that would take years to occur naturally. The tests must have high precision, and the experimental conditions must be appropriate for each type of material since the behavior will vary (Michel and Billington 2012; Latos-Brozio and Masek 2020). Techniques used to perform accelerated weathering seek to cause stress to the material by reproducing environmental conditions (Pickett 2018). Besides, accelerated weathering testing can use different types of lamps, wavelength ranges, and exposure times considering the standard methods ISO 4892–1 and ASTM G151 (González-López et al. 2020).

The main techniques evaluate the deterioration caused by sunlight, and the xenon arc test can be used for the weathering process of internal and external solar exposure of materials. Another testing is related to ultraviolet exposure, which simulates the

Table 1 Standard tests for accelerated weathering in different materials

Standard test	Types of materials	References
AATCC TM186	Textile materials	AATCC 186 (2015)
ASTM D4101	Polypropylene materials	ASTM D4101 (2017)
ASTM D4329/ ISO 29664	Plastic materials	ASTM D4329 (2013); ISO 29664 (2010)
ASTM D5208	Photodegradable plastic materials	ASTM D5208 (2014)
ASTM D4811	Non-vulcanized rubber	ASTM D4811 (2016)
ASTM F1164	Transparent plastic materials	ASTM F1164 (2019)
ASTM F1945	Inner lining materials	ASTM F1945 (2011)
DIN 75,220	Automotive components	DIN 75220 (1992)
ISO 11507	Paints and varnishes	ISO 11507 (2007)

deterioration of materials in natural sunlight. The carbon arc test verifies the optical properties' resistance when the material is exposed to light and heat (Pickett 2018).

Degradation rates are strongly affected by the intensity of visible light. Xenon, metal-halide, or carbon arc lamps have been used for photo-degradation, exhibiting strong absorption bands below 250 nm. The rate of photodegradation is faster in: carbon arc lamps > metal halide lamps > xenon lamps > external exposure (González-López et al. 2020). Carbon arc lamps were developed to prevent the fading of textiles. The xenon arc light source is surrounded by an internal quartz filter and an external borosilicate glass filter. This light source can greatly distort the chemical changes that occur during accelerated weathering compared to outdoor exposure (Nichols 2018).

In addition to the lamps that simulate solar radiation, the QUV and Q-SUN machines have been used for accelerated weathering tests. With the use of QUV and Q-SUN equipment, standardization of weather conditions is possible. The main difference is that the QUV uses UV at wavelengths between 300 and 400 nm, while the Q-SUN system can use the entire spectrum of sunlight, including UV, visible light, and IR. Thus, Q-SUN simulates degradation conditions similar to the natural environment. However, it is important to control irradiance on Q-SUN machines, as the xenon arc lamp is less spectrally stable. Therefore, calibration radiometers are installed to maintain the spectrum (Sang et al. 2020).

The choice of method depends on the material and the environmental conditions to which it will be exposed. In this context, several standard methodologies are available for different types of materials (Table 1).

4 Studies of Accelerated Weathering on Degradation of the Bio-Composites

Composites reinforced with natural fibers have a growing interest in researchers as a sustainable and biodegradable alternative to conventional polymers. Bio-composites have advantages over conventional materials, such as lightness, low manufacturing cost, renewability, and recyclability. Moreover, bio-composites contribute to the preservation of the ecosystem (Chee et al. 2019). However, polymers or natural fibers are prone to degradation when exposed to different environmental conditions. After the weathering periods, bio-composites may change various properties, such as discoloration, surface roughness, loss of mechanical and thermal stability (Fei et al. 2016). Therefore, accelerated weathering assesses the state and extent of degradation, exposing bio-composites to simulated conditions that are somehow related to outdoor exposure (Pickett et al. 2019).

4.1 Morphology and Visual Appearance

The combined effects of ultraviolet solar radiation, humidity, and temperature oscillations can cause weakening and photodegradation of the polymeric matrix (Vasconscelos et al. 2020). The free radical reaction mechanism shows that the aging of polymers is an automatic catalytic process. The products of the reactions involved can increase the number of reactive species, occurring the auto-acceleration of photo-oxidative degradation (Celina et al. 2019).

Campo et al. (2020) evaluated the morphology of the bio-composite formed of poly (lactic acid) (PLA) and agave fibers (*Agave tequilana* Weber var. Azul). The accelerated weathering test in the bio-composite was performed using the QUV machine. The samples were subjected to 2 h of cyclic exposure to UV light (340 nm fluorescent UV lamp) at 55 °C and 2 h of condensation at 50 °C for 600 h. After accelerated weathering exposure, the results of micrographs showed that gap between the polymer and fibers appeared and increased the pull-out effect of fibers in the bio-composite. These effects are related to the degradation caused by the absorption of UV radiation and moisture at the bio-composite interface. Furthermore, it was observed that accelerated weathering affected the color of the samples, mainly the PLA, which changed from transparent to white.

Sawpan et al. (2019) developed a bio-composite with PLA and hemp fibers and evaluated the appearance properties of the material after the action of accelerated weathering. The samples were subjected to cyclic exposures of 8 h of exposure to UV light (340 nm fluorescent UV lamp) at 60 °C followed by 0.25 h of water spray without light and 3.75 h of condensation at 50 °C. The results show that the color fading from brown to white in bio-composites, caused by the UV degradation of lignin and leaching of impurities from hemp fibers.

4.2 Molecular Characteristics

The chemical properties, crystallinity, and molecular weight of bio-composites are also affected by exposure to UV radiation, humidity, and temperature. Moreover, the results obtained in the weathering process are dependent on the type of material. Photolysis and hydrolysis mechanisms can occur during the accelerated weathering process, randomly breaking the polymer chains (Tsuji et al. 2006). The effects of reducing and increasing molecular weight are also caused by polymeric fission and crosslinking, respectively (Azwa et al. 2013). The extent and rate of degradation depend on the initial molecular weight of the polymer. Shorter chains are easily degraded, while longer chains are more difficult to break (Chávez-Montes et al. 2015).

The scission of the polymeric chain results in increased crystallinity. The degree of crystallinity influences the degradation kinetics. The shorter chains produced during the scission have greater mobility and are easily crystallized, which increases embrittlement and hinders the diffusion of water (Zhou and Xanthos 2008). Crosslinking does not affect crystallinity and is induced by UV. The scission occurs in the amorphous phase of the polymer and is controlled by the diffusion of oxygen (Stark and Matuana 2004). Lv et al. (2017) observed that the accelerated weathering affected the crystallinity of the composite formed by starch, PLA, and wood flour. According to the authors, there may have been greater mobility of the shorter chains obtained from the polymer fission, indicating that the process destroyed the crystalline structure of the PLA.

Photodegradation occurs by two mechanisms in the materials, the first and second-order kinetics. If the molecular weight decreases proportionally to its current value, the process is described by the first-order degradation kinetics (Chávez-Montes et al. 2015). However, if the reduction in molecular weight is proportional to the square of the current molecular weight, the second-order equation of the Norrish II mechanism describes this process (Zaidi et al. 2010; Santonja-Blasco et al. 2013).

4.3 Mechanical Properties

The accelerated weathering studies on mechanical properties simulate the mechanism of degradation of composites (Azwa et al. 2013). The mechanical performance after weathering of bio-composites produced with natural fibers depends on the fiber volume fraction, aspect ratio, fiber orientation, dispersion level, and the state of interfacial adhesion (González-López et al. 2020). Lila et al. (2019) developed the PLA bio-composite containing 20% bagasse fibers to assess the effects of accelerated weathering on mechanical properties. The authors observed an increase of tensile and flexural strength of the bio-composite up to 8 weeks of exposure to temperature cycles. Moreover, tensile strength and modulus increased by 5.2% and 4.3% after 4 weeks of exposure time, respectively, while the flexural strength enhanced by 5.1%

and modulus by 13.4%. A substantial decrease in the tensile and flexural strength of the bio-composite was observed after 12 weeks.

Exposure of bio-composites to moisture conditions can also influence mechanical properties. Dayo et al. (2020) developed bio-composites with hemp fibers and polybenzoxazine and exposed this material to moisture absorption during accelerated weathering testing. Besides, the authors analyzed the impact caused on the tensile strength, flexion, and strength properties. The bio-composite showed low moisture absorption that varied between 3.8 and 6.0%. Exposure to wet conditions reduced the tensile strength from 14.2 to 21.8% compared to control samples, which were not exposed to accelerated weather. The flexion modulus values of the bio-composites showed 8–13% compared to unconditioned samples. Bio-composites showed a 17% increase in impact strength compared to the control sample. Moisture absorption during weathering conditions made the fibers more flexible and resistant, which improved the impact strength.

4.4 Thermal Properties

The accelerated weathering process is also used to check the effects of temperature, UV radiation, and humidity on the material aging. The heating and cooling cycles of weathering can cause cracks and increased crystallinity (Lila et al. 2019). Differential scanning calorimetry (DSC) analysis may indicate changes in the melting temperature of materials as a function of increased crystal mobility (Yatigala et al. 2018). Spiridon et al. (2016) evaluated the effects of weathering on the thermal characteristics of the PLA and cellulose fibers bio-composite. The material was exposed to artificial light from a mercury lamp ($200 < \lambda < 700$ nm) at 30 °C, 60% humidity for 600 h. The results show that the addition of cellulose fibers into the PLA matrix improved thermal stability and crystallinity, as the glass transition temperature and crystallinity index increased by 3 °C and 9.6%, respectively. According to the DSC analysis, the melting temperature of the bio-composites also increased after weathering. Thus, the authors concluded that the combined action of temperature, humidity, and UV results in the embrittlement of the surface and the increase in the melting temperature of bio-composites.

Yorseng et al. (2020) used natural kenaf/sisal fibers to produce composites with a bioepoxy matrix and evaluate thermal stability after the weathering. The material was exposed to the accelerated weathering test containing two cycles with temperature of 63 °C, UV radiation of 0.35 w/m^2 and humidity of 30%. The first cycle was exposed to UV light for 1.42 h, and the second was operated with UV light and water spray for 0.18 h. The results of the thermogravimetric analysis showed that all composites are stable at 295 °C after weathering. Through the DSC curves, it was observed that the melting temperature increased after the accelerated weathering testing. The authors confirm that these results are due to the reinforcement of natural fibers to the bioepoxy matrix.

5 Effects of Nanofillers on Degradation of Composites

The polymer blending is an effective alternative to improve the thermal stability, printability, barrier, and mechanical properties of several materials. Besides, fillers and additives can be used to accelerate or slow down the process of polymer degradation (Antunes et al. 2020a). In this sense, nanofillers are increasingly incorporated into polymeric materials (Han et al. 2018). The addition of titanium oxide nanoparticles, zinc oxide nanoparticles, nano-clays, and carbon nanotubes has been used to improve polymer properties (Luo et al. 2019). According to Nikolic et al. (2016), if good dispersion is achieved together with good compatibility with the polymer, nanoparticles can have a positive effect on the material's performance in the long run.

The degradation rate of PLA has limited its applicability (Zhou et al. 2018). Luo et al. (2019) observed that the biodegradation of PLA under composting conditions could be controlled by titanium oxide (TiO_2) nano-fillers addition. The relative hydrophilicity of the TiO_2 nanoparticles (TiO_2Nps) facilitates the absorption of moisture. Thus, TiO_2Nps contribute to the penetration of water in the polymeric matrix. Therefore, the hydrolytic degradation and photodegradation of PLA are accelerated (Wu and Wu 2006; Farah et al. 2016). In addition to acting as UV protection agent, TiO_2Nps promote the formation of hydroxyl radicals from the water, triggering the chain split and accentuating the polymer degradation (Antunes et al. 2020b; Park et al. 2019). Nano-clays are also able to modify the degradation kinetics of PLA (Olewnik-Kruszkowska et al. 2015). According to Sajna et al. (2016), the nano-clay reinforcement creates a labyrinth-like structure, which decreases the rate of water diffusion and increases resistance to accelerated weathering. In the study developed by Kaynak and Sarı (2016), it was found that the intercalated/exfoliated layers of nano-clay acted as a barrier. Thus, the flexion and traction modules of nano-clay bio-composites were less affected than the bio-composite without nano-clay.

Nano-clay was also used to develop low-density polyethylene (LDPE) composite films for food packaging applications. Nano-clay contributed to the stability of LDPE and improved thermal and barrier properties. However, nano-clays have been found to accelerate the UV oxidation of LDPE. The surface roughness, the chemiluminescence index, and the carbonyl index increased with exposure of the material to UV. The authors also concluded that the mineral oxide ions constituted in nano-clays accelerated the photo-oxidation degradation of LDPE (Han et al. 2018).

There is a growing demand for the use of wood plastic composite in outdoor environments, where they are subject to degradation caused by UV radiation, temperature, and humidity. In this context, nano zinc oxide (ZnO) has been studied to contribute to the resistance to degradation of these composites (Rasouli et al. 2016). Rasouli et al. (2016) evaluated the effect of using ZnO on the degradation of wood composite with high-density polyethylene exposed to artificial weathering. The study found that the number of cracks in the surfaces, loss of tensile strength, and changes in the contact angle decreased due to the presence of ZnO.

Epoxy/timber composites have also stood out for applications in outdoor conditions (Zarras et al. 2016). Multi-walled carbon nanotubes in polymers can improve the performance of epoxy resin material. These nanotubes provide a higher modulus, less elongation, higher fracture toughness, higher abrasion, and wear resistance of the material. Moreover, nanotubes can improve the resistance of polymers to weathering due to their high UV absorption potential (Nowack et al. 2013) and their ability to decrease the moisture and oxygen permeability of materials (Schlagenhauf et al. 2014). In a study by Awad et al. (2018), it was found that the incorporation of carbon nanotubes with multiple walls in an epoxy resin conferred improvements in the mechanical properties (56% for tensile strength and 65% for modules) of the material.

In this way, compared to conventional micro and macro fillers, nanofillers generally exhibit a superior improvement in the properties of composites. Nanoparticles are increasingly incorporated into a wide variety of polymeric materials with favorable matrix-fill interaction that results in improved physical, chemical, and electrical properties. Filling of nanoscale also contributes to modifying the morphology of material and improve the miscibility/compatibility of polymer blending (Scaffaro and Botta 2014).

6 Conclusions and Future Perspective

Weathering causes the degradation of bio-composites through photo-radiation, thermal degradation, photo-oxidation, and hydrolysis. These processes, through the incidence of UV radiation, and temperature and humidity cycles result in molecular changes, thermal and mechanical properties of bio-composites. Studies of accelerated weathering of bio-composites containing natural fibers show that fibers influence thermal stability, increase tensile and flexural strength, affect crystallinity and molecular weight. The fiber content also affects the absorption of UV radiation and moisture from the composites, which can cause the weakening of the matrix and color fading.

Reinforcements can attenuate the loss of mechanical properties and is related to their structural integrity and the state of interfacial adhesion. Carbon nanotubes and zinc oxide nanoparticles, for example, showed act as a protective barrier during the weathering attack, retarding the degradation process of polymers. Titanium oxide nanoparticles can act as UV protection agents but contribute to accentuating the polymer degradation. Therefore, it is interesting to use nanofillers as reinforcements in bio-composites because they can accelerate or slow down the degradation process, depending on the material composition and environmental conditions to which they are exposed.

References

AATCC 186 (2015) AATCC 186: test method for weather resistance: UV light and moisture exposure

Antunes A, Popelka A, Aljarod O, Hassan MK, Luyt AS (2020a) Effects of rutile–TiO_2 nanoparticles on accelerated weathering degradation of poly(lactic acid). Polymers 12:1096. https://doi.org/10.3390/polym12051096

Antunes A, Popelka A, Aljarod O, Hassan MK, Kasak P, Luyt AS (2020b) Accelerated weathering effects on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and PHBV/TiO_2 nanocomposites. Polymers 12:1743. https://doi.org/10.3390/polym12081743

ASTM D4101 (2017) ASTM D4101—17e1 standard classification system and basis for specification for polypropylene injection and extrusion materials

ASTM D4329 (2013) ASTM D4329—13 standard practice for fluorescent ultraviolet (UV) lamp apparatus exposure of plastics

ASTM D4811 (2016) ASTM D4811/D4811M—16 standard specification for nonvulcanized (Uncured) rubber sheet used as roof flashing

ASTM D5208 (2014) ASTM D5208—14 standard practice for fluorescent ultraviolet (UV) exposure of photodegradable plastics

ASTM F1164 (2019) ASTM F1164—19 standard test method for evaluation of transparent plastics exposed to accelerated weathering combined with biaxial stress

ASTM F1945 (2011) ASTM F1945—05(2011) Standard practice for determining the lightfastness of ink jet prints exposed to indoor fluorescent lighting (Withdrawn 2020)

ASTM G154 (2016) ASTM G154—16 standard practice for operating fluorescent ultraviolet (UV) lamp apparatus for exposure of nonmetallic materials

ASTM G177 (2020) ASTM G177—03(2020) standard tables for reference solar ultraviolet spectral distributions: hemispherical on 37° tilted surface

Awad SA, Fellows CM, Mahini SS (2018) Effects of accelerated weathering on the chemical, mechanical, thermal and morphological properties of an epoxy/multi-walled carbon nanotube composite. Polym Test 66:70–77. https://doi.org/10.1016/j.polymertesting.2017.12.015

Aziz N, Mat Nor NA, Mohd-Adnan AF, Taha RM, Arof AK (2016) Colour properties of poly(vinyl alcohol)–anthocyanin blends. Opt Quantum Electron 48:451. https://doi.org/10.1007/s11082-016-0715-7

Azwa ZN, Yousif BF, Manalo AC, Karunasena W (2013) A review on the degradability of polymeric composites based on natural fibres. Mater Des 47:424–442. https://doi.org/10.1016/j.matdes.2012.11.025

Campo ASM, Robledo-Ortíz JR, Arellano M, Rabelero M, Pérez-Fonseca AA (2020) Accelerated weathering of polylactic acid/agave fiber biocomposites and the effect of fiber–matrix adhesion. J Polym Environ 1–11. https://doi.org/10.1007/s10924-020-01936-z

Celina M, Linde E, Brunson D, Quintana A, Giron N (2019) Overview of accelerated aging and polymer degradation kinetics for combined radiation-thermal environments. Polym Degrad Stabil 166:353–378. https://doi.org/10.1016/j.polymdegradstab.2019.06.007

Chávez-Montes W, González-Sánchez G, López-Martínez E, Lira-Gómez P, Ballinas-Casarrubias L, Flores-Gallardo S (2015) Effect of artificial weathering on PLA/nanocomposite molecular weight distribution. Polymers 7:760–776. https://doi.org/10.3390/polym7040760

Chee SS, Jawaid M, Sultan MTH, Alothman OY, Abdullah LC (2019) Accelerated weathering and soil burial effects on colour, biodegradability and thermal properties of bamboo/kenaf/epoxy hybrid composites. Polym Test 79:106054. https://doi.org/10.1016/j.polymertesting.2019.106054

Dayo AQ, Babar AA, Qin QR, Kiran S, Wang J, Shah AH, Zegaoui A, Ghouti HA, Liu WB (2020) Effects of accelerated weathering on the mechanical properties of hemp fibre/polybenzoxazine based green composites. Compos Part A Appl Sci Manuf 128:105653. https://doi.org/10.1016/j.compositesa.2019.105653

DIN 75220 (1992) DIN 75220—applied technical services

Farah S, Anderson D, Langer R (2016) Physical and mechanical properties of PLA, and their functions in widespread applications—a comprehensive review. Adv Drug Deliv Rev 107:367–392. https://doi.org/10.1016/j.addr.2016.06.012

Fei P, Xiong H, Cai J, Liu C, Zia-ud-Din YuY (2016) Enhanced the weatherability of bamboo fiber-based outdoor building decoration materials by rutile nano-TiO_2. Constr Build Mater 114:307–316. https://doi.org/10.1016/j.conbuildmat.2016.03.166

Gao T, He Z, Hihara LH, Mehr HS, Soucek MD (2019) Outdoor exposure and accelerated weathering of polyurethane/polysiloxane hybrid coatings. Prog Org Coatings 130:44–57. https://doi.org/10.1016/j.porgcoat.2019.01.046

Ghanbarzadeh B, Almasi H (2013) Biodegradable polymers. In: Chamy R (ed) Biodegradation—life of science. InTech, Valparaiso, p 200

Gijsman P (2018) Polymer stabilization. In: Handbook of environmental degradation of materials, 3rd Edit. Elsevier, pp 369–395

González-López ME, Campo ASM, Robledo-Ortíz JR, Arellano M, Pérez-Fonseca AA (2020) Accelerated weathering of poly (lactic acid) and its biocomposites: a review. Polym Degrad Stabil 179:109290. https://doi.org/10.1016/j.polymdegradstab.2020.109290

Grossman GW (1977) Correlation of laboratory to natural weathering. J Coatings Technol 49:45–54

Han C, Zhao A, Varughese E, Sahle-Demessie E (2018) Evaluating weathering of food packaging polyethylene-nano-clay composites: release of nanoparticles and their impacts. NanoImpact 9:61–71. https://doi.org/10.1016/j.impact.2017.10.005

ISO 11507 (2007) ISO—ISO 11507:2007—paints and varnishes—exposure of coatings to artificial weathering—exposure to fluorescent UV lamps and water

ISO 29664 (2010) ISO—ISO 29664:2010—plastics—artificial weathering including acidic deposition

Kavitha G, Kurinjimalar C, Sivakumar K, Kaarthik M, Aravind R, Palani P, Rengasamy R (2016) Optimization of polyhydroxybutyrate production utilizing waste water as nutrient source by *Botryococcus braunii* Kütz using response surface methodology. Int J Biol Macromol 93:534–542. https://doi.org/10.1016/j.ijbiomac.2016.09.019

Kaynak C, Sarı B (2016) Accelerated weathering performance of polylactide and its montmorillonite nanocomposite. Appl Clay Sci 121–122:86–94. https://doi.org/10.1016/j.clay.2015.12.025

Kiryukhin MV, Lau HH, Goh SH, The C, Korzh V, Sadovoy A (2018) A membrane film sensor with encapsulated fluorescent dyes towards express freshness monitoring of packaged food. Talanta 182:187–192. https://doi.org/10.1016/j.talanta.2018.01.085

Kuntzler SG, Costa JAV, Morais MG (2018) Development of electrospun nanofibers containing chitosan/PEO blend and phenolic compounds with antibacterial activity. Int J Biol Macromol 117:800–806. https://doi.org/10.1016/j.ijbiomac.2018.05.224

Lankone RS, Ruggiero E, Goodwin DG, Vilsmeier K, Mueller P, Pulbere S, Challis K, Bi Y, Westerhoff P, Ranville J, Fairbrother DH, Sung L-P, Wohlleben W (2020) Evaluating performance, degradation, and release behavior of a nanoform pigmented coating after natural and accelerated weathering. NanoImpact 17:1–9. https://doi.org/10.1016/j.impact.2019.100199

Latos-Brozio M, Masek A (2020) The application of natural food colorants as indicator substances in intelligent biodegradable packaging materials. Food Chem Toxicol 135:110975. https://doi.org/10.1016/j.fct.2019.110975

Lila MK, Shukla K, Komal UK, Singh I (2019) Accelerated thermal ageing behaviour of bagasse fibers reinforced poly (lactic acid) based biocomposites. Compos Part B Eng 156:121–127. https://doi.org/10.1016/j.compositesb.2018.08.068

Luo Y, Lin Z, Guo G (2019) Biodegradation assessment of poly (lactic acid) filled with functionalized titania nanoparticles (PLA/TiO_2) under compost conditions. Nanoscale Res Lett 14:1–10. https://doi.org/10.1186/s11671-019-2891-4

Lv S, Liu X, Gu J, Jiang Y, Tan H, Zhang Y (2017) Effect of glycerol introduced into PLA based composites on the UV weathering behavior. Constr Build Mater 144:525–531. https://doi.org/10.1016/j.conbuildmat.2017.03.209

Michel AT, Billington SL (2012) Characterization of poly-hydroxybutyrate films and hemp fiber reinforced composites exposed to accelerated weathering. Polym Degrad Stab 97:870–878. https://doi.org/10.1016/j.polymdegradstab.2012.03.040

Mohseni M, Ramezanzadeh B, Yari H (2011) Effects of environmental conditions on degradation of automotive coatings. In: New trends and developments in automotive industry. InTech, pp 267–296

Moreira JB, Lim L-T, Zavareze ER, Dias ARG, Costa JAV, Morais MG (2019) Antioxidant ultrafine fibers developed with microalga compounds using a free surface electrospinning. Food Hydrocoll 93:131–136. https://doi.org/10.1016/j.foodhyd.2019.02.015

Nichols ME (2018) Paint weathering tests. In: Handbook of environmental degradation of materials, 3rd edn. Elsevier, pp 51–67

Nikolic M, Nguyen HD, Daugaard AE, L€of D, Mortensen K, Barsberg S, Sanadi AR (2016) Influence of surface modified nano silica on alkyd binder before and after accelerated weathering. Polym Degrad Stabil 126:134–143. https://doi.org/10.1016/j.polymdegradstab.2016.02.006

Nowack B, David RM, Fissan H, Morris H, Shatkin JA, Stintz M, Zepp R, Brouwer D (2013) Potential release scenarios for carbon nanotubes used in composites. Environ Int 59:1–11. https://doi.org/10.1016/j.envint.2013.04.003

Olewnik-Kruszkowska E, Koter I, Skopinska-Wisniewska J, Richert J (2015) Degradation of polylactide composites under UV irradiation at 254 nm. J Photochem Photobiol Chem 311:144–153. https://doi.org/10.1016/j.jphotochem.2015.06.029

Park Y, Jin S, Park Y, Kim SM, Noda I, Chae B, Jung YM (2019) Studies on chemical IR images of poly(hydroxybutyrate-co-hydroxyhexanoate)/poly(ethylene glycol) blends and two-dimensional correlation spectroscopy. Polymers 11:507. https://doi.org/10.3390/polym11030507

Pickett JE (2018) Weathering of plastics. In: Myer K (ed) Handbook of environmental degradation of materials. Elsevier, Third Edit, pp 163–184

Pickett JE, Kuvshinnikova O, Sung L-P, Ermi BD (2019) Accelerated weathering parameters for some aromatic engineering thermoplastics. Polym Degrad Stabil 166:135–144. https://doi.org/10.1016/j.polymdegradstab.2019.05.028

Rasouli D, Dintcheva NT, Faezipour M, Mantia FPL, Farahani MRM, Tajvidi M (2016) Effect of nano zinc oxide as UV stabilizer on the weathering performance of wood-polyethylene composite. Polym Degrad Stab 133:85–91. https://doi.org/10.1016/j.polymdegradstab.2016.08.004

Rivera-Briso LA, Serrano-Aroca Á (2018) Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate): enhancement strategies for advanced applications. Polymers 10:732. https://doi.org/10.3390/polym10070732

Sajna V, Nayak SK, Mohanty S (2016) Weathering and biodegradation study on graft copolymer compatibilized hybrid bionanocomposites of poly(lactic acid). J Mater Eng Perform 25:2895–2906. https://doi.org/10.1007/s11665-016-2151-z

Sang T, Wallis C, Hill G, Britovsek GJP (2020) Polyethylene terephthalate degradation under natural and accelerated weathering conditions. Eur Polym J 136:109873. https://doi.org/10.1016/j.eurpolymj.2020.109873

Santonja-Blasco L, Ribes-Greus A, Alamo RG (2013) Comparative thermal, biological and photodegradation kinetics of polylactide and effect on crystallization rates. Polym Degrad Stabil 98:771–784. https://doi.org/10.1016/j.polymdegradstab.2012.12.012

Sawpan MA, Islam MR, Beg MDH, Pickering K (2019) Effect of accelerated weathering on physico-mechanical properties of polylactide bio-composites. J Polym Environ 27:942–955. https://doi.org/10.1007/s10924-019-01405-2

Scaffaro R, Botta L (2014) Nanofilled thermoplastic—thermoplastic polymer blends. In: Thomas S, Shanks R, Chandrasekharakurup S (eds) Nanostructured polymer blends. Elsevier, Oxford p, pp 133–160

Schlagenhauf L, Nüesch F, Wang J (2014) Release of carbon nanotubes from polymer nanocomposites. Fibers 2:108–127. https://doi.org/10.3390/fib2020108

Silva CK, Mastrantonio DJS, Costa JAV, Morais MG (2019) Innovative pH sensors developed from ultrafine fibers containing açaí (*Euterpe oleracea*) extract. Food Chem 294:397–404. https://doi.org/10.1016/j.foodchem.2019.05.059

Spiridon I, Darie RN, Kangas H (2016) Influence of fiber modifications on PLA/fiber composites. Behavior to accelerated weathering. Compos Part B: Eng 92:19–27. https://doi.org/10.1016/j.compositesb.2016.02.032

Stark NM, Matuana LM (2004) Surface chemistry changes of weathered HDPE/wood–flour composites studied by XPS and FTIR spectroscopy. Polym Degrad Stabil 86:1–9. https://doi.org/10.1016/j.polymdegradstab.2003.11.002

Sun Y, Yuan J, Zhou T, Zhao Y, Yu F, Ma J (2020) Laboratory simulation of microplastics weathering and its adsorption behaviors in an aqueous environment: a systematic review. Environ Pollut 265:114864. https://doi.org/10.1016/j.envpol.2020.114864

Tsuji H, Echizen Y, Nishimura Y (2006) Enzymatic degradation of poly(l-lactic acid): effects of UV irradiation. J Polym Environ 14:239–248. https://doi.org/10.1007/s10924-006-0023-6

Vasconcelos GCMSD, Carvalho LHD, Barbosa R, Idalino RDCDL, Alves TS (2020) Effects of weathering on mechanical and morphological properties cork filled green polyethylene eco-composites. Polímeros 30:1–11. https://doi.org/10.1590/0104-1428.04919

Wu T-M, Wu CY (2006) Biodegradable poly(lactic acid)/chitosan-modified montmorillonite nanocomposites: preparation and characterization. Polym Degrad Stab 91:2198–2204. https://doi.org/10.1016/j.polymdegradstab.2006.01.004

Xie N, Li H, Zhang H, Zhang X, Jia M (2020) Effects of accelerated weathering on the optical characteristics of reflective coatings for cool pavement. Sol Energy Mater Sol Cells 215:110698. https://doi.org/10.1016/j.solmat.2020.110698

Yatigala NS, Bajwa DS, Bajwa SG (2018) Compatibilization improves performance of biodegradable biopolymer composites without affecting UV weathering characteristics. J Polym Environ 26:4188–4200. https://doi.org/10.1007/s10924-018-1291-7

Yorseng K, Rangappa SM, Pulikkalparambil H, Siengchin S, Parameswaranpillai J (2020) Accelerated weathering studies of kenaf/sisal fiber fabric reinforced fully biobased hybrid bioepoxy composites for semi-structural applications: Morphology, thermo-mechanical, water absorption behavior and surface hydrophobicity. Constr Build Mater 235:117464. https://doi.org/10.1016/j.conbuildmat.2019.117464

Zaidi L, Kaci M, Bruzaud S, Bourmaud A, Grohens Y (2010) Effect of natural weather on the structure and properties of polylactide/Cloisite 30B nanocomposites. Polym Degrad Stabil 95:1751–1758. https://doi.org/10.1016/j.polymdegradstab.2010.05.014

Zarras P, Goodman PA, Stenger-Smith JD (2016) Functional polymeric coatings: synthesis, properties, and applications. In: Zuzuarregui A, Morant-Miñana MC (eds) Research perspectives on functional micro- and nanoscale coatings. IGI Global, Hershey pp 78–104

Zhou Q, Xanthos M (2008) Nanoclay and crystallinity effects on the hydrolytic degradation of polylactides. Polym Degrad Stabil 93:1450–1459. https://doi.org/10.1016/j.polymdegradstab.2008.05.014

Zhou YH, Lei L, Yang B, Li JB, Ren J (2018) Preparation and characterization of polylactic acid (PLA) carbon nanotube nanocomposites. Polym Test 68:34–38. https://doi.org/10.1016/j.polymertesting.2018.03.044

Effects of Natural Weathering on Aesthetics, Thermal and Mechanical Properties of Completely Biodegradable Composites

Clement Matthew Chan, Steven Pratt, and Bronwyn Laycock

Abstract The emergence of biodegradable plastics as the polymer matrix for natural fibre composites has been rapid, due to the concerns over the accumulation of nondegradable plastic waste in the environment. Given the market growth in exterior applications, there is a need to understand the behaviour of these emerging materials under natural weathering conditions before these materials can be commercialised. In this chapter, we have provided an overview of the natural weathering behaviour of representative completely biodegradable composites. The effects of natural weathering on completely biodegradable composites are no far different from those on natural fibre composites with conventional non-degradable matrices. Any influence of biodegradation from the biopolymer matrices was not evident under natural weathering conditions for at least 2 years. Physical and mechanical deteriorations of the composites were observed after a few months of exposure, the severity depending predominantly on the fibre content. Overall, the conclusion is that the accessibility of the natural fibres and the rate of moisture ingress into the bulk matrix controls the stability of the biodegradable composites upon natural weathering.

1 Introduction

The demand for natural fibre composites has been burgeoning in the past decades, with applications ranging from packaging material to structural components such as decking. Petroleum-derived and non-biodegradable polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) are among the most commonly used polymer matrices in the current natural fibre composites market (Marketsandmarkets 2019). The use of such non-degradable matrices makes the final composite products non-degradable and, at the same time, these composites are challenging to recycle in conventional plastic recycling facilities due to their complex structure and use of hybrid ingredients. In recent years, there is increasing awareness and concern

C. M. Chan (✉) · S. Pratt · B. Laycock
School of Chemical Engineering, The University of Queensland, St Lucia, QLD 4072, Australia
e-mail: c.chan@uq.edu.au

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_10

regarding the end-of-life management and environmental impact of these natural fibre composites. Therefore, the demand for a shift towards the use of renewable and biodegradable materials as the polymer matrix to yield a new class of completely biodegradable composites while not losing performance is growing (Faruk et al. 2012; 2014; Gurunathan et al. 2015; Satyanarayana et al. 2009).

2 What Are Biopolymers/Biodegradable Polymers?

Before we can consider the properties of completely biodegradable composites, we need to understand what constitutes a biodegradable polymer. Biodegradable polymeric materials or, more simply in this chapter, biopolymers, are polymers that can be degraded into water, carbon dioxide and residual biomass by living microorganisms or bacteria through biological activity. According to the most recent standards, a broad range of polymers can be regarded as biopolymers, including those which are synthesised into polymers in plants (e.g. thermoplastic starch), animals (e.g. proteins) and bacteria (e.g. polyhydroxyalkanoate (PHA)), as well as those from synthetic routes (e.g. polylactic acid (PLA), polycaprolactone (PCL), poly(butylene adipate-*co*-terephthalate) (PBAT) and polybutylene succinate (PBS)). The thermal and mechanical properties of these polymers are summarised in Table 1. The biopolyesters, including PHA, PLA, PBAT and PBS, have mechanical properties that are similar to conventional polyolefins such as PP, low-density polyethylene (LDPE) and high-density polyethylene (HDPE), with PHA and PLA being more brittle. They are also relatively hydrophobic in nature, which is an attractive property for outdoor applications. Thermoplastic starch is the most hydrophilic of the biopolymers. It is predominantly used in polymer blends to add oxygen and carbon dioxide barrier properties (Cooper 2013). The most common biopolymers used in the plastics industry are PLA, poly(3-hydroxybutyrate) (P(3HB), a common PHA homopolymer), thermoplastic starch and PCL, which have been entering the market in different sectors ranging from packaging to structural applications (Halley and Dorgan 2011).

3 Applications of Biopolymers in Natural Fibre Composites

A composite is a hybrid material formed by combining two or more materials to yield a new class of material with different properties. It takes advantage of the high modulus fibres to overcome the low modulus and low thermal stability of virgin plastics. Ceramics and glass fibres have been the fibre of choice. Recently, there has been a shift to the use of organic fillers, predominantly lignocellulosic fibres to replace traditional inorganic fillers as they pose advantages including low-cost, light weight and sustainability being both bio-renewable and biodegradable (Faruk et al. 2012). The use of biopolymers as the polymer matrix is attractive as it takes advantage

Table 1 Thermal and mechanical properties of common biopolymers and (as reference) commodity grade nondegradable polyolefins (Brostow 2007; de Matos Costa et al. 2020; Drobny 2012; Gigli et al. 2016; Jian et al. 2020; Jiménez et al. 2012; Laycock et al. 2014; Van de Velde and Kiekens 2002)

Polymer type	Density	Melting temperature, T_m (°C)	Glass transition temperature, T_g (°C)	Tensile strength (MPa)	Tensile Young's modulus (GPa)
PHA (Laycock et al. 2014)	1.18–1.26	64–181	−13–18	1.8–51	0.14–8.7
PLA (Van de Velde and Kiekens 2002)	1.21–1.25	150–162	45–60	21–60	0.35–3.5
PCL (Van de Velde and Kiekens 2002)	1.11–1.15	58–65	−65 to −60	21–42	0.21–0.44
Starch (Jiménez et al. 2012)	1.26–1.28	Amorphous	31–98	3.1–30	0.17–1.5
PBAT (de Matos Costa et al. 2020; Jian et al. 2020)	1.22	115–125	−27 to −32	18–23	0.78–0.84
PBS (Gigli et al. 2016)	1.24–1.26	111–115	−37 to −18	31–35	0.34–0.54
PP (Brostow 2007; Drobny 2012)	0.90–0.91	160–169	−14 to −6	28–40	1.1–2.0
HDPE (Brostow 2007; Drobny 2012)	0.95–0.97	130–137	−125 to −90	20–40	0.70–1.4
LDPE (Brostow 2007; Drobny 2012)	0.92–0.93	105–125	−125 to −90	7–17	−0.30

of both ingredients being biodegradable, thereby further expanding applications to relatively short-term uses such as packaging.

Among all the biopolymers, PLA, PHA, thermoplastics starch and PBS have been predominantly used in natural fibre composite applications, where there is already a substantial amount of literature on their physical and mechanical properties of such biocomposites, with a focus on process and property optimisations (Chan et al. 2018; Gurunathan et al. 2015; Satyanarayana et al. 2009). Given that the target applications for completely biodegradable composites include both indoor and outdoor environments, the durability of these materials under representative 'in-service' conditions need to be explicitly assessed. The natural weathering of natural fibre composites of conventional PP and PE are well-documented (Azwa et al. 2013; Badji et al. 2017; Fabiyi et al. 2008; Homkhiew et al. 2014), where the deterioration of both physical and mechanical properties is commonly observed. Observations

include the discolouration or photo-bleaching of the composite surface from brown to white (Badji et al. 2017), the development of a higher degree of surface roughness (Badji et al. 2017), the formation of surface cracking (Fabiyi et al. 2008), and these when combined lead to a drop in mechanical performance (Homkhiew et al. 2014). Moisture, UV effects and fungal attack all play a role in determining the weatherability of composite materials. Given the increasing demand on the shift towards the use of biopolymers as the matrix, concerns about their long-term weatherability and stability are raised. Therefore, this chapter aims to provide an overview of the effect of natural weathering on the aesthetic, thermal, and mechanical properties of biopolymer based biocomposites, with data from natural weathering studies on representative biodegradable composites being presented and the controlling factors being analysed.

It should be noted that accelerated weathering tests have been the preferred testing method for biocomposites in the literature, as opposed to natural weathering aging, as the latter requires time and will encounter the challenge of inconsistency. However, with the focus of this chapter being on the exposure to real-life outdoor 'in-service' conditions, such studies from accelerated weathering are not considered. For a discussion of this topic, a review by Chang, Mohanty and Misra (Chang et al. 2020) provides a comprehensive summary of the accelerated weathering of completely biodegradable composites.

4 Natural Weathering of Completely Biodegradable Composites

4.1 Visual Changes Due to Natural Weathering

The UV light from natural sunlight can induce the photo-oxidative degradation of both the polymer matrices and the fibre constituents (Matuana et al. 2011). This is a decomposition process that breaks down the chemical structure of the materials, and can occur via multiple pathways involving free radical chemistry and oxidative processes, since the energy from the shortest wavelength of solar radiation is enough to scission C–C, C–N, C–O and N–H bonds (Kockott 1999). Such bond scission can result in photobleaching of chromophores as well as eventual degradation of mechanical properties. Figure 1 illustrates the changes in aesthetic properties of composites of poly(3-hydroxybutyrate-*co*3-hydroxyvalerate) (PHBV), a copolymer of PHA, and wood flour (WF) at 3 different loadings (0, 20 and 50 wt%), and PLA and wood flour from a natural weathering study of samples placed on an inclined stainless-steel rack for a duration of 12 months (Chan et al. 2019). Whitening was observed on the surface exposed to UV sunlight for all composites, independent of loading.

These colour changes could be quantified using a spectrometer and expressed using the CIE Lab system, which consists of L^*, a^* and b^* colour coordinates.

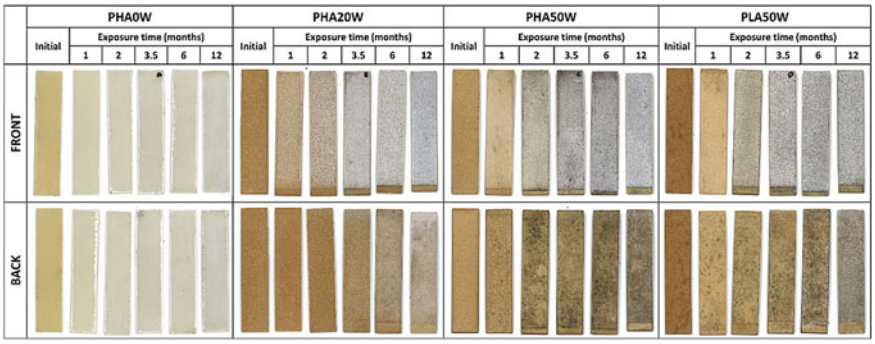


Fig. 1 Visual appearance of PHBV/WF (0, 20 and 50 wt% WF) and PLA/WF (50 wt%) composite samples when exposed to natural weathering. FRONT (top row): the surface facing the sun; BACK (bottom row): the surface in the shade. Figure adapted with permission from (Chan et al. 2019) and modified, Elsevier, copyright 2019

The changes in colour properties (ΔL^*, Δa^* and Δb^*) of the of PHBV/WF and PLA/WF are presented in Fig. 2. L^* represents the lightness, such that a positive ΔL^* means that the specimen is lighter in colour. a^* represents the red-green direction, such that a shift towards red is represented by a positive Δa^* and b^* represents the yellow-blue direction such that a shift towards yellow is represented by a positive Δb^*. The aesthetic properties upon natural weathering were also captured in a study of PBS composites with kenaf bast fibre (KBF) at 5 different loadings (0, 10, 20, 30 and 40 wt%) for a duration of 6 months (Ahmad Thirmizir et al. 2010). All the composites across the studies showed positive ΔL^* values after the first few months of exposure (Fig. 2a), and the degree of whitening increased with increasing fibre loading. This implies that the whitening of the composites is dominated by the photo-bleaching of the fibre constituents. In terms of yellowness, all PHBV/WF and PLA/WF samples showed steep decreases in yellowness over the first 3.5 months of natural weathering and then stabilised (Fig. 2c). The UV-activated reduction of

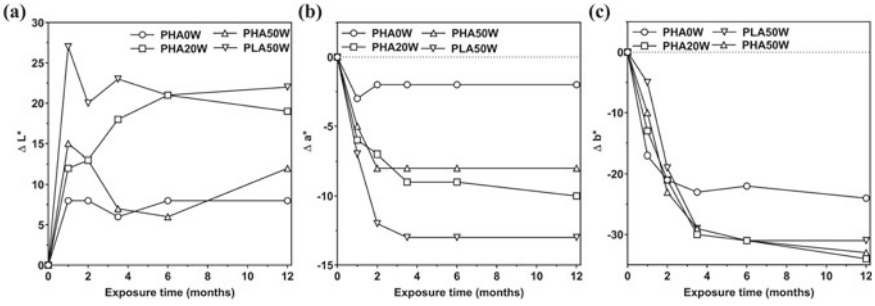


Fig. 2 Colour changes in CIE Lab colour parameters of the surface facing the sun of PHBV/WF (0, 20 and 50 wt% WF) and PLA/WF (50 wt%) composite samples when exposed to natural weathering. Figure adapted with permission from (Chan et al. 2019) and modified, Elsevier, copyright 2019

paraquinones (the oxidation product of lignin) to hydroquinones has been proposed to explain the decrease in yellowness (Chan et al. 2019). Unlike PHBV/WF and PLA/WF composites, the yellowness of PBS/KBF composites first increased in the first 2 months of natural weathering then decreased (Ahmad Thirmizir et al. 2010). The formation of paraquinones through the oxidation of lignin can be associated with the yellowing observed in the early stage of exposure (Muasher and Sain 2006). Photo-bleaching then dominated, in a similar fashion to PHBV/WF and PLA/WF composites. The initial increase in yellowness was not shown in those composites due to the more severe photo-bleaching of the polyesters, as shown by positive ΔL^* and negative Δb^* values from PHBV (Fig. 2).

The aesthetic properties of the composite surface in the shade were also affected by natural weathering. Black regions associated with mould growth were evidenced from PHBV/WF and PLA/WF composites within 2 months of natural weathering (Chan et al. 2019). Apart from UV irradiation, the specimens have also experienced natural wet-dry cycles through rainfall and sunlight periods. Lignocellulosic materials are susceptible to moisture absorption due to their hygroscopic nature. The retained moisture facilitated the growth of filamentous fungal hyphae and spherical spores, which are commonly seen in decayed wood without appropriate protection or coating (Hammer et al. 2014; Xu et al. 2015). Overall, fibre loading plays a dominating role in determining the aesthetic properties of composites upon natural weathering through exposure to UV irradiation from sunlight and rainfall.

4.2 Effect of Natural Weathering on Thermal Properties

The thermal properties of biopolymers are also affected by natural weathering, especially the polymer crystallinity of semi-crystalline polymers (Laycock et al. 2017). In the context of composites, natural fibres act as nucleating agents that promote the crystal growth of the polymer matrix, resulting in increased crystallisation and smaller crystal spherulites (Reinsch and Kelley 1997). Such fibres could therefore influence the effects of the weathering process on thermal properties. However, such effects have not been commonly assessed in natural weathering studies on biocomposites, with only a few natural weathering studies reporting the trends in thermal properties.

In one such study, the melting temperatures of the neat PHBV and its composites with WF remained unchanged throughout the 12-month natural weathering period (Chan et al. 2019). Neat PLA also showed constant melting temperature after 60 days of natural weathering (Zaidi et al. 2010). It is well-established in the literature that the exposure to UV irradiation led to crosslinking of polymer chains of aromatic biopolyesters such as PBAT (Mistretta et al. 2020; Stloukal et al. 2012). While for linear biopolyesters, including PHBV and PLA, photochemical reactions provoked chain scissions mainly through the photochemical reactions of the carbonyl groups (C=O) with absorptions bands between 190–280 nm (Sakai and Tsutsumi 2010). Both PHA (Sadi et al. 2010; Wei and McDonald 2016) and PLA (Ikada 1997; Sakai

and Tsutsumi 2010) showed molecular weight loss when exposed to UV irradiation at 280–400 nm wavelength through Norrish Type I and Type II reactions (free radical initiation and chain scissioning) (Zaaba and Jaafar 2020). The wavelength spectrum of sunlight on the ground extends from approximately 280 to 3000 nm and could initiate photochemical reaction of the C=O bonds but the intensity may not be enough to see an effect on the bulk properties of the polymer (Sakai and Tsutsumi 2010). Therefore, the influence from the exposure to sunlight irradiation was not enough to alter the bulk lamellar structures of these biopolymer crystals (Wei and McDonald 2016).

The melt crystallisation temperatures of PHBV and PHBV/WF composites showed a step increase after 1 month of natural weathering and then stayed constant (Fig. 3b). This means that the polymer chains require less "cooling" energy to form crystals. As stated above, although limited under natural weathering, exposure to UV irradiation promotes chain scission reactions of PHBV and still led to a slight loss in molecular weight (Chan et al. 2019). Higher chain mobility of the short polymer chains could explain the phenomenon, i.e. when the PHBV is cooling from the melt, less energy is required for the arrangement of chains to highly ordered crystals.

No clear trends were observed with respect to the enthalpy of melting (ΔH_m) values over the 12-month natural weathering of PHBV and PHBV/WF composites (Fig. 3c). The crystallinity of biopolymers has been shown to be directly proportional to ΔH_m such that ΔH_m values can be used as a good estimation of the bulk crystallinity (Chen and Hwang 1995). The results showed that natural weathering had limited effect on the bulk crystallinity of the PHBV matrices. On the other hand, the degree of crystallinity of PLA in PLA/nanoclay composites increased after 30 days of exposure. According to the literature, the amorphous regions have been shown to be more sensitive to UV-induced chain scission and chain rearrangement (Kaynak and Dogu 2016). The increment in crystallinity of PLA could be due to both the rearrangement of the amorphous PLA chains to spherulites under UV irradiation and cold crystallisation to form crystals during the cool periods of the natural weathering cycles (Ahmad Sawpan et al. 2019). The differences between the two matrices could

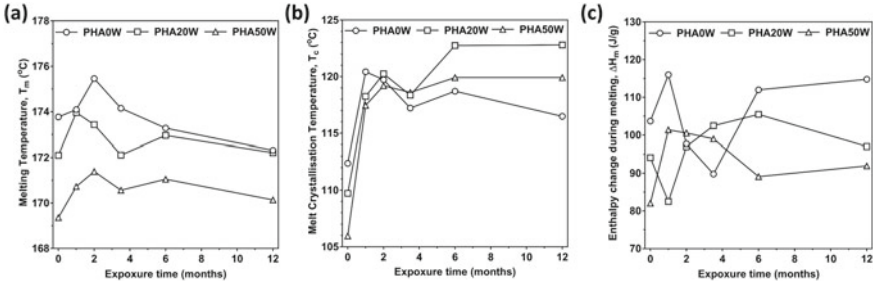


Fig. 3 The (**a**) peak melting temperature, (**b**) melt crystallisation temperature and (**c**) enthalpy change during melting values of all unaged and weathered PHBV and PHBV/WF composite samples at different exposure times. Figure adapted with permission from (Chan et al. 2019) and modified, Elsevier, copyright 2019

be explained by the lower crystallinity, in other words more amorphous regions, of the PLA before aging when compared to the PHBV matrix used in the study (at 1 mol% HV content).

4.3 Effect of Natural Weathering on Mechanical Properties

Material performance during outdoor natural weathering is one of the most important aspects, given the need to evaluate the durability of completely biodegradable composites for outdoor applications. In one study, the changes in mechanical properties of PHBV/WF and PLA/WF composites throughout a 12-month natural weathering period were fully characterised (Chan et al. 2019, 2020). The tensile strength and modulus, and strain at break trends are presented in Fig. 4a–c, respectively. The mechanical properties of PHBV were unchanged during the 12 months of natural weathering exposure. The whitening of PHBV did not lead to the change in mechanical properties, suggesting that the photo-bleaching reaction was not severe enough to alter the bulk properties of the polymer matrix. On the other hand, the tensile strength and modulus of PHBV/WF and PLA/WF composites at 50 wt% loading decreased throughout the exposure period, with PLA composites suffering a more substantial deterioration in mechanical performance when compared to PHBV composites. Another study showed that the PLA lost 43% of the tensile strength and 21% of tensile modulus after 8 weeks of exposure to natural weathering conditions (Yew et al. 2009). The differences can be explained by the contribution from the mechanical deterioration of the polymer matrix through photo-oxidation in a similar way to other polymers such as polypropylene (Abu-Sharkh and Hamid 2004).

For PLA degradation, the literature coupled the photodegradation with the hydrolytic degradation which is favoured within the amorphous regions (Zaaba 2020), which could explain the loss in mechanical properties from PLA but not from PHA under natural weathering.

Same as the aesthetic properties, fibre loading has a significant effect on the outdoor mechanical stability of composites. The tensile strength and stiffness of PHBV composites with 20 wt% WF decreased less substantially over the exposure period than those containing 50 wt% WF (Chan et al. 2019). These observations align with the trends reported from a study on PBS/kenaf bast fibre (KBF) composites with up to 40 wt% fibre content (Ahmad Thirmizir et al. 2010). The losses in mechanical properties upon natural weathering were more severe than for PBS alone when the fibre loading was higher than 20 wt%. It is noteworthy that most of the composite plaques used these studies were uncoated, such that the mechanism of the mechanical deterioration is similar to that for uncoated wood articles (Reinprecht 2016). At higher fibre content, the hygroscopic fibres are not perfectly encapsulated by the polymer matrix and can be exposed to the atmosphere during the natural weathering period. Such exposure to rainfall could lead to the swelling of fibres and the growth of fungal cells, where both could introduce localised defects that caused the early failure under load in weathered composites.

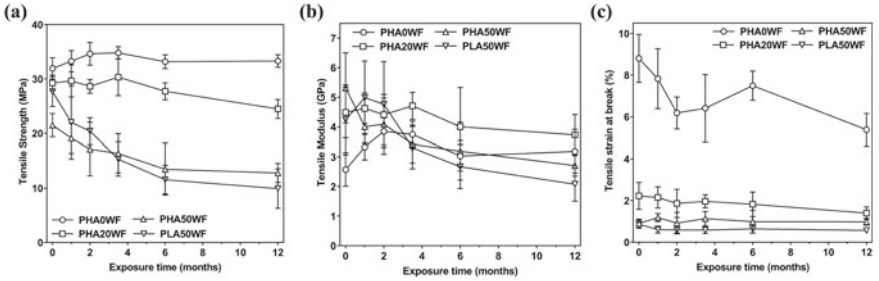


Fig. 4 The (**a**) tensile strength, (**b**) tensile modulus and (**c**) tensile strain at break of PHBV/WF (0, 20 and 50 wt% WF) and PLA/WF (50 wt%) composite samples when exposed to natural weathering. Figure adapted with permission from (Chan et al. 2019) and modified, Elsevier, copyright 2019

4.4 Effect of Natural Weathering on Composite Structure

The surface roughness and bulk macrostructure of the composites upon natural weathering have been shown to be key in determining the durability of completely biodegradable composites (Chang et al. 2020). Apart from the surface aesthetic changes as outlined in Sect. 5, natural weathering exposure severely deteriorated the surface of completely biodegradable composites across different combinations of polymer matrices and fibres (Ahmad Thirmizir et al. 2010; Chan et al. 2019; Singh et al. 2000; Siti Norasmah Surip 2018). Figure 5 captures the gradual changes in the roughness of PHBV/WF and PLA/WF composite surfaces facing the sun over time. Exposure to the natural weather created voids and cracks on the surface of both the PHBV and PLA composites at 50 wt% WF content (row 3 and 4 in Fig. 5). Six months exposure to natural weather also created voids and blisters across the surface of the PLA composites with Kenaf bast fibres (KBF) and Kenaf core fibres (KCF) (Siti Norasmah Surip 2018) (Fig. 6). The blister effect was also seen in neat PLA after exposure, but it was substantially less severe than for the samples with fibres. It was clearly shown that the blisters and voids created were concentrated around the fibres, with subsequent surface deterioration and crack propagating from these defects around the exposed fibres on the surface. This is mainly caused by the stress built up from the moisture-induced swelling and shrinkage of the fibres at the fibre-matrix interface (Chan et al. 2019). As a result, increased amount of fibres within the matrix were then exposed to the atmosphere. The accumulated effect led to the formation of a network of cracks and dents across the composite surface, as clearly observed from the SEM micrograms of PHBV and PLA composites at 50 wt% WF content after 12 months of exposure (Fig. 5). Similar surface roughness observation was also reported from a study on PBS composites with 30 wt% kenaf bast fibre (KBF) after 6 months of exposure (Ahmad Thirmizir et al. 2010). The surface roughness was interpreted to be introduced by the degradation of natural fibre, potentially through fungal colonization (Ahmad Thirmizir et al. 2010; Chan et al. 2019).

At lower (20 wt%) fibre contents, the encapsulation effects were shown once again for PHBV/WF composites (Fig. 5 row 2). As can be seen, only a small number of voids were formed throughout the exposure period of 12 months. The fibres were more perfectly sealed by the relatively hydrophobic PHBV matrix, and as such the fibre was protected from moisture absorption. Therefore, less severe surface deterioration was observed. The neat PHBV plaques, which were free of fibres, were also free of observable cracks and defects throughout the exposure period. This highlights the important role of the fibre in determining the natural weathering effects of completely biodegradable composites.

The bulk macrostructure of the PHA and PLA composites with WF before and after 12 months of natural weathering was observed by optical microscopy (Chan et al. 2019). Across all composites, at different WF contents, the effect of natural weathering on the bulk macrostructure was not significant. Despite the observed surface deterioration from PHA and PLA composites with 50 wt% WF content, the bulk structure was mostly maintained throughout the exposure period. Porosity and cracks penetrated only up to approximately 0.4 mm into the matrix after 12 months of natural weathering. The composites absorbed moisture from rainfall through the surface of the composite, predominantly via the hygroscopic fibres. However, the moisture diffusion rate is very slow through the polymer matrix. The partially embedded WF in the bulk composite matrix was untouched and free from moisture. Without the fibre swelling effects, the core of the composite sample maintained an intact structure upon natural weathering (Fig. 7).

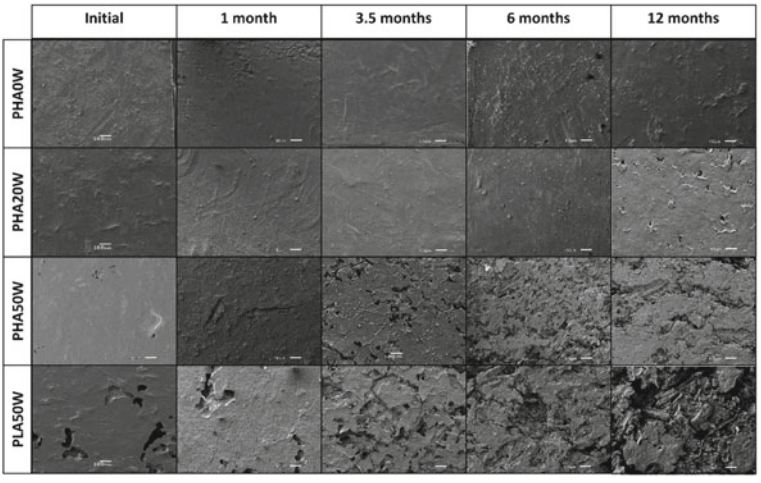


Fig. 5 SEM images of the surface facing the sun of PHBV/WF (0, 20 and 50 wt% WF) and PLA/WF (50 wt%) composite samples when exposed to natural weathering. Figure adapted with permission from Chan et al. (2019) and modified, Elsevier, copyright 2019

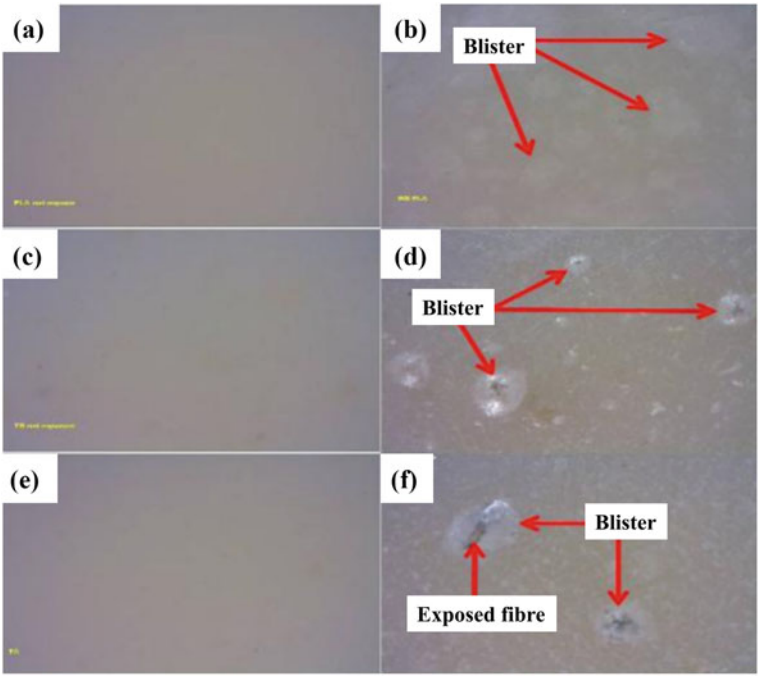


Fig. 6 SEM images of the surface facing the sun of composite samples before aging (left column) and after 6 months under natural weathering conditions (right column): (**a**), (**b**) PLA before and after aging; (**c**), (**d**): PLA/kenaf bast fibre (2 wt% KBF); (**e**), (**f**): PLA/kenaf core fibre (2 wt% KCF). Figure adapted with permission from (Siti Norasmah Surip 2018) and modified, IJTech, copyright 2018

5 Controlling Factors in Natural Weathering

So far, we have presented the properties trends of representative completely biodegradable composites under natural weathering. The next step is to identify the controlling factors, so as to be able to understand the durability of these materials in outdoor applications, under the exposure to natural rainfall and UV radiation. Data showed that the influence of biodegradation of the biopolymer matrices was not evident over the very extended period of weathering, suggesting that the common biopolymers in composite matrices are otherwise stable when they are not exposed to microbial activities and/or substantial amounts of moisture. Likewise, there was no evidence of biodegradation for the PHBV, PLA and PBS composites influencing the natural weathering processes for a substantial period of time.

On the other hand, it is obvious across all data that fibre loading had massive effects on the durability of the composites upon natural weathering. This is attributed to the hygroscopic nature of the natural fibres and the degree of exposure of these fibres to the atmosphere, especially rainfall. The deterioration process upon natural weathering appears to be primarily governed by the mechanism of moisture ingress

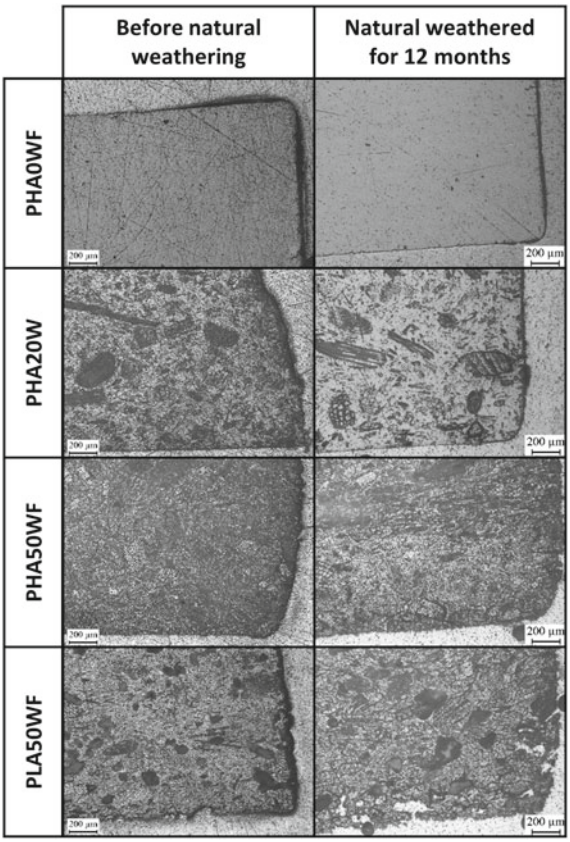


Fig. 7 Optical microscopy images of the cross-section of PHBV/WF (0, 20 and 50 wt% WF) and PLA/WF (50 wt%) composite samples before aging (left column) and after 12 months under natural weathering conditions (right column). Figure adapted with permission from (Chan et al. 2019) and modified, Elsevier, copyright 2019

into the composite matrix, as it is for nondegradable polymer/biofibre composites (Azwa et al. 2013), with biopolymer matrices being mostly hydrophobic, unlike the hydrophilic natural fibres, causing these two materials to swell at different degrees on moisture uptake.

The prolonged presence of moisture also promoted mould growth. Both of these mechanisms thus led to the introduction of defects along the fibre-polymer interface. Such defects could act as initiation points for crack propagation through into the bulk, leading to physical and mechanical deteriorations during the natural weathering period. Figure 8 provides a schematic illustrating the likely controlling factors that contribute to the natural weathering of natural fibre composites (Chan et al. 2019). The encapsulation of natural fibres plays a vital role in determining the natural weathering behaviour of biocomposites. At lower fibre contents, there is a higher chance of fibre shielding from the processing of the composite. Their durability under natural weathering is therefore higher.

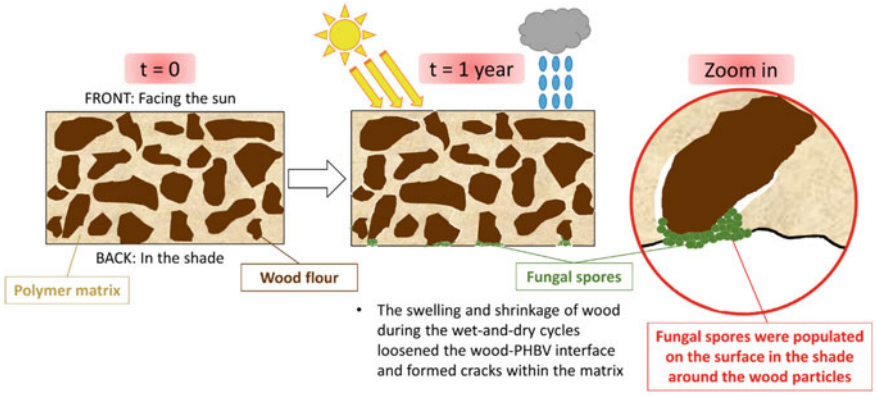


Fig. 8 Schematic diagram illustrating the controlling factors contributing to the natural weathering of PHBV/WF composites. Figure adapted with permission from (Chan et al. 2019), Elsevier, copyright 2019

6 Summary

The accumulation of nondegradable plastics, which are the polymers of choice in traditional natural fibre composites, in the environment is an important issue of our time, and the magnitude of this issue is projected to increase exponentially given the current burgeoning production rate. Moreover, these composite products are, at the same time, challenging to recycle in conventional plastic recycling facilities due to their complex structure and use of hybrid ingredients. Therefore, there has been a growing demand for the use of biodegradable polymer matrices in natural fibre composites including exterior applications. It is thus imperative that we need to consider their performance under 'in-service' conditions.

In this chapter, we have provided an overview of the natural weathering behaviour of representative completely biodegradable composites. They experienced physical and mechanical deteriorations after a few months of exposure in a similar fashion to the traditional natural fibre composites with conventional non-degradable matrices. Their natural behaviour is controlled by the accessibility of the hygroscopic natural fibres and the rate of moisture ingress into the bulk composite matrix. The biodegradation of the biopolymer matrices was not evident under natural weathering conditions without the presence of an active microbial community such as those found in soil. Strategies to improve the stability of natural fibre biocomposites without losing the unique advantage of complete biodegradability include but are not limited to the application of hydrophobic biopolymer-based coating to seal the natural fibre from the atmosphere, and the use of compatibilisation techniques to functionalise the hydrophilic surface of the natural fibre and/or strengthen the biopolymer-fibre interface to limit the rate of moisture ingress.

References

Abu-Sharkh BF, Hamid H (2004) Degradation study of date palm fibre/polypropylene composites in natural and artificial weathering: mechanical and thermal analysis. Polym Degrad Stab 85:967–973

Ahmad Sawpan M, Islam MR, Beg MDH, Pickering K (2019) Effect of accelerated weathering on physico-mechanical properties of polylactide bio-composites. J Polym Environ 27:942–955

Ahmad Thirmizir MZ, Mohd Ishak ZA, Mat Taib R, Rahim S, Mohamad Jani S (2010) Natural Weathering of Kenaf Bast Fibre-Filled Poly(Butylene Succinate) composites: effect of fibre loading and compatibiliser addition. J Polym Environ 19:263–273

Azwa ZN, Yousif BF, Manalo AC, Karunasena W (2013) A review on the degradability of polymeric composites based on natural fibres. Mater Des 47:424–442

Badji C, Soccalingame L, Garay H, Bergeret A, Bénézet J-C (2017) Influence of weathering on visual and surface aspect of wood plastic composites: correlation approach with mechanical properties and microstructure. Polym Degrad Stab 137:162–172

Brostow W (2007) Mechanical properties. In: Mark JE (ed) Physical properties of polymers handbook, pp 423–445. Springer New York, New York, NY

Chan CM, Pratt S, Halley P, Richardson D, Werker A, Laycock B et al (2019) Mechanical and physical stability of polyhydroxyalkanoate (PHA)-based wood plastic composites (WPCs) under natural weathering. Polym Test 73:214–221

Chan CM, Vandi L-J, Pratt S, Halley P, Richardson D, Werker A et al (2018) Composites of wood and biodegradable thermoplastics: a review. Polym Rev 58:444–494

Chan CM, Vandi L-J, Pratt S, Halley P, Richardson D, Werker A et al (2020) Mechanical stability of polyhydroxyalkanoate (PHA)-based wood plastic composites (WPCs). J Polym Environ 28:1571–1577

Chang BP, Mohanty AK, Misra M (2020) Studies on durability of sustainable biobased composites: a review. RSC Adv 10:17955–17999

Chen H-L, Hwang JC (1995) Some comments on the degree of crystallinity defined by the enthalpy of melting. Polymer 36:4355–4357

Cooper T (2013) Developments in plastic materials and recycling systems for packaging food, beverages and other fast-moving consumer goods. In: Farmer N (ed) Trends in packaging of food, beverages and other fast-moving consumer goods (FMCG): Markets, materials and technologies. Woodhead Publishing, Cambridge, UK, pp 58–107

de Matos Costa AR, Crocitti A, Hecker de Carvalho L, Carroccio SC, Cerruti P, Santagata G (2020) Properties of biodegradable films based on poly(butylene Succinate) (PBS) and poly(butylene adipate-co-terephthalate) (PBAT) blends. Polymers 12:2317–2333

Drobny JG (2012) Polymeric Materials. In: Drobny JG (ed) Polymers for electricity and electronics. John Wiley & Sons Inc., Hoboken, NJ, pp 27–133

Fabiyi JS, McDonald AG, Wolcott MP, Griffiths PR (2008) Wood plastic composites weathering: visual appearance and chemical changes. Polym Degrad Stab 93:1405–1414

Faruk O, Bledzki AK, Fink H-P, Sain M (2012) Biocomposites reinforced with natural fibers: 2000–2010. Prog Polym Sci 37:1552–1596

Faruk O, Bledzki AK, Fink H-P, Sain M (2014) Progress report on natural fiber reinforced composites. Macromol Mater Eng 299:9–26

Gigli M, Fabbri M, Lotti N, Gamberini R, Rimini B, Munari A (2016) Poly(butylene succinate)-based polyesters for biomedical applications: a review. Eur Polymer J 75:431–460

Gurunathan T, Mohanty S, Nayak SK (2015) A review of the recent developments in biocomposites based on natural fibres and their application perspectives. Compos A Appl Sci Manuf 77:1–25

Halley PJ, Dorgan JR (2011) Next-generation biopolymers: advanced functionality and improved sustainability. MRS Bull 36:687–691

Hammer EC, Balogh-Brunstad Z, Jakobsen I, Olsson PA, Stipp SLS, Rillig MC (2014) A mycorrhizal fungus grows on biochar and captures phosphorus from its surfaces. Soil Biol Biochem 77:252–260

Homkhiew C, Ratanawilai T, Thongruang W (2014) Effects of natural weathering on the properties of recycled polypropylene composites reinforced with rubberwood flour. Ind Crops Prod 56:52–59
Ikada E (1997) Photo- and Bio-degradable Polyesters. Photodegradation Behaviors of Aliphatic Polyesters. J Photopolym Sci Technol 10:265–270
Jian J, Xiangbin Z, Xianbo H (2020) An overview on synthesis, properties and applications of poly(butylene-adipate-co-terephthalate)–PBAT. Adv Indus Eng Polym Res 3:19–26
Jiménez A, Fabra MJ, Talens P, Chiralt A (2012) Edible and biodegradable starch films: a review. Food Bioprocess Technol 5:2058–2076
Kaynak C, Dogu B (2016) Effects of accelerated weathering in polylactide biocomposites reinforced with microcrystalline cellulose. Int Polym Proc 31:410–422
Kockott D (1999) Weathering. In M Dekker (ed) Handbook of polymer testing: physical methods. CRC Press, New York
Laycock B, Halley P, Pratt S, Werker A, Lant P (2014) The chemomechanical properties of microbial polyhydroxyalkanoates. Prog Polym Sci 39:397–442
Laycock B, Nikolić M, Colwell JM, Gauthier E, Halley P, Bottle S et al (2017) Lifetime prediction of biodegradable polymers. Prog Polym Sci 71:144–189
Marketsandmarkets (2019) Wood-plastic composites market: global industry trends, share, size, growth, opportunity and forecast 2019–2024. http://www.marketsandmarkets.com/Market-Reports/wood-plastic-composite-market-170450806.html. Accessed Feb 2020.
Matuana LM, Jin S, Stark NM (2011) Ultraviolet weathering of HDPE/wood-flour composites coextruded with a clear HDPE cap layer. Polym Degrad Stab 96:97–106
Mistretta MC, La Mantia FP, Titone V, Botta L, Pedeferri M, Morreale M (2020) Effect of ultraviolet and moisture action on biodegradable polymers and their blend. J Appli Biomater Funct Mater 18:1–8
Muasher M, Sain M (2006) The efficacy of photostabilizers on the color change of wood filled plastic composites. Polym Degrad Stab 91:1156–1165
Reinprecht L (2016) Biological Degradation of Wood. In: Reinprecht L (ed) Wood deterioration, protection and maintenance. John Wiley & Sons, Oxford, UK, p 62
Reinsch VE, Kelley SS (1997) Crystallization of poly(hydroxybutyrate-co-hydroxyvalerate) in wood fiber-reinforced composites. J Appl Polym Sci 64:1785–1796
Sadi RK, Fechine GJM, Demarquette NR (2010) Photodegradation of poly(3-hydroxybutyrate). Polym Degrad Stab 95:2318–2327
Sakai W, Tsutsumi N (2010) Photodegradation and Radiation Degradation. In: Grossman RF, Nwabunma D, Auras R, Lim L-T, Selke SEM, Tsuji H (eds) Poly(Lactic Acid): synthesis, structures, properties, processing, and applications. John Wiley & Sons Inc., pp 413–421
Satyanarayana KG, Arizaga GGC, Wypych F (2009) Biodegradable composites based on lignocellulosic fibers—an overview. Prog Polym Sci 34:982–1021
Singh B, Gupta M, Verma A (2000) The durability of jute fibre-reinforced phenolic composites. Compos Sci Technol 60:581–589
Surip SN, Raihan WN, Jaafar W (2018) Comparison study of the bio-degradation property of polylactic acid (PLA) green composites reinforced by kenaf fibers. Int J Technol 9:1205–1215
Stloukal P, Verney V, Commereuc S, Rychly J, Matisova-Rychlá L, Pis V et al (2012) Assessment of the interrelation between photooxidation and biodegradation of selected polyesters after artificial weathering. Chemosphere 88:1214–1219
Van de Velde K, Kiekens P (2002) Biopolymers: overview of several properties and consequences on their applications. Polym Testing 21:433–442
Wei L, McDonald AG (2016) Accelerated weathering studies on the bioplastic, poly(3-hydroxybutyrate-co-3-hydroxyvalerate). Polym Degrad Stab 126:93–100
Xu K, Feng J, Zhong T, Zheng Z, Chen T (2015) Effects of volatile chemical components of wood species on mould growth susceptibility and termite attack resistance of wood plastic composites. Int Biodeterior Biodegradion 100:106–115
Yew GH, Chow WS, Mohd Ishak ZA, Mohd Yusof AM (2009) Natural weathering of poly (Lactic Acid): effects of rice starch and epoxidized natural rubber. J Elastomers Plast 41:369–382

Zaaba NF, Jaafar M (2020) A review on degradation mechanisms of polylactic acid: hydrolytic, photodegradative, microbial, and enzymatic degradation. Polym Eng Sci 60:2061–2075

Zaidi L, Kaci M, Bruzaud S, Bourmaud A, Grohens Y (2010) Effect of natural weather on the structure and properties of polylactide/Cloisite 30B nanocomposites. Polym Degrad Stab 95:1751–1758

Effect of Aging and UV Exposure on Mechanical Properties of Natural Fiber Composites

Ajitanshu Vedrtnam, Dheeraj Gunwant, Harsha Verma, and Kishor Kalauni

Abstract The natural fiber-reinforced composites (NFCs) are used to make sustainable eco-friendly products with properties comparable to synthetic materials. However, NFCs are susceptible to aging-induced degradation in environmental conditions such as moisture and ultra violet (UV) exposure. Therefore, it is imperative to understand the aging phenomenon of NFCs and the mechanical properties degradation due to aging and UV exposure. This chapter provides an insight into the effects of aging and UV exposure on the mechanical properties of NFCs. The chapter consists of a comprehensive literature review, simplified procedure for aging and UV exposure tests, a case study and a finite element method (FEM) based model for studying the effect of aging and UV exposure on NFCs. It was evident that with an increase in UV exposure time, the mechanical properties deteriorate significantly as a result of matrix erosion, cracking, and photo-degradation. A further insight into the previous work of one of the authors was provided to understand aging in wood-plastic composites (WPCs). The wood-plastic composites (WPCs) experience a noticeable reduction in the tensile strength (TS), bending strength (BS) and wear resistance after weathering for 13 weeks. In the present work, the sugarcane dry leaves composites (SDLRPCs) also showed a reduction in the TS, BS, and Mode I plane strain fracture toughness (K_{1C}) after 80 h of UV exposure. The FEM-based micromechanical model was constituted to visualize the state of stress within the NFCs. It predicted that after UV exposure, the NFCs such as SDLRPCs have a higher tendency to undergo matrix shear yielding near the crack tip.

A. Vedrtnam (✉)
Departamento de Arquitectura, Universidad de Alcalá, 28801 Madrid, Spain
e-mail: ajitanshu.m@invertis.org

A. Vedrtnam · D. Gunwant · K. Kalauni
Department of Mechanical Engineering, Invertis University, Bareilly, UP 243001, India

D. Gunwant
GET Group of Institutions, Bazpur, Uttarakhand, India

H. Verma
Department of Polymer and Process Engineering, SRE Campus, IIT Roorkee, Roorkee, India

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_11

Keywords Aging · UV exposure · Composite · Tensile strength · FE model

Abbreviations

NFs	Natural fibers
NFCs	Natural fiber-reinforced composites
WPCs	Wood-plastic composites
SDLRPCs	Sugarcane dry leaves composites
PVA	Polyvinyl alcohol
PP	Polypropylene
FEM	Finite element method
FE	Finite element
TS	Tensile strength
BS	Bending strength
IS	Impact strength
T_g	Glass-transition temperature
K_{1C}	Mode I plane strain fracture toughness
G_{1C}	Fracture energy

1 Introduction

The demand for sustainable bio-based materials is constantly fuelled by the circular economy motivations and stringent environmental regulations worldwide (Mohanty et al. 2000, 2002; Netravali and Chabba 2003; Avérous and Pollet 2012). Composite materials form an important class of materials that offer a unique blend of properties that are not available naturally. The composites are viable alternatives to conventional materials due to light weight, high strength and energy-saving in the applications ranging from musical instruments to highly sophisticated artificial prosthetics (Mohanty et al. 2000; Li et al. 2020). Bio-composites are the materials derived from NFs viz. hemp, flax, animal hair fibers, and petroleum-based non-biodegradable or biodegradable polymer matrix. Materials derived from the combination of a biodegradable polymer matrix and synthetic fibers such as glass, carbon, etc. are also considered as bio-composite. NFs are derived from three basic sources: lignocellulose based materials, minerals, and animals (Saxena et al. 2011). Fibers derived from lignocellulose based materials are categorized into wood and non-wood fibers. Although wood fibers are abundantly available in nature, non-wood fibers obtained from bast/stem, leaf, fruits, and stalk are also gaining popularity. Out of these, bast fibers obtained from the phloem of plants present in their stem are the stiffest (Majeed et al. 2013). Therefore, it can be asserted that composites derived from recyclable and biodegradable biological matter that are commercially viable can be considered

sustainable biocomposites. Additionally, bio-composites are environment friendly as they do not increase the net environmental CO_2 upon decomposition. Sincere efforts for obtaining optimal blend have been reported in the literature. The utilization of NF reinforced composites in the automobile industry was explained in detail by (Hassan et al. 2017). NFs are finding applications mainly in door cladding, linings, and floor panels as well as soundproofing and automotive tires. The influence of fiber content and treatments on mechanical properties has been reported in the literature for kenaf (Ochi 2008; Akil et al. 2011; El-Shekeil et al. 2012), hemp (Lu and Oza 2013; Sepe et al. 2018; Sair et al. 2018), ramie (Li et al. 2012; Kumar and Anand 2019), and corn (Liu et al. 2019) and rice (Ghofrani et al. 2015). However, mechanical properties of NFCs depend on moisture, fiber physical properties, defects, internal structure, and microfibrillar geometry and fiber/matrix interfacial properties (Campilho 2015).

The fiber/matrix interfacial adhesion plays a vital role in deciding the overall physico mechanical properties of the biocomposite. The matrix plays an important role in holding the fibers together and protecting them from harsh environmental conditions. It also facilitates the load transfer among fibers by providing them connectivity (Saheb and Jog 1999; Gowda et al. 2018). The main prerequisite for effective load transfer between fiber and matrix is the intimate contact between them. This leads to the challenge of selecting proper matrix material compatible with the natural fiber. Generally, metals, ceramics, and polymers can be used as matrix materials for composites. However, in the case of NF-based composites, petroleum-based polymers are extensively studied in the literature (Campilho 2015; Gowda et al. 2018). The polymeric matrices are a natural choice for matrix materials due to their low density, low thermal and electrical conductivity, high corrosion resistance, and good aesthetic appeal. At the same time, they also suffer from drawbacks such as poor transverse strength and lower operating temperature range (Verma 2012). Numerous efforts have been directed towards incorporating NFs into biodegradable and non-biodegradable polymeric matrices (Yu et al. 2009; Zhong et al. 2011; Bajpai et al. 2013b; Asgher et al. 2017; Mancini et al. 2019; Naeem et al. 2020). The NF reinforcement in biodegradable matrices such as PLA (Yu et al. 2009; Zhong et al. 2011; Bajpai et al. 2013b), cellulose (Naeem et al. 2020), PVA (Asgher et al. 2017; Mancini et al. 2019), and non-biodegradable matrices such as PP (Zampaloni et al. 2007; Sullins et al. 2017) and epoxy (Reddy et al. 2015; Premnath 2018; Sood and Dwivedi 2018) have been reported in the literature.

Although fascinating theoretically, in practice the use of NFs for the development of polymeric composites is limited by various challenges including Polymer-NF incompatibility, agglomeration tendency, high moisture absorption, poor fire, and UV resistance, and unavailability of established manufacturing processes. Due to this, the use of NFCs in sunlight, changing weather, static/dynamic loads, moisture, and gases can lead to their degradation. Therefore, these challenges must be acknowledged dexterously to achieve high-performance of NFCs for engineering applications. The polar groups present in the NFs favour moisture absorption lowering the interfacial strength. The composites subjected to moisture absorption are susceptible to a weak interface between hydrophobic matrix and hydrophilic NFs leading to failure through fiber swelling and delamination (Araújo et al. 2008; Dittenber

and GangaRao 2012). The aromatic groups present in the polymeric matrix when subjected to UV rays, undergo bond rupture and superficial micro-cracks leading to degradation of properties.

Despite the low-cost of NFCs, a variety of costly processes are sometimes necessary to alleviate the issues associated with their practical applications. It is therefore necessary to understand the effects of factors viz. environmental aging and UV exposure on the mechanical properties of NFCs. This chapter explores the effects of aging and UV exposure on the mechanical properties of NFCs. The mechanism of degradation associated with these two factors is probed and correlated with their effect on the mechanical properties of composites. The effects of weathering and UV exposure on the mechanical properties of WPCs and SDLRPCs have been presented. Finally, the use of a FE modeling approach for analyzing the effect of UV exposure on the SDLRPC is presented. This chapter will be beneficial for the scientific and technical community who intend to work on the development of high-performance durable NFC products.

2 NFCs and Aging Phenomenon

Plant-based NFs are naturally available composites consisting of cellulose fibrils ingrained within the lignin matrix (see Fig. 1). Each fiber possesses a layered structure with one primary and three secondary walls. The mechanical properties of the fiber are governed by the thickness of the middle layer of the secondary wall. Other ingredients of NFs include oils and waxes, pectin, and lumen, giving them the typical hollow structure (John and Thomas 2008; Liu et al. 2012). Table 1 shows the chemical composition of selected NFs.

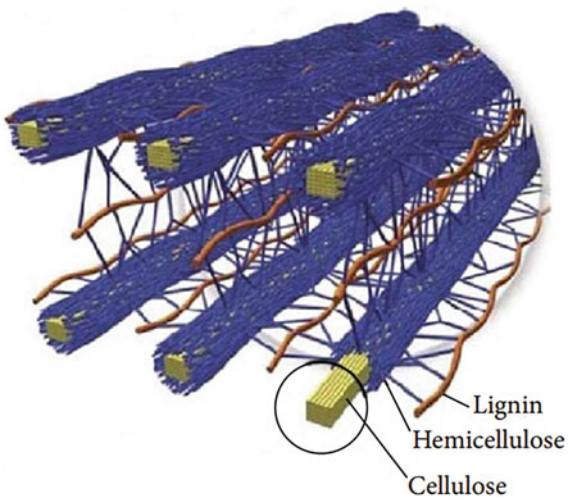


Fig. 1 The inner structure of natural fiber (Mamtaz et al. 2016)

Table 1 Chemical composition of some of the NFs (Lalit et al. 2018)

S. No.	Natural fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)
1	Banana	48–60	10.2–15.9	14.4–21.6	2.1–4.1
2	Bamboo	48.2–73.8	12.5–73.3	10.2–21.4	0.37
3	Flax	64.1	16.7	2	1.8
4	Jute	64.4	12	0.2	11.8
5	Ramie	68.6	13.1	0.6	1.9
6	Pineapple	57.5–74.3	80.7	4.4–10.1	1.1
7	Sisal	65.8	12	9.9	0.8
8	Kenaf	37–49	18–24	15–21	8.9
9	Hemp	55–80.2	12–22.4	2.6–13	0.9–3.0
10	Coir	19.9–36.7	11.9–15.4	32.7–53.3	4.7–7.0

The change in properties of polymer composites over time is referred to as the aging process. Aging can be broadly categorized into physical aging, chemical aging, and mechanical aging. Physical aging occurs during the dispersal of material towards thermodynamic equilibrium after the rapid cooling of the polymer below its T_g. The physical aging directly affects the properties of polymers such as moduli, strength, and ductility within the glassy range (Hutchinson 1995). The durability of polymeric composites is compromised as most polymeric composites remain mainly in their glassy range during their lifetime.

Chemical aging involves the combination of thermo-oxidative, hydrolytic, and thermal aging. It activates cross-linking and chain scission in the polymeric matrix. While oxidation and cross-linking are the prominent chemical aging mechanisms within the operating range of composites, at the higher temperature, thermo-oxidation also becomes active. Chemical aging is also likely to cause higher cross-linking density and hence unwarranted densification of material resulting in higher T_g. These changes are undesirable from the polymeric composites to satisfy specific structural requirements (Martin 2008).

Mechanical aging is an irreversible phenomenon that is manifested in composites as matrix cracking, interfacial degradation, fracture of fiber, and plastic deformation. The mechanical properties are significantly affected by the mechanical aging phenomenon. Mechanical aging depends upon factors such as moisture, temperature, critical degradation mechanisms (physical, chemical, and mechanical processes), and accelerated aging mechanisms (Lévêque et al. 2005; Martin 2008).

3 Effect of Aging on Mechanical Properties of NFCs

The degradation of NFCs due to aging has been reported abundantly in the literature. The effect of aging on mechanical properties of Prosopis juliflora fiber-reinforced

palm seed powder-filled polymer composites was reported (Sakthi Balan et al. 2020). A decrease in TS and hardness has been reported with an increase in aging time. Kenaf/sisal fabric reinforced bio-epoxy composites subjected to accelerated weathering tests displayed a significant reduction in TS, elongation at break as well as impact properties (Yorseng et al. 2020). The main reason for the lowering of mechanical properties is bio-epoxy degradation. The TS of unweathered neat epoxy was 53.49 MPa which was reduced by 52.12% to 25.61 MPa for weathered neat epoxy. The accelerated weathering had a severe negative effect on the impact property of bio-epoxy. The impact strength (kJ/m^2) of neat epoxy was 17.90 which was reduced to 5.30 (a reduction of 70%) after weathering. Although the weathering showed little effect on the water absorption behavior of composites, the main issue noticed was the inconsistent water absorption behavior. The effect of aging on the mechanical properties of flax reinforced PLA composites was investigated by (Regazzi et al. 2016). The dynamic elastic modulus decreased up to 38.60% at 50 °C after 144 h of aging. Both water absorption and high temperature lead to increased polymer chain mobility paving way for the deeper penetration of moisture into the matrix. Hygro-thermal aging affects lignocellulosic composites by moisture diffusion, fiber swelling followed by microcrack formation, leaching of hydrophilic substances and finally fiber/matrix debonding upon drying. The moisture absorption can be significantly reduced through proper surface treatment such as alkalization, acetylation, silanization, and alkali-silanization. The moisture absorption and weight increment percentage of flax fiber-reinforced polymer composites were reduced up to 45.80 and 42.20% respectively by suitable treatment (Wang and Petrů 2019). Chemically treated composites displayed improved storage modulus throughout the temperature range. The storage modulus of treated composites improved up to 49.40% over the control sample after 16 days of hygrothermal aging at 30 °C. Similarly, the storage modulus at 100 °C was enhanced up to 197.10% after identical aging conditions. The chemical treatment helps by discouraging the moisture uptake and simultaneously improving the fiber/matrix interfacial bonding.

X-ray tomography was employed for visualizing the effect of hygrothermal aging on jute fiber reinforced PLA composites (Jiang et al. 2019). The cracking of the matrix was invisible till stage III (28–56 days) and there was a small effect on the TS and modulus of the samples. As the sample passed stage III, moisture uptake was significantly enhanced due to macro-crack formation. Figure 2 shows the presence of a large number of cracks in a high-resolution tomography image of composite samples after 42 days of hygrothermal aging. The TS decreased by >12% in 0–7 days and the tensile modulus reduced by >25% after 28 days of aging. The increase in porosity due to matrix hydrolysis followed by internal cracking and embrittlement was mainly attributed to the loss of mechanical properties.

The effects of factors such as soil, river water, sub-zero temperature, and sunlight on nettle fiber-mat reinforced PP composites have been reported (Bajpai et al. 2013a). The neat PP matrix displayed TS of 32.56 MPa which is reduced by 20.06, 17.07, 12.64, 2.89, and 21.09% after exposure to river water, diesel oil,—8 °C temperature, soil, and sunlight for 512 h. The sample exposed to river water exposure reported a 5.67% increase in weight as compared to unexposed samples after 512 h of exposure.

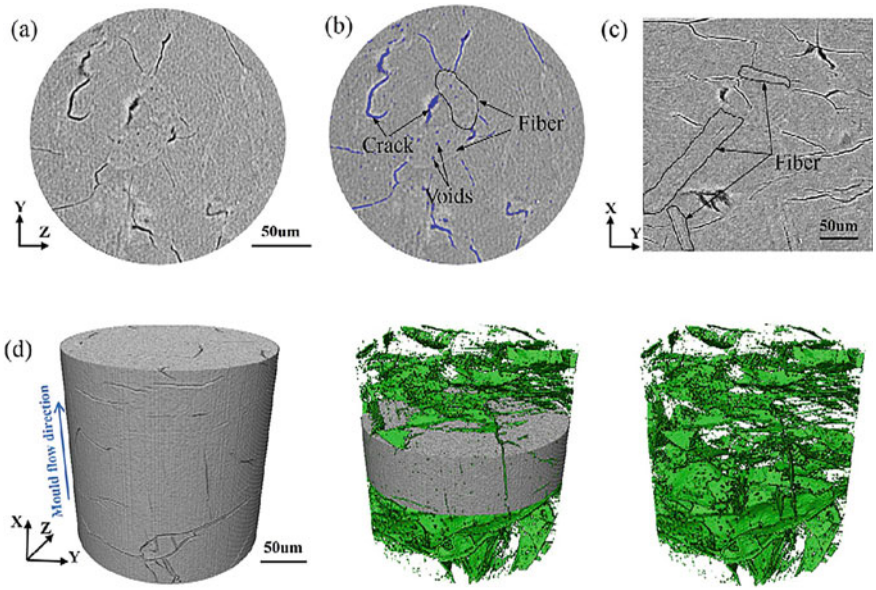


Fig. 2 High-resolution tomography image of jute/poly (lactic) acid composite sample after 42 days of hygrothermal aging (with image segmentation) (Jiang et al. 2019)

On the other hand, soil exposed samples were least affected both in terms of TS and weight gain.

The detrimental effects of water and alkali solution (KOH, NaOH and $Ca(OH)_2$ pH = 13.5) have been reported on jute/basalt/epoxy composites (Ma et al. 2018). The jute fabric was NaOH and silane (SiH_4) treated to enhance the fiber/matrix interfacial strength by removing the hydrophilic cellulose hydroxyl group from fibers. The water uptake behaviour was according to the classic Fick's law with the rapid uptake in the first two weeks and then levelling off. The higher temperature was observed to be more detrimental to the TS of the composites. A 45 days immersion in solution at 40 °C led to a 22.50 and 16.30% reduction in the TS of alkali-treated and silane treated composites. At 40 °C temperature both water as well as alkali solutions reduced Young's modulus of jute/epoxy composites slightly. Similarly, basalt/epoxy composites reported up to a 39 and 38% decrease in TS at temperatures of 20 and 40 °C respectively. The jute/epoxy composites immersed in 5% NaOH solution have been reported to undergo weight gain of up to 17.20% after 3 months (Lila et al. 2018). Within the same period and identical solution, the TS decreased by up to 28.80%. This is attributed to the dissolution of hemicellulose into the NaOH solution resulting in cavity formation and thinning of fibers leading to subsequent fracture. The composite samples immersed in petrol and peanut oil showed similar behaviour mainly due to the absorption of organic solvents into the voids. Accelerated aging leads to the fading of the texture of NFCs due to the decomposition of lignin into simpler water-soluble components (Beckert and Lauke 1998; Hon and Shiraishi 2000). The differential

swelling and shrinkage cause matrix cracking and the formation of milky patches in the case of hemp fiber PLA composites (Islam et al. 2010). A drastic reduction in tensile and flexural strengths from 61 and 115 MPa for unexposed to 8 and 13 MPa for exposed samples respectively was reported. Similarly, Young's modulus and flexural modulus were reduced from 8 and 6 GPa for unexposed to 1 and 2 GPa for exposed samples. The K_{1C} value of untreated fiber composites was reduced drastically from 3.2 MPa $\sqrt{m}$ to just 0.6 MPa $\sqrt{m}$ (Islam et al. 2010). The reduction in mechanical properties of composites is attributed to the development of swelling stress due to differential expansion of fiber and the matrix.

4 Effect of UV Exposure on NFCs

The NFC used in the automobile industry is generally affected by photo-degradation when exposed to UV radiation. The UV exposure can break down cellulose, lignin, and hemicellulose content of the NFs, affecting the fiber/matrix interfacial bonding. The weak interfacial bonding results in lower mechanical properties and eventually reduces the efficiency of the NFCs. The effect of UV radiation on the tensile behaviour of nettle fiber reinforced PP composites w.r.t. time (64, 128, 256, and 512 h) was reported (Bajpai et al. 2013a). The nettle fiber mat reinforced PP matrix composites were prepared by the compression moulding process. It was reported that the increase in UV exposure time was inversely related to the TS of composites. The weight and TS of samples were decreased by 21.02 and 0.14% respectively after 512 h of exposure. The photo-oxidation induced polymer chain splitting phenomenon in UV exposed samples was primarily responsible for the deterioration of the mechanical properties of composites. A similar phenomenon and subsequent property degradation were observed in mercerized and bleached sugarcane bagasse reinforced high impact polystyrene composites (Beninia et al. 2011). The accelerated weathering effect was produced by irradiating samples using a fluorescent bulb UVB-13 with an irradiance of 0.76 W/m^2. The samples were exposed for 8 h at 60 °C temperature followed by water condensation for 4 h at 50 °C. The SEM analysis confirmed that the fibers were degraded due to accelerated weathering with negligible effect on the fiber-matrix interface. The TS of exposed composites was reduced accompanied by a proportionate increase in the tensile modulus. The presence of lignin in mercerized fiber composites rendered them more susceptible to accelerated weathering as compared to the bleached fiber composites. The effect of UV radiation on the mechanical properties of treated sisal fiber reinforced PP composites fabricated via a solution mixing technique was studied (Joseph et al. 2002). The decrease in TS after 2–12 weeks of exposure is attributed to the UV radiation-induced chain-scission phenomenon. The degradation phenomenon is mainly located on the surface of composites as the oxygen is used up before it can diffuse into the polymer. Due to high molecular weight, complete crystallization of PP is impossible and which favours the photo-oxidation in the non-crystalline or amorphous region. The wood flour and kenaf fiber-reinforced high-density polyethylene (HDPE) composites

displayed a significant decrease in bending stiffness and strength after sunlight and rain exposure (Lundin et al. 2002). The bending stiffness and strength decrease by 42 and 24% respectively due to exposure for 2000 h. For the same exposure time and conditions, the bending stiffness and strength of wood floor reinforced composites was decreased by 33 and 20% respectively. Flax fabric reinforced epoxy composites showed up to 29.90, 34.90, 10, and 10.20% decrease in TS, modulus, flexural strength, and modulus respectively (Yan et al. 2015). The composites displayed signs of degraded fiber-matrix adhesion in SEM analysis. Severe physical degradation signs were such as discoloration, matrix erosion and cracking were visible after 1500 h of exposure.

Effects of four iron oxide pigments on the mechanical properties of the composites after weathering were studied (Zhang et al. 2010). The pigmented wood fiber reinforced HDPE composite samples were subjected to UV accelerated weathering for 2000 h. The mechanical properties of the composites decreased after accelerated weathering. In some cases, UV exposure may promote the crosslinking reaction in the polymer matrix. Studies on the mechanical properties of natural flour reinforced HDPE composites (Lopez et al. 2006). Short as well as long term laboratory tests and natural conditions were conducted to determine the effect of UV and moisture on the mechanical properties. The TS of composites improved under both UVA and UVB radiation. The TS of NFC was improved by 6% after 4000 h of exposure to UVA radiation. After 2000 h of exposure, the TS of wood was improved by 46.02% due to the positive effect of UV radiation on the lignin.

5 Testing Procedure for UV Exposure and Aging

Authors have utilised different procedures for UV exposure and aging tests along with the standard tests. This section gives an overview of simplified testing procedures for UV degradation and the aging tests of NFCs.

5.1 UV Degradation in Weathering Chambers

A fluorescent UV apparatus is used in an artificial UV test post confirming that its spectral power distribution qualifies the standard practices (Vedrtnam et al. 2019). The NFC specimens prepared for the testing should be sized to fit specimen holders and racks of exposure apparatus. It should be ensured that the holder should support the minimum specimen area, and the unexposed area should not be used as a part of the test area. The device should be programmed to follow the recommended exposure cycles specified for fluorescent UV exposures. A periodic evaluation of the test specimen should be done in order to determine the variation in magnitude and change of property in accordance with exposure time and radiant exposure. Finally,

the exposed specimens should be compared with unexposed specimens to evaluate the difference in properties.

5.2 UV Degradation in Outdoor Weathering Conditions

In outdoor conditions, the results of tests conducted for less than 12 months depend on the season of the year. The initial steps include selecting the test site, angle of the exposure rack, and holder type. The precautions must be taken that the fasteners used to attach specimens to the test rack should be secure as well as allow the specimens to have expansion or contraction with respect to thermal changes, moisture absorption, moisture desorption, or plasticizer loss. Radiometers should be mounted at identical tilt and azimuth angles to test specimens. Before starting the experiment, initial appearance and physical-property of the specimen should be recorded. The specimens should be mounted on racks for the prescribed time, solar radiant energy, or total UV radiant energy following the standards (Vedrtnam et al. 2019). While taking periodic data of samples, a standard procedure of cleaning, visual examination, conditioning, and testing of the specimens should be followed. For a visual comparison of exposed specimens at various exposure levels, specimens should be compared with unexposed file specimens.

5.3 Thermal Aging of Specimen

The first and foremost requirement for thermal aging involves a controlled horizontal or vertical airflow oven, having forced-draft circulation with substantial constant fresh air intake. The specimens are conditioned before testing in accordance with the requirements of the test method for evaluating the required properties. For each particular test and temperature, it is recommended that all materials must be exposed at the same time in the same oven. Before carrying out the aging process, the exposure time, temperature should be selected as per the recommended standards. Periodic evaluation of data should be done to find the change in properties of the specimen at various levels of exposure.

5.4 Water Aging of Specimen

Like thermal aging, water aging also requires specimens' conditioning before testing. Initially, the specimen's initial weight and dimensions before exposure should be recorded. The specimen should be placed inside and immersed into a closed container of distilled water. For boiling-water immersion, specimens should be entirely immersed in a container of boiling distilled water. The specimens should

be timely removed at a fixed interval from the water, wiped free of surface moisture with a dry cloth, weighed, and dimensions measured for collecting the data. After recording the data, the specimens should be immediately placed inside their respective container. When the specimens reach their saturation level, they should be removed from the container. The difference between the saturated weight and the dry weight will be considered as the water absorbed by the specimen. At saturation condition, a graph of the increase in weight as a function of the square root of each immersion time should be prepared. Any observations regarding warping, cracking, or change in the appearance of the specimens should also be reported.

6 Effect of Aging and UV Exposure: Case Study and FE Modelling

This section includes a case study along with a previous study of one of the authors demonstrating the effect of aging and UV exposure on the mechanical properties of NFCs. The effect of aging on WPCs was significantly studied by researchers (Kokta et al. 1983; Yang et al. 2015). The degradation of mechanical properties of WPCs due to aging and UV exposure is widely reported in the literature (Tamrakar and Lopez-Anido 2011; Peng et al. 2015; Friedrich and Luible 2016; Turku et al. 2017). In the previous work of one of the authors, the varying concentrations (10, 15, and 20%) of Babool, Mango, Sheesham, and Mahogany dust were used as reinforcements in the PP matrix for preparing WPC samples (Fig. 3) via injection molding technique (Vedrtnam et al. 2019). The mixture of wood dust and the PP matrix was put into the nozzle and passed through the plunger of the injection molding machine at 200–240 °C. Subsequently, the mixture was poured into the mold to occupy the mold structure. Five samples were prepared for each testing i.e., TS, BS, impact strength (IS), and wear of WPCs. The prepared samples were exposed to natural weather for thirteen weeks between July and September as per ASTM D 1435-99. The average values of these mechanical properties with the effect of aging are given in Table 2.

Fig. 3 WPC samples and set up for weathering and aging test

Table 2 Mechanical properties of WPCs before and after aging (Vedrtnam et al. 2019)

Wood type	Wt. percent (%)	TS (MPa)		BS (MPa)		IS (kJ/m^2)		Wear (g)	
		Before aging	After aging	Before aging	After aging	Before aging	After aging	Before aging	After aging
Babool	10	21.50	18.99	43.14	39.12	2.33	2.14	9.50	10.73
	15	21.07	16.65	41.44	34.55	3.30	2.70	7.50	8.10
	20	18.33	14.02	39.66	29.83	2.45	1.80	6.00	9.55
Mango	10	16.63	15.88	31.50	29.19	3.92	3.54	10.50	10.66
	15	16.58	13.71	30.97	25.66	4.29	3.40	7.00	7.91
	20	16.22	12.02	37.96	28.03	3.90	2.94	5.50	6.11
Sheesham	10	18.25	16.66	35.86	33.11	2.20	1.99	10.00	10.22
	15	18.17	15.12	36.30	28.59	4.53	3.79	7.00	7.98
	20	16.19	12.99	34.30	26.03	3.18	2.36	5.50	7.12
Mahogany	10	17.07	14.95	35.79	32.98	2.57	2.29	8.50	9.60
	15	16.78	14.40	37.28	30.22	2.08	1.61	7.00	8.11
	20	15.32	12.18	36.39	27.56	4.04	2.99	6.50	7.77

It is clear from the results that the TS, BS, IS as well as wear resistance of the WPCs were decreased significantly after aging. The TS of 10, 15, and 20% Babool wood dust reinforced composites was decreased by 11.67, 20.98, and 23.51%. For the same concentration, the BS and IS decreased by 9.32, 16.63, and 24.79% and 8.15, 18.18, and 26.53% respectively. After aging, the highest wear degradation of 59.17% was noticed for 20% Babool wood dust reinforced composites. The Mango wood dust reinforced PP composites displayed a wider range of variation in TS. The minimum and maximum reductions were 4.51% for 10% and 25.89% for 20% Mango wood dust reinforced composites. The largest reduction of 26.16% in BS was noticed at 20% Mango wood dust concentration which is the highest for all four types of woods. The IS of Mango wood dust reinforced composites reduced by 9.69, 20.75, and 24.62% at Mango wood dust concentrations of 10, 15, and 20%. On the other hand, 10% Mango wood dust reinforced composites displayed a minimum wear degradation of 1.52% as compared to all four types of woods. This implies that at this concentration, the Mango wood dust can be considered the best reinforcement as far as wear resistance is considered. The Sheesham wood dust reinforced composites displayed an 8.71, 16.79, and 19.77% decrease at concentrations of 10, 15, and 20% respectively after aging. For the same concentration, the BS and IS of Sheesham wood dust reinforced composites decreased by 7.67, 21.24, 24.11%, and 9.55, 16.34, 25.79%. The composites containing 10% Sheesham wood dust displayed better wear resistance with just a 2.2% decrease in mass after aging. This is next only to Mango wood dust reinforced composites. The Mahogany wood reinforced composites displayed 14.95, 14.4, and 12.18% reduction in the TS at 10, 15, and 20% concentration. The IS and BS were reduced by 10.89, 22.60, 25.99%, and 7.85, 18.94, 24.26% at 10, 15, and 20% Mahogany wood concentration respectively. The wear degradation was noticed to be 12.94, 15.86, and 19.54% at 10, 15, and 20% Mahogany wood concentration.

The TS, BS as well as IS reduced significantly after aging and this reduction increases with wood dust concentration. Similar results are observed for the wear resistance of the composites. All the composites registered a reduction in wear resistance due to aging. Overall, the composites with 10% of Mango and Mahogany wood powders have experienced lesser wear as compared to others. This is attributed to the change in crystallinity of PP matrix, oxidation on composite surfaces, and the mechanism of wood powder mixing in the matrix (Peng et al. 2015; Migneault et al. 2015; Friedrich and Luible 2016; Turku et al. 2017; Vedrtnam et al. 2019). It has been observed that the composites with 10% wood powder display a smaller reduction in TS, BS, and IS, irrespective of the type of wood powder. The reason behind this is the PP matrix has completely encapsulated the wood powder to protect it from UV and humidity. These results are in line with the earlier reported results (Ren et al. 2015; Peng et al. 2015; Migneault et al. 2015; Catto et al. 2016). Furthermore, Fig. 4a, b show the SEM micrographs of WPC samples with and without aging. It can be seen that the wood particles are evenly dispersed in the PP matrix. The presence of void at the fiber/matrix interface is visible due to as a result of wood powder pull out. This is attributed to the hydrophilic nature of powder and the hydrophobic nature of PP which leads to property mismatch at interfacial locations. After aging,

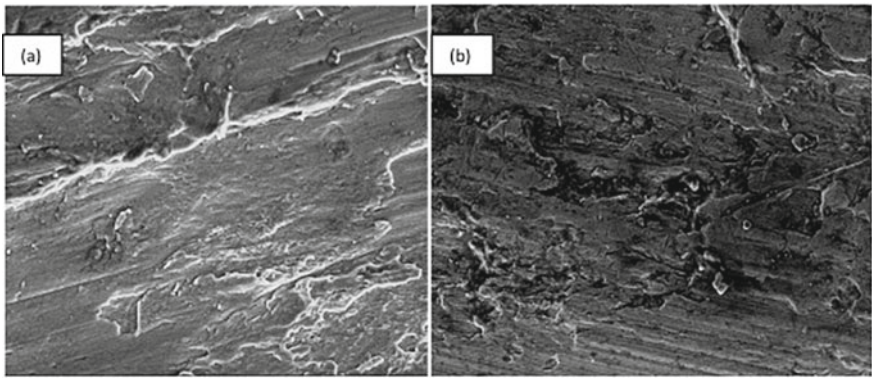


Fig. 4 SEM micrographs WPC samples with 20% Sheesham wood flour **a** without **b** with aging

the deterioration of the matrix of WPC samples due to aging is visible in the SEM micrographs.

The completely damaged and removed interface can be seen from the SEM micrograph of WPCs after aging. Aging induced decomposition of the matrix due to severely damaged interface is the main reason for the reduction in mechanical properties (Ren et al. 2015). Figure 5 shows the SEM micrographs WPC samples post UV exposure using an artificial source. The process of UV exposure is described in (Vedrtnam et al. 2019). The deterioration of the matrix material is visible in the micrograph which is responsible for the inferior mechanical properties of the WPCs.

Extensive superficial roughening is visible on the exposed surface of WPC samples after 13 weeks of natural aging. The rough surface generated indicating deterioration of the matrix as a result of UV exposure is evident from the micrographs. The reduction in mechanical properties is attributed to the fiber/matrix interface degradation following UV aging (Martin 2008).

6.1 Case Study: Aging and UV Exposure on Mechanical Properties of SDLRPCs

India is an agricultural country and every year more than 18 million tonnes of sugarcane leaves are produced (Jutakanoke et al. 2012). In general, these waste sugarcane dry leaves (SDLs) are usually left and burnt in an open atmosphere, emitting a voluminous amount of hazardous gases. The SDLRPCs are prepared from these waste sugarcane dry leaves and the effects of aging on various properties were evaluated. A part of the experimental results of this case study is reported in previous work of the authors (Ji Yadav et al. 2020). In addition to those results, new experimental results and a FE model is constituted for having an insight into the behavior of SDLRPCs subjected to aging and UV exposure.

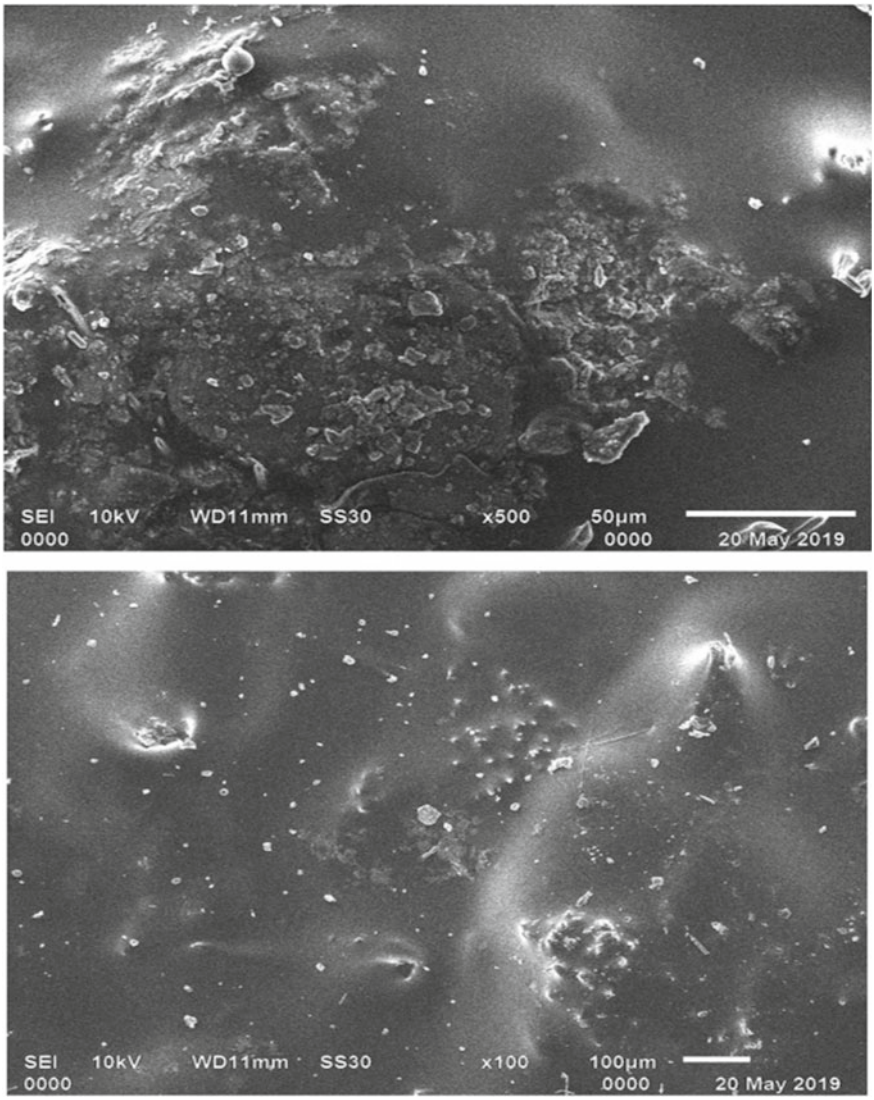


Fig. 5 SEM micrographs of WPC samples post UV exposure using an artificial source

The SDLRPCs containing 2–8 vol.% of sugarcane dry leaves (SDLs) were fabricated by the method described in (Ji Yadav et al. 2020). The pristine epoxy, as well as SDLRPCs, was exposed to UV rays under a controlled environment for 80 h before testing. Figure 6a shows the variation of tensile properties with SDL concentration for unexposed as well as exposed samples. There was a continuous enhancement in Young's modulus of SDLRPCs with SDL concentration. The neat UV unexposed samples displayed Young's modulus of 3500 MPa. This value improved by 4.40,

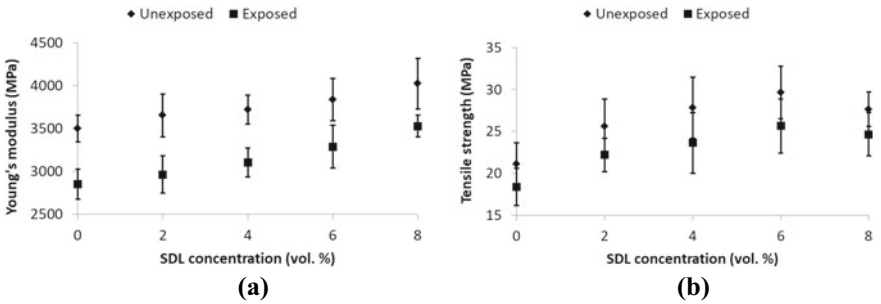


Fig. 6 Variation of **a** Young's modulus and **b** TS of unexposed as well as exposed SDLRPC samples with SDL concentration

6.31, 9.69, and 15% as the SDL concentration varied from 0, 2, 4, 6, and 8 vol.% respectively. On the other hand, UV exposed neat epoxy displayed Young's modulus of 2850 MPa which is 18.85% lower than unexposed samples. This value improved up to 4.03, 8.84, 15.36 and 23.83% at SDL concentrations ranging 0–8 vol.%. Figure 6b shows the variation of TSs of unexposed as well as exposed SDLRPC samples. SDL addition improved the TS up to 6 vol.% due to effective stress transfer between the matrix and reinforcement. The maximum TS of the unexposed sample is observed to be 29.65 MPa at 6 vol.% SDL concentration. On the other hand, the maximum TS of the unexposed sample are observed 25.66 MPa (about 13.50% lower than the unexposed sample). As expected, the TS of exposed samples is lower than the unexposed samples at all SDL concentrations.

The lower tensile properties of exposed samples are attributed to the UV rays-induced photo-degradation of polymer-based matrix (Jutakanoke et al. 2012). The aromatic groups present in epoxy-based polymers are prone to breaking under UV rays of wavelength ≈300 nm. The high energy UV rays break the C–O, C–C, and O–O bonds leading to chain scission forming free radicals. These free radicals lead to the accelerated degradation of epoxy and hence a significant reduction in mechanical properties (Woo et al. 2007; Nikafshar et al. 2017).

The K_{1C} and G_{1C} values of composites, as well as pristine epoxy samples, were determined using the SENB fracture test. The samples with a single edge notch were subjected to three-point bending loading as per ASTM D-5045 standard using the Tinius Olsen make UTM. The K_{1C} value was calculated using the Eq. (1):

$$K_{IC} = \left(\frac{F}{BW^{\frac{1}{2}}}\right) f(x) \tag{1}$$

where 'F' is the maximum applied load, 'B' is the thickness of the specimen, 'W' is the width of the specimen, 'a' is the pre-crack length, and 'f(x)' is the geometry factor which is calculated using the Eq. (2):

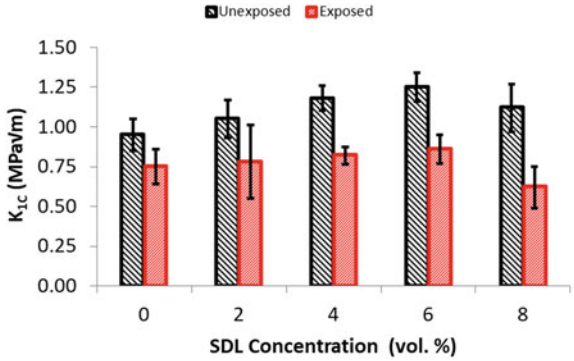


Fig. 7 Variation of K_{1C} of unexposed and exposed SDLRPC samples

$$f(x) = 6\sqrt{x}\left[\frac{1.99 - x(1-x)\left(2.15 - 3.93x + 2.7x^2\right)}{(1+2x)(1-x)^{\frac{3}{2}}}\right] \tag{2}$$

where, x = a/W.

Figure 7 shows the variation of K_{1C} with SDL proportion on unexposed and exposed samples.

The addition of SDL into epoxy has a positive effect on the K_{1C} of both unexposed and exposed samples. A gradual enhancement in K_{1C} can be noticed in both cases. Unexposed pristine epoxy shows a K_{1C} value of 0.95 MPa$\sqrt{}$m. This improved gradually up to 31.6% to a value of 1.25 MPa$\sqrt{}$m at 6 vol.% SDL in proportion. Enhancement in the K_{1C} value of SDLRPCs is attributed to various toughening mechanisms such as pull-out, fiber breakage, etc. (Wang et al. 2007). Similar results have been reported for fracture toughness polyester-based hemp and jute fiber composites (Hughes et al. 2002). On the other hand, an exposed pristine epoxy sample displayed a K1C value of just 0.75 MPa$\sqrt{}$m. The SDLRPC samples displayed modest improvement in K1C value with SDL concentration. The value was improved by 4, 9.33, and 14.66% at 2, 4, and 6 vol.% SDL proportion respectively. On further increase in SDL proportion, the K_{1C} value of composites dropped by 17.33% below pristine epoxy. The modest increase in K_{1C} is attributed to the photo-degradation of the epoxy matrix due to UV exposure. The UV exposure being a surface phenomenon, results in the decomposition of the surface without the direct decomposition of fibers. This degradation is often visualized as superficial micro-cracks present in the composite post-exposure (Woo et al. 2007).

The thermogravimetric characteristics of pristine epoxy and unexposed as well as exposed SDLRPC samples (6 vol.%) were evaluated. The analysis was conducted using the EXSTAR TG/DTA 6300 instrument under a nitrogen environment. Figure 8a and b show the results of the thermogravimetric analysis of pristine epoxy, unexposed, and exposed SDLRPC (6 vol.% proportion) samples. Table 3 summarizes the thermal behavior of pristine epoxy as well as SDLRPC samples. The T_5, T_{50}, and T_{80} refer to the temperatures at 5, 50, and 80% degradation respectively.

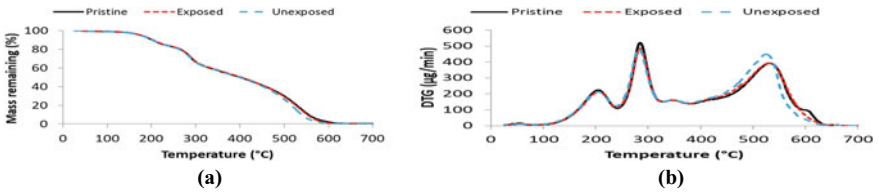


Fig. 8 **a** Percentage mass remaining and **b** DTG curve for pristine epoxy and SDLRPC at 6 vol.% SDL proportion under different conditions

Table 3 Data of thermogravimetric analysis

S. No.	Sample	T_5 (°C)	T_{50} (°C)	T_{80} (°C)	R_{max} (µg/min)	T_I (°C)	T_{II} (°C)	R_{700} (°C)
1	Pristine epoxy	176.28	400.18	528.12	521.34	284.56	532.44	0.26
2	Unexposed	177.07	403.36	525.49	484.62	284.93	531.07	−0.36
3	Exposed	174.96	398.20	516.14	482.69	282.29	524.52	−0.14

R_{max} refers to the maximum rate of degradation, T_I and T_{II} refer to the temperatures at the two DTG peaks and R_{700} refers to the char residue at 700 °C.

It is evident that pristine epoxy and composites decomposed in two steps. The first 2.5% of degradation is attributed primarily to the loss of adsorbed water. The pristine epoxy displayed 5% decomposition at a temperature of 176.28 °C which dropped slightly to 177.07 and 174.96 °C in case of unexposed and exposed composites respectively. The 50% decomposition temperature of pristine epoxy was 400.18 °C which slightly increased to 403.36 °C in case of unexposed sample and dropped again to 398.20 °C in case of exposed samples. The 80% decomposition temperature of pristine epoxy was 528.12 °C which dropped to 525.19 °C for unexposed and 516.14 °C for the exposed sample. As far as R_{max} is considered, the pristine epoxy displayed the highest value of 521.34 µg/min which was reduced to 484.62 and 482.69 µg/min respectively for unexposed and exposed samples. Thermal decomposition of pristine epoxy produced a char residue (R_{700}) of 0.26%. On the other hand, the unexposed and exposed sample displayed an R_{700} of −0.36 and −0.14% respectively. It can be inferred from the DTG curve that the exposed samples display a higher decomposition rate particularly in the second step of decomposition. Nevertheless, it can be adjudged from the results of the thermal analysis that the developed composites are thermally stable in both unexposed as well as the exposed state.

The structure of pristine epoxy unexposed as well as exposed composites was determined via powder X-Ray diffraction (XRD) technique. XRD was performed on a Rigaku make diffractometer using CuKα radiation having $\lambda = 1.541$ Å. The test setup was operated at 40 kV and 20 mA with a scanning range of 5°–100° and a scanning rate of 0.5°/min. Figure 9 shows the XRD patterns for pristine epoxy and well as unexposed and exposed SDLRPC samples at 6 vol.% SDL proportion. Both pristine, as well as unexposed composites, display a prominent peak at 18.16°

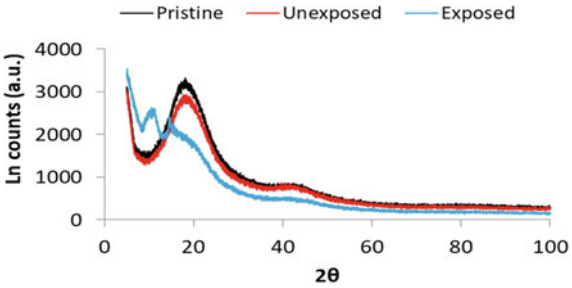


Fig. 9 XRD spectra of pristine epoxy as well as unexposed and exposed SDLRPC sample at 6 vol.% SDL proportion

corresponding to the epoxy. This implies that SDLs dispersed in epoxy via this processing technique have a negligible effect on the amorphous structure of epoxy. On the other hand, the exposed composite sample displayed a significantly different structure characterized by two peaks. This might be due to the accumulation of moisture and decomposition of SDLs within the epoxy matrix.

6.2 FE Modelling

FE models were constituted to determine the effect of UV exposure on the mechanical behaviour of SDLRPCs. The properties of unexposed as well as exposed epoxies were determined experimentally and properties of SDLs were determined as explained in (Ji Yadav et al. 2020). The properties of constituents used in FE modeling are shown in Table 4.

A FE model considering the periodic distribution of SDLs in the epoxy matrix was used for understanding the effect of matrix degradation on the concentration of von Mises stress. Figure 10 shows the FE model and boundary conditions used for stress analysis. Solid 186 elements available in the ANSYS library were used for the discretization of the model.

Figures 11a, b and 12a, b show the concentration of von Mises stress in the FE model under uniaxial and hydrostatic stress conditions respectively. The hydrostatic state of stress is present in the vicinity of the crack tip. Whereas, the uniaxial stress state is present away from the crack tip (Gunwant et al. 2018). Under uniaxial loading, the epoxy matrix is under lower stress for unexposed samples. The epoxy matrix in the case of the unexposed sample was subjected to 137.76 MPa which increased

Table 4 Material properties of various constituents used in the FE analysis (Ji Yadav et al. 2020)

S. No.	Constituent	Status	Young's modulus (MPa)	Poisson's ratio
1	Epoxy	Unexposed	3500	0.35
2	Epoxy	Exposed	2850	0.35
3	SDLs	–	9650.14	0.33

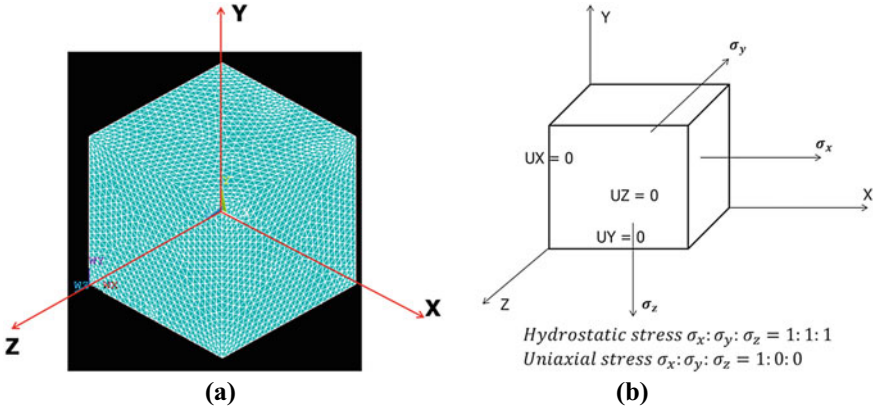


Fig. 10 **a** FE model **b** boundary and loading conditions

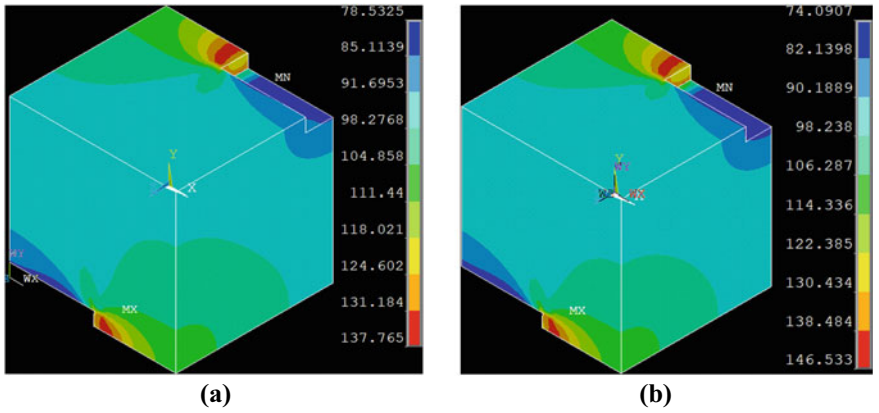


Fig. 11 von Mises stress contours in the epoxy matrix under uniaxial pressure of 100 MPa for **a** unexposed and **b** exposed SDLRPCs

by 6.36% to 146.533 MPa for exposed samples. Similarly, maximum von Mises stress in epoxy was 51.88 MPa for unexposed samples under hydrostatic loading. This increased by 20.41% to 62.47 MPa for exposed SDLRPC samples implying an increased tendency of matrix shear yielding in the vicinity of crack-tip after exposure. The increase in stress concentration post UV exposure is attributed to the lowering of Young's modulus of epoxy due to photo-degradation. Alternatively, the stress raising effect of SDLs is enhanced under crack-tip stress when the modulus of the epoxy is reduced i.e. after matrix degradation. Another noticeable point is that under uniaxial loading, the bulk of the epoxy matrix is under significantly higher stress concentration. The highest stress concentration occurs at the SDL-epoxy interface in a plane normal to the loading direction. On the other hand, under hydrostatic loading,

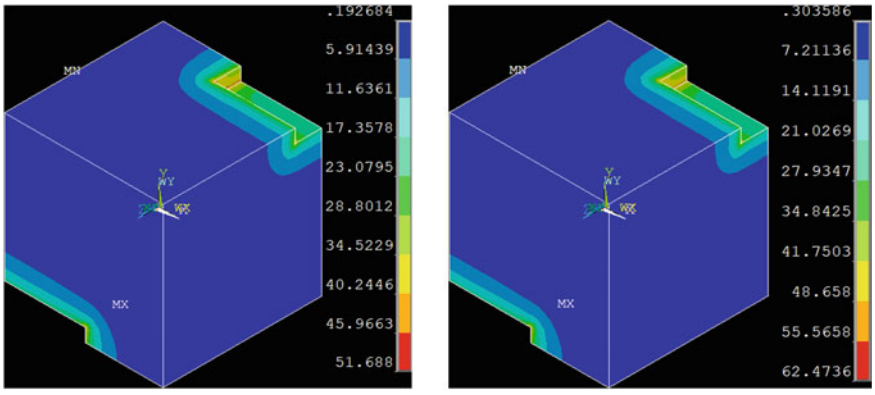


Fig. 12 von Mises stress contours in the epoxy matrix under hydrostatic pressure of 100 MPa for **a** unexposed and **b** exposed SDLRPCs

the stress concentration takes place at the SDL-epoxy interface while the bulk of the matrix is under smaller stress.

Figure 13a, b shows the simulation results for an unexposed and exposed SDLRPC sample (6 vol.%) obtained after subjecting the model to failure load under three-point bending. Corresponding values are presented in Table 5. The loading and boundary

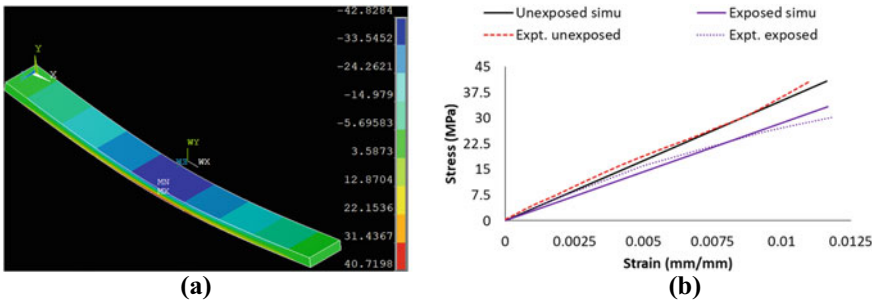


Fig. 13 **a** Stress distribution in flexural test and **b** experimental and predicted stress–strain curves under flexural loading

Table 5 Experimental and simulation results of flexural tests

S. No.	Status	Flexural stress (MPa)		% Difference	Flexural strain (mm/mm)		% Difference
		Experimental	Simulation		Experimental	Simulation	
1	Unexposed	40.60	40.72	0.3	0.0112	0.0116	3.57
2	Exposed	30.11	33.26	10.46	0.011	0.0118	7.27

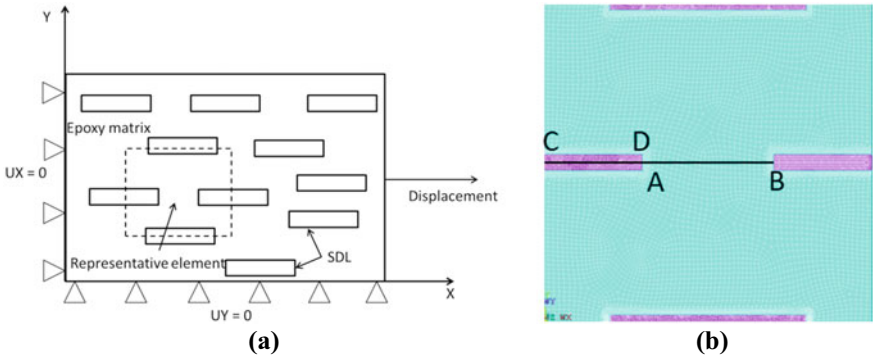


Fig. 14 **a** Distribution of SDLs within the epoxy matrix, **b** corresponding FE simulation model for SDLRPC showing paths

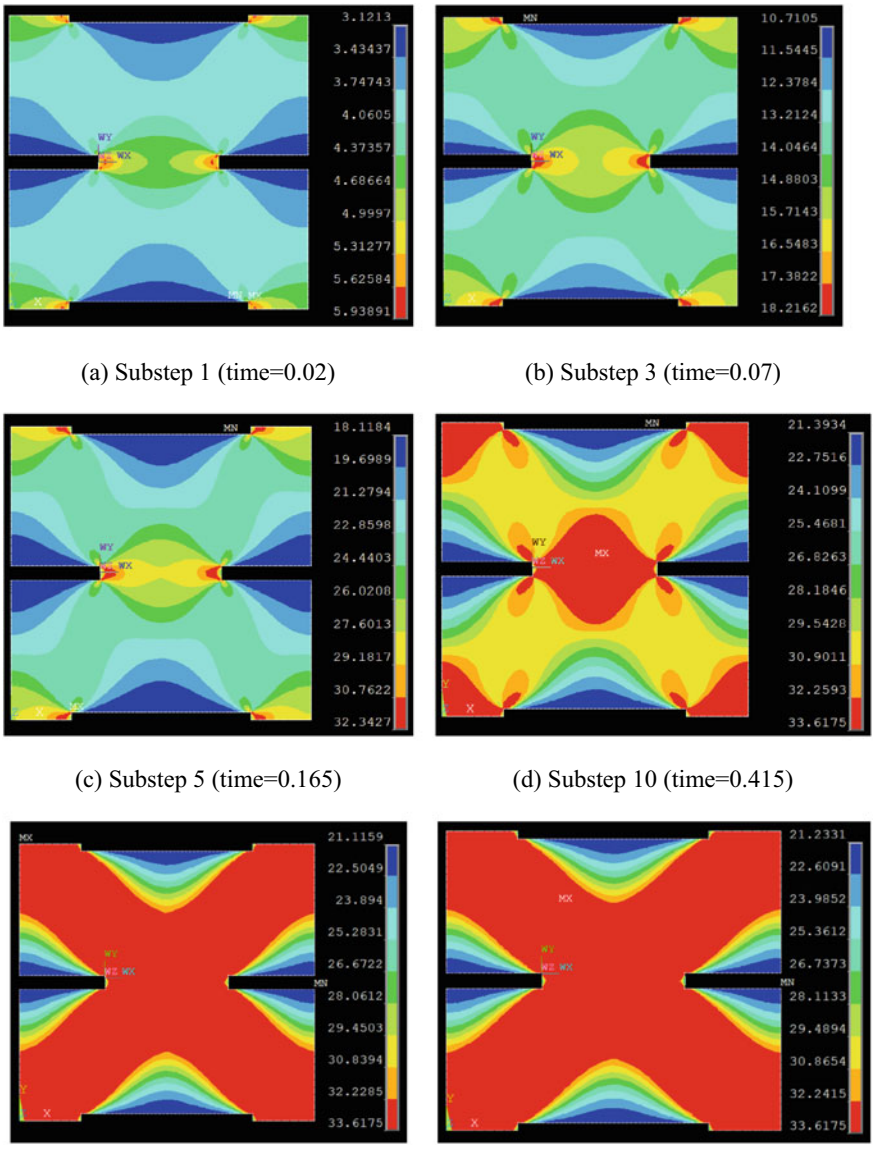
conditions for simulation were kept similar to the actual loading scenario to maintain coherence among experimental and simulation results.

The simulated and experimental stress–strain curves are in good agreement with each other. The percentage difference between experimental and simulation results is also within admissible limits establishing that flexural behavior of SDLRPCs can be predicted using FEM.

To visualize the development of the plastic zone in UV exposed samples, another two-dimensional model is proposed. The SDLs were considered to be uniformly distributed within the epoxy matrix. A square domain of dimensions $L \times L$ mm^2 was chosen as the representative area element as shown in Fig. 14a. Figure 14b shows the meshed FE model consisting of SDLs embedded in the epoxy matrix developed in ANSYS. The experimental tensile stress–strain curve for pristine epoxy was input into the program through the inbuilt multi linear elasto plastic material model. The SDLs were modelled as a linearly elastic material.

The right edge of the model was subjected to a uniform displacement of 0.55 mm to develop plastic strain in the matrix and capture the shear yielding phenomenon. For a better understanding of the yielding phenomenon, the von Mises stresses within the matrix as well as SDLs were mapped onto paths AB and CD respectively. The mapped results are presented graphically as the function of distance along with paths AB and CD. The mechanical properties of the constituents are given in Table 2.

Upon solving the model under given boundary conditions and loads, the solution converged after 22 sub steps. Figure 15a–f show the process of matrix yielding in gradual stages. The increase in the size of high von Mises stress locations corresponds to a progressive increase in the yield region size with the applied load. The matrix yielding pattern is altered due to the presence of rigid SDL inclusions. In the matrix, the von Mises stress is concentrated in front of the leading edge of SDL. It can be seen that due to the symmetry of the model and the identical size of SDLs, the damage initiation zones are uniformly located. Figure 9b, c shows the systematic formation of shear bands originating due to interaction between nearby SDLs. The process of



(a) Substep 1 (time=0.02) (b) Substep 3 (time=0.07)

(c) Substep 5 (time=0.165) (d) Substep 10 (time=0.415)

(e) Substep 15 (time=0.655) (f) Substep 22 (time=1)

Fig. 15 Contour plots for von Mises stress distribution at different substeps

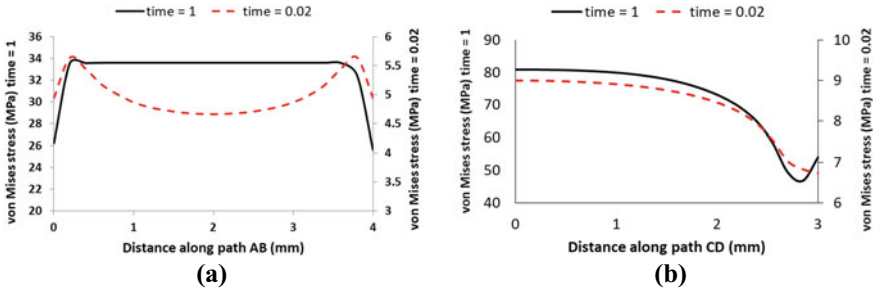


Fig. 16 Variation of von Mises stress along with the path **a** AB and **b** CD

shear banding between two neighboring SDLs can be visualized from Fig. 12d where the high-stress zones of adjacent SDLs coalesce into a single damage initiation zone. As shown in Fig. 12e–f this shear damage initiation zone finally culminates into an X-shaped shear band as the matrix reaches its failure point. On the other hand, the region of the matrix just above the longer edge of SDL was shielded from an increase in von Mises stress and thus safeguarded against yielding.

Figure 16 shows the variation of von Mises stress along with path AB (matrix) and CD (particle) at times 0.02 and 1 (substeps 1 and 22). Originally, the variation of stress resembled a bathtub indicating high stress at the SDL-epoxy interface and comparatively smaller stress in the matrix (Fig. 16a). This is in line with the contour plots of von Mises stress developed at the interface just ahead of the SDL (Fig. 15a–f). As the solution is completed, the maximum stress in the matrix reached is 33.615 MPa. On the other hand, along the same path AB, the curve resembles a straight line as the solution is completed. This indicates that under uniaxial loading, the matrix will gradually start yielding and reach its ultimate point. Figure 16b shows the variation of von Mises stress within SDL for $t = 0.02$ and 1. The von Mises stress in SDL is substantially higher than that in the matrix. Considering the complex interaction between SDL with the epoxy matrix as well as neighboring SDLs, the stress distribution within SDL plays a vital role in particle fracture. Depending upon interfacial bonding, particle size, orientation, and stress applied the failure of SDL may initiate when stress reaches a critical value. The maximum stress induced within the SDL is approximately 80 MPa which is more than double the stress-induced in the epoxy matrix. In the presence of a large number of SDLs (higher volume fraction), the plastic zone size is expected to be limited due to plastic strain developed near adjacent particles. These conditions might facilitate the fracture of SDL depending upon their strength and SDL/epoxy interaction.

7 Conclusions

The use of NFs in composite fabrication is being promoted as an alternative to synthetic fibers. This chapter has provided an overview of the effects of UV radiation and aging on the mechanical properties of NFCs. The aging phenomenon can be characterized by physical, chemical, and mechanical aging processes. The aging phenomenon adversely affects the mechanical properties of NFCs mainly due to matrix degradation but the degradation depends on the constituents of the NFCs. For instance, up to 52 and 70% reduction in TS and IS respectively have been reported in kenaf/epoxy composites. The hemp/PLA composites displayed 86.88, 88.70, and 81.25% reduction in the tensile and flexural strengths and K_{1C} values respectively. The wood flour composites underwent a 33 and 20% reduction in bending stiffness and strength after 2000 h of UV exposure. The loss in properties can be partially avoided via the suitable chemical treatment of fibers before composite fabrication. The chemical treatments such as NaOH and SiH_4 improve the moisture resistance along with improved fiber/matrix adhesion. As far as WPCs are considered, the TS, TS, and impact strength are reduced, and wear erosion increased significantly after the aging process. WPCs fabricated with 10% of Mango and Mahogany wood dust showed better wear resistance and mechanical properties as compared to other wood dust. This is due to adequate encapsulation of wood dust by PP matrix leading to proper wetting of wood dust at this concentration. The SDLRPCs fabricated via mixing 2–8 vol.% SDLs into epoxy matrix displayed a similar reduction in mechanical properties after UV exposure for 80 h. The photo-degradation of matrix upon UV exposure and matrix cracking is mainly responsible for such behavior. However, both and unexposed as well as exposed SDLRPC samples showed similar decomposition behavior in the thermogravimetric analysis. The FE model constituted for stress analysis showed the stress concentration within the epoxy matrix for unexposed as well as exposed samples. Under hydrostatic loading, the von Mises stress within the epoxy matrix increased by 20.41% after UV exposure as compared to unexposed samples. This implies that in the vicinity of crack-tip the tendency of the epoxy matrix to undergo shear yielding increases after exposure. Another FE model constituted for determining the bending properties of SDLRPC containing 6 vol.% SDLs showed good agreement between experimental and simulation results. Finally, a two-dimensional elasto-plastic FE model has shown the formation of shear bands due to aging/UV exposure the NFCs.

References

Akil HM, Omar MF, Mazuki AAM et al (2011) Kenaf fiber reinforced composites: a review. Mater Des 32:4107–4121. https://doi.org/10.1016/j.matdes.2011.04.008

Araújo JR, Waldman WR, De Paoli MA (2008) Thermal properties of high density polyethylene composites with natural fibres: coupling agent effect. Polym Degrad Stab 93:1770–1775. https://doi.org/10.1016/j.polymdegradstab.2008.07.021

Asgher M, Ahmad Z, Iqbal HMN (2017) Bacterial cellulose-assisted de-lignified wheat straw-PVA based bio-composites with novel characteristics. Carbohyd Polym 161:244–252. https://doi.org/10.1016/j.carbpol.2017.01.032

Avérous L, Pollet E (2012) Biodegradable polymers. In: Avérous L, Pollet E (eds) Environmental silicate nano-biocomposites. Springer, London, pp 13–39

Bajpai PK, Meena D, Vatsa S, Singh I (2013a) Tensile behavior of nettle fiber composites exposed to various environments. J Nat Fibers 10:244–256. https://doi.org/10.1080/15440478.2013.791912

Bajpai PK, Singh I, Madaan J (2013b) Tribological behavior of natural fiber reinforced PLA composites. Wear 297:829–840. https://doi.org/10.1016/j.wear.2012.10.019

Beckert W, Lauke B (1998) Critical discussion of the single-fibre pull-out test: does it measure adhesion? In: Parts of this paper were presented as a lecture at the sixth international conference on composite interfaces (ICCI-VI) held at Zichron Yaacov, Israel, in May 1996.1. Compos Sci Technol 57:1689–1706. https://doi.org/10.1016/S0266-3538(97)00107-3

Beninia KCCC, Voorwald HJC, Cioffi MOH (2011) Mechanical properties of HIPS/sugarcane bagasse fiber composites after accelerated weathering. Procedia Eng 10:3246–3251. https://doi.org/10.1016/j.proeng.2011.04.536

Campilho RDSG natural fiber composites. CRC Press

Catto AL, Montagna LS, Almeida SH et al (2016) Wood plastic composites weathering: effects of compatibilization on biodegradation in soil and fungal decay. Int Biodeterior Biodegrad 109:11–22. https://doi.org/10.1016/j.ibiod.2015.12.026

Dittenber DB, GangaRao HVS (2012) Critical review of recent publications on use of natural composites in infrastructure. Compos A Appl Sci Manuf 43:1419–1429. https://doi.org/10.1016/j.compositesa.2011.11.019

El-Shekeil YA, Sapuan SM, Abdan K, Zainudin ES (2012) Influence of fiber content on the mechanical and thermal properties of Kenaf fiber reinforced thermoplastic polyurethane composites. Mater Des 40:299–303. https://doi.org/10.1016/j.matdes.2012.04.003

Friedrich D, Luible A (2016) Investigations on ageing of wood-plastic composites for outdoor applications: a meta-analysis using empiric data derived from diverse weathering trials. Constr Build Mater 124:1142–1152. https://doi.org/10.1016/j.conbuildmat.2016.08.123

Ghofrani M, Mokaram KN, Ashori A, Torkaman J (2015) Fiber-cement composite using rice stalk fiber and rice husk ash: mechanical and physical properties. J Compos Mater 49:3317–3322. https://doi.org/10.1177/0021998314561813

Gowda TGY, Sanjay MR, Bhat KS et al (2018) Polymer matrix-natural fiber composites: an overview. Cogent Eng 5:1446667. https://doi.org/10.1080/23311916.2018.1446667

Gunwant D, Sah P, Zaidi MGH (2018) Morphology and micromechanics of liquid rubber toughened epoxies. e-Polymers 18. https://doi.org/10.1515/epoly-2018-0141

Hassan F, Zulkifli R, Ghazali M, Azhari C (2017) Kenaf fiber composite in automotive industry: an overview. Int J Adv Sci Eng Inf Technol 7:315. https://doi.org/10.18517/ijaseit.7.1.1180

Hon DNS, Shiraishi N (2000) Wood and cellulosic chemistry, revised, and expanded. CRC Press

Hughes M, Hill CAS, Hague JRB (2002) The fracture toughness of bast fibre reinforced polyester composites. Part 1. Evaluation and analysis. J Mater Sci 37:4669–4676. https://doi.org/10.1023/A:1020621020862

Hutchinson JM (1995) Physical aging of polymers. Prog Polym Sci 20:703–760. https://doi.org/10.1016/0079-6700(94)00001-I

Islam MS, Pickering KL, Foreman NJ (2010) Influence of accelerated ageing on the physico-mechanical properties of alkali-treated industrial hemp fibre reinforced poly(lactic acid) (PLA) composites. Polym Degrad Stab 95:59–65. https://doi.org/10.1016/j.polymdegradstab.2009.10.010

Ji Yadav SK, Vedrtnam A, Gunwant D (2020) Experimental and numerical study on mechanical behavior and resistance to natural weathering of sugarcane leave reinforced polymer composite. Constr Build Mater 262:120785. https://doi.org/10.1016/j.conbuildmat.2020.120785

Jiang N, Yu T, Li Y et al (2019) Hygrothermal aging and structural damage of a jute/poly (lactic acid) (PLA) composite observed by X-ray tomography. Compos Sci Technol 173:15–23. https://doi.org/10.1016/j.compscitech.2019.01.018

John MJ, Thomas S (2008) Biofibres and biocomposites. Carbohyd Polym 71:343–364. https://doi.org/10.1016/j.carbpol.2007.05.040

Joseph PV, Rabello MS, Mattoso LHC et al (2002) Environmental effects on the degradation behaviour of sisal fibre reinforced polypropylene composites. Compos Sci Technol 62:1357–1372. https://doi.org/10.1016/S0266-3538(02)00080-5

Jutakanoke R, Leepipatpiboon N, Tolieng V et al (2012) Sugarcane leaves: pretreatment and ethanol fermentation by Saccharomyces cerevisiae. Biomass Bioenerg 39:283–289. https://doi.org/10.1016/j.biombioe.2012.01.018

Kokta BV, Chen R, Daneault C, Valade JL (1983) Use of wood fibers in thermoplastic composites. Polym Compos 4:229–232. https://doi.org/10.1002/pc.750040407

Kumar R, Anand A (2019) Fabrication and mechanical characterization of Indian ramie reinforced polymer composites. Mater Res Express 6:055303. https://doi.org/10.1088/2053-1591/aaff12

Lalit R, Mayank P, Ankur K (2018) Natural fibers and biopolymers characterization: a future potential composite material. Strojnícky Časopis J Mech Eng 68:33–50. https://doi.org/10.2478/scjme-2018-0004

Lévêque D, Schieffer A, Mavel A, Maire J-F (2005) Analysis of how thermal aging affects the long-term mechanical behavior and strength of polymer–matrix composites. Compos Sci Technol 65:395–401. https://doi.org/10.1016/j.compscitech.2004.09.016

Li M, Pu Y, Thomas VM et al (2020) Recent advancements of plant-based natural fiber–reinforced composites and their applications. Compos B Eng 200:108254. https://doi.org/10.1016/j.compositesb.2020.108254

Li X, He L, Zhou H et al (2012) Influence of silicone oil modification on properties of ramie fiber reinforced polypropylene composites. Carbohyd Polym 87:2000–2004. https://doi.org/10.1016/j.carbpol.2011.10.023

Lila MK, Singh B, Pabla BS, Singh I (2018) Effect of environmental conditioning on natural fiber reinforced epoxy composites. Mater Today Proc 5:17006–17011. https://doi.org/10.1016/j.matpr.2018.04.105

Liu K, Takagi H, Osugi R, Yang Z (2012) Effect of lumen size on the effective transverse thermal conductivity of unidirectional natural fiber composites. Compos Sci Technol 72:633–639. https://doi.org/10.1016/j.compscitech.2012.01.009

Liu Y, Xie J, Wu N et al (2019) Influence of silane treatment on the mechanical, tribological and morphological properties of corn stalk fiber reinforced polymer composites. Tribol Int 131:398–405. https://doi.org/10.1016/j.triboint.2018.11.004

Lopez JL, Sain M, Cooper P (2006) Performance of natural-fiber–plastic composites under stress for outdoor applications: effect of moisture, temperature, and ultraviolet light exposure. J Appl Polym Sci 99:2570–2577. https://doi.org/10.1002/app.22884

Lu N, Oza S (2013) A comparative study of the mechanical properties of hemp fiber with virgin and recycled high density polyethylene matrix. Compos B Eng 45:1651–1656. https://doi.org/10.1016/j.compositesb.2012.09.076

Lundin T, Falk RH, Felton C (2002) Accelerated weathering of natural fiber-thermoplastic composites: effects of ultraviolet exposure on bending strength and stiffness. In: Sixth international conference on woodfiber-plastic composites: May 15–16, 2001. Forest Products Society, Madison, WI , pp 87–93. c2002: ISBN: 0892529181

Ma G, Yan L, Shen W, et al (2018) Effects of water, alkali solution and temperature ageing on water absorption, morphology and mechanical properties of natural FRP composites: plant-based jute vs. mineral-based basalt. Compos Part B Eng 153. https://doi.org/10.1016/j.compositesb.2018.09.015

Majeed K, Jawaid M, Hassan A et al (2013) Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. Mater Des 46:391–410. https://doi.org/10.1016/j.matdes.2012.10.044

Mamtaz H, Fouladi MH, Al-Atabi M, Narayana Namasivayam S (2016) Acoustic absorption of natural fiber composites. J Eng. https://www.hindawi.com/journals/je/2016/5836107/. Accessed 31 May 2020

Mancini E, Antonelli MG, Zobel PB, Sasso M (2019) Characterization and analytical parametrization of composite in cellulose fibre and PVA matrix. Compos B Eng 172:496–505. https://doi.org/10.1016/j.compositesb.2019.05.093

Martin R (ed) (2008) Ageing of composites, 1st edn. Woodhead Publishing

Migneault S, Koubaa A, Perré P, Riedl B (2015) Effects of wood fiber surface chemistry on strength of wood–plastic composites. Appl Surf Sci 343:11–18. https://doi.org/10.1016/j.apsusc.2015.03.010

Mohanty AK, Misra M, Drzal LT (2002) Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. J Polym Environ 10:19–26. https://doi.org/10.1023/A:1021013921916

Mohanty AK, Misra M, Hinrichsen G (2000) Biofibres, biodegradable polymers and biocomposites: an overview. Macromol Mater Eng 276–277:1–24. https://doi.org/10.1002/(SICI)1439-2054(20000301)276:1%3c1::AID-MAME1%3e3.0.CO;2-W

Naeem MA, Siddiqui Q, Khan MR et al (2020) Bacterial cellulose-natural fiber composites produced by fibers extracted from banana peel waste. J Ind Text. https://doi.org/10.1177/1528083720925848

Netravali A, Chabba S (2003) Composites get greener. Mater Today 6:22–29. https://doi.org/10.1016/S1369-7021(03)00427-9

Nikafshar S, Zabihi O, Ahmadi M et al (2017) The effects of UV light on the chemical and mechanical properties of a transparent epoxy-diamine system in the presence of an organic UV absorber. Materials 10:180. https://doi.org/10.3390/ma10020180

Ochi S (2008) Mechanical properties of kenaf fibers and kenaf/PLA composites. Mech Mater 40:446–452. https://doi.org/10.1016/j.mechmat.2007.10.006

Peng Y, Liu R, Cao J (2015) Characterization of surface chemistry and crystallization behavior of polypropylene composites reinforced with wood flour, cellulose, and lignin during accelerated weathering. Appl Surf Sci 332:253–259. https://doi.org/10.1016/j.apsusc.2015.01.147

Premnath A (2018) Impact of surface treatment on the mechanical properties of sisal and jute reinforced with epoxy resin natural fiber hybrid composites. J Nat Fibers 16:1–11. https://doi.org/10.1080/15440478.2018.1432002

Reddy KO, Maheswari CU, Reddy KR et al (2015) Effect of chemical treatment and fiber loading on mechanical properties of Borassus (Toddy Palm) fiber/epoxy composites. Int J Polym Anal Charact 20:612–626. https://doi.org/10.1080/1023666X.2015.1054084

Regazzi A, Corn S, Ienny P et al (2016) Reversible and irreversible changes in physical and mechanical properties of biocomposites during hydrothermal aging. Ind Crops Prod 84:358–365. https://doi.org/10.1016/j.indcrop.2016.01.052

Ren Y, Wang Y, Wang L, Liu T (2015) Evaluation of intumescent fire retardants and synergistic agents for use in wood flour/recycled polypropylene composites. Constr Build Mater 76:273–278. https://doi.org/10.1016/j.conbuildmat.2014.12.004

Saheb DN, Jog JP (1999) Natural fiber polymer composites: a review. Adv Polym Technol 18:351–363. https://doi.org/10.1002/(SICI)1098-2329(199924)18:4%3c351::AID-ADV6%3e3.0.CO;2-X

Sair S, Oushabi A, Kammouni A et al (2018) Mechanical and thermal conductivity properties of hemp fiber reinforced polyurethane composites. Case Stud Constr Mater 8:203–212. https://doi.org/10.1016/j.cscm.2018.02.001

Sakthi Balan G, Ravichandran M, Santhosh Kumar V (2020) Study of ageing effect on mechanical properties of prosopis juliflora fibre reinforced palm seed powder filled polymer composite. Aust J Mech Eng 1–13. https://doi.org/10.1080/14484846.2020.1806194

Saxena M, Pappu A, Sharma A, et al (2011) Composite materials from natural resources: recent trends and future potentials. In: Tesinova P (ed) Advances in composite materials—analysis of natural and man-made materials. InTech

Sepe R, Bollino F, Boccarusso L, Caputo F (2018) Influence of chemical treatments on mechanical properties of hemp fiber reinforced composites. Compos B Eng 133:210–217. https://doi.org/10.1016/j.compositesb.2017.09.030

Sood M, Dwivedi G (2018) Effect of fiber treatment on flexural properties of natural fiber reinforced composites: a review. Egypt J Pet 27:775–783. https://doi.org/10.1016/j.ejpe.2017.11.005

Sullins T, Pillay S, Komus A, Ning H (2017) Hemp fiber reinforced polypropylene composites: the effects of material treatments. Compos B Eng 114:15–22. https://doi.org/10.1016/j.compositesb.2017.02.001

Tamrakar S, Lopez-Anido RA (2011) Water absorption of wood polypropylene composite sheet piles and its influence on mechanical properties. Constr Build Mater 25:3977–3988. https://doi.org/10.1016/j.conbuildmat.2011.04.031

Turku I, Keskisaari A, Kärki T et al (2017) Characterization of wood plastic composites manufactured from recycled plastic blends. Compos Struct 161:469–476. https://doi.org/10.1016/j.compstruct.2016.11.073

Vedrtnam A, Kumar S, Chaturvedi S (2019) Experimental study on mechanical behavior, biodegradability, and resistance to natural weathering and ultraviolet radiation of wood-plastic composites. Compos B Eng 176:107282. https://doi.org/10.1016/j.compositesb.2019.107282

Verma D (2012) Bagasse fiber composites: a review. J Mater Environ Sci 3:1079–1092

Wang B, Panigrahi S, Tabil L, Crerar W (2007) Pre-treatment of flax fibers for use in rotationally molded biocomposites. J Reinf Plast Compos 26:447–463. https://doi.org/10.1177/0731684406072526

Wang X, Petrů M (2019) Effect of hygrothermal aging and surface treatment on the dynamic mechanical behavior of flax fiber reinforced composites. Materials 12:2376. https://doi.org/10.3390/ma12152376

Woo RSC, Chen Y, Zhu H et al (2007) Environmental degradation of epoxy–organoclay nanocomposites due to UV exposure. Part I: photo-degradation. Compos Sci Technol 67:3448–3456. https://doi.org/10.1016/j.compscitech.2007.03.004

Yan L, Chouw N, Jayaraman K (2015) Effect of UV and water spraying on the mechanical properties of flax fabric reinforced polymer composites used for civil engineering applications. Mater Des 71:17–25. https://doi.org/10.1016/j.matdes.2015.01.003

Yang T-H, Yang T-H, Chao W-C, Leu S-Y (2015) Characterization of the property changes of extruded wood–plastic composites during year round subtropical weathering. Constr Build Mater 88:159–168. https://doi.org/10.1016/j.conbuildmat.2015.04.019

Yorseng K, Rangappa SM, Pulikkalparambil H et al (2020) Accelerated weathering studies of kenaf/sisal fiber fabric reinforced fully biobased hybrid bioepoxy composites for semi-structural applications: morphology, thermo-mechanical, water absorption behavior and surface hydrophobicity. Constr Build Mater 235:117464. https://doi.org/10.1016/j.conbuildmat.2019.117464

Yu T, Li Y, Ren J (2009) Preparation and properties of short natural fiber reinforced poly(lactic acid) composites. Trans Nonferrous Metals Soc China 19:s651–s655. https://doi.org/10.1016/S1003-6326(10)60126-4

Zampaloni M, Pourboghrat F, Yankovich SA et al (2007) Kenaf natural fiber reinforced polypropylene composites: a discussion on manufacturing problems and solutions. Compos A Appl Sci Manuf 38:1569–1580. https://doi.org/10.1016/j.compositesa.2007.01.001

Zhang Z, Du H, Wang W, Wang Q (2010) Property changes of wood-fiber/HDPE composites colored by iron oxide pigments after accelerated UV weathering. J for Res 21:59–62. https://doi.org/10.1007/s11676-010-0009-z

Zhong J, Li H, Yu J, Tan T (2011) Effects of natural fiber surface modification on mechanical properties of poly(lactic acid) (PLA)/sweet sorghum fiber composites. Polym Plast Technol Eng 50:1583–1589. https://doi.org/10.1080/03602559.2011.557817

Fatigue Life Prediction of Bio-composites Subjected to Environmental Aging

G. Jeevi, R. Karthikeyan, Nalini Ranganathan, M. Abdul Kader, and Sanjay K. Nayak

Abstract In last few decades, the manufacturing and application of natural fiber reinforced polymeric composites have remarkable achievements to replace the non-bidegradable petroleum based materials. The demand for natural composites is drastically increasing, and became a notable material to use for extensive range of applications such as automotive, aviation, consumer products, and civil engineering, etc. Many investigations and studies have been reported to expand the mechanical and durability performance of biocomposites to compete with conventional composites. Comparatively enormous number of failure mechanisms occurs in fibre reinforced composite arises, and the fatigue life distributions of composites at various constant stress levels are determined using various models. In this chapter, the different methodologies adapted to determine the fatigue life of biocomposites were discussed. The fatigue behavior of biocomposites when subjected to different aging mechanisms under various service conditions and environments were reviewed. Further the chapter also detailed the long-term durability of biocomposites in different dynamic and static stresses under various environments namely corrosive stresses, mechanical stresses, electric stress, thermal stress and photo stress.

Keywords Fatigue life · Biocomposites · Environmental aging · Mechanical properties · Stress cycle

1 Introduction

In recent years, natural polymer composites have been involved in various structural applications and have superior mechanical properties. In general, biocomposites are composed of two or more distinct constituent of materials namely reinforcement and

R. Karthikeyan · N. Ranganathan (✉) · M. A. Kader
Advanced Research School for Technology and Product Simulation, TVK Industrial Estate, Guindy, Chennai, India

G. Jeevi · S. K. Nayak
Central Institute of Plastics Engineering & Technology (CIPET), TVK Industrial Estate, Guindy, Chennai, India

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_12

matrix, one being a naturally derived material (Mohammed et al. 2015). The natural fiber reinforcements may be cotton, sisal, hemp, flax, jute, viscose, kenaf and wood etc.; and organic matrices are corn zein, gelatin, chitosan, gluten, collagen, synthetic polymers are esters based polymer and polyvinyl alcohol (PVA) (Kozlowski and Wladyka-Przybylak 2004; Dhaliwal 2019). Bio-composites have advantages of more renewability, biodegradability and sustainability in nature; and have created much more interest in research and industrial areas (Mohanty et al. 2002). Furthermore, these composites are being widely used in structural application because of their good mechanical performance and lower cost (Gurunathan et al. 2015; Shesan et al. 2019). However, the exposure of composites to harsh environments such as UV light, elevated temperature, moisture, saline or sea water etc., tends to affect the mechanical performance of the composites, particularly while used in long term load bearing applications (Liu et al. 2020; Mahato et al. 2014).

The interdependent action such as high temperature, moisture penetration, frozen-in residual stresses and other combative agents will strongly affect the morphological behavior of the composites and its bonding interfaces between the fiber and matrix (Apicella et al. 1983). Bio-composites can be used productively in more industrial and mechanical applications such as higher production of products with short life span of 1–2 years (non-durable) or products with short-term and long-term indoor applications (GhaffarianHoseini et al. 2013; Netravali and Chabba 2003). The study of Maudood et al. (2019) stated that bio-composites are primarily used for applications due to their low durability, and immediate degradation in the hard and humid environment, which is a major drawback of biocomposites for outdoor usage. Bazli et al., study reported that the degradation of mechanical performance in composites under aggressive sea water environmental conditions (Bazli et al. 2019). The loss of fiber confinement due to matrix cracking and wear is the principal mechanism for the degradation of matrix influential properties (Nakamura et al. 2006). The wear and fatigue failure ultimately results in lowering the life-cycle of the composites. Therefore, the study on fatigue behavior of the composites is very important, particularly for bio-composites when subjected to long-term load bearing applications.

The modes of fatigue failures in composite have more complexity due to inhomogenous and anisotropic nature of composites. In fatigue test, the number of cycles to fail depends on stress variables, stress rate, fatigue cycling mode, environmental conditions and material compositions. In polymer composites, the fatigue tests are conducted for the suggestions of load level, frequency setup, allowable stress, amplitude and factor of safety to predict the service life of structure or components (Degrieck and Van Paepegem 2001).

In this chapter, fatigue failure of bio-composites are reviewed and reported with measure of reload application, such as total life cycle or number of cycles to failure or the crack growth life approach correlate with the environmental parameters such as solvents, mechanical load, temperature, UV radiation and electric charges etc.

2 Overview of Biocomposites

Biocomposites are by different kind of natural polymers such as bio-based polymers and petro-based polymers reinforced with matrices and inexpensive biofillers namely flour, biomass, or biosourced carbon, etc. However, the sustainable biocomposites are not only developed using plant fibers but also using agro-waste (Sadh et al. 2018; Mohanty et al. 2018). Both thermoplastic and thermoset polymers are often utilized with various bio-based fibres (biofibre), bio fillers or reinforcements to shape biocomposites. It is classified into three major groups (Chang et al. 2020) as described in Fig. 1:

(a) Non-degradable composites,
(b) Biodegradable composites, and
(c) Non-biodegradable composites.

In automotive applications, the usage of bio-fibers are used in manufacturing various components such as dashboards, door panels, seat cushions, interior parts and other exterior body parts (Koronis et al. 2013; Huda et al. 2008). Due to several environmental considerations, the automobile sector focused to adapt bio-based composites in manufacturing the components instead of traditional composites. Bio-based composites has more beneficial than synthetic composites in terms of energy consumption, life cycle assesment (LCA), and environmental impacts (Yates and Barlow 2013).

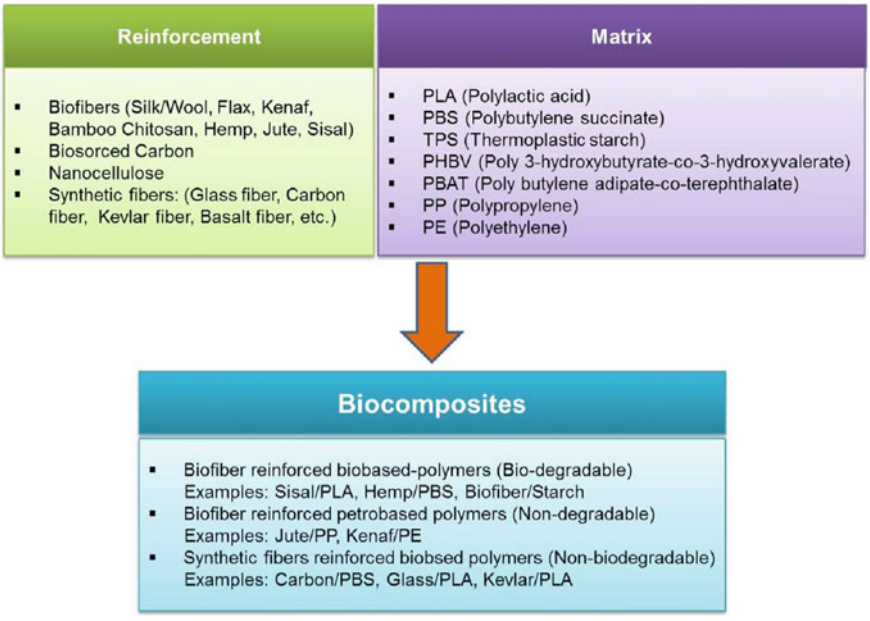


Fig. 1 Three major groups of bio-composites and their examples

Table 1 Types of aging due to different environmental attacks

Types of aging	Attribution
Natural	Aging occurs by environmental conditions
Thermo-oxidative	Aging of plastics at higher temperature in oxygen rich environment
Biological	Aging through the action of living organisms (bacteria/fungus)
Mechanical	Aging due to constant dynamic and static loads (fatigue load)
Ozone	Aging due to ozone
Photo-oxidative	Aging through the effect of visible and UV light spectrum in oxygen rich environment
Chemical	Aging by chemical substances
Artificial	Aging in artificially modified conditions
Thermal	Aging through heat/temperature

Miller (2018) reported that PHBV natural composites has lower carbon foot prints, hence became an attractive component to replace the synthetic composites in automotive sectors. Further, these composites found advantages in acoustic properties (Hassan et al. 2020; Tang and Yan 2017), non-abrasiveness and biodegradable properties, etc. Biocomposites reduces the environmental pollution by degrading under appropriate composite condition. Thereby, it became an undesirable material to use in loang term load bearing applications. The types of aging factors that attributes to different environmental attacks are enumerated in Table 1.

The components of biofibers namely the Lignin and hemicellulose are prone to UV degradation moisture degradation respectively (Beg and Pickering 2008). The different types of polymers exhibit dissimilar degradation behavior based on molecular breakdown with respect to rate of oxidation. The composite degradation occurs either in mechanical or chemical form, the factor to the degradation directly depends on temperature, acid contact, environmental oxidation, ultra violet radiation etc. The degradation of composites under various scenarios reduces the material performance, which in turn the reliability and its durability (Brebu 2020). The prolonged exposure of composites to these environments reduces the endurance limit of the material.

3 Prediction of Fatigue Strength on Bio-composites

Fatigue is a dynamic phenomenon, which tends to initiate as a micro-crack on the materials or products and on repeated loading and unloading, the micro-crack propagates into a macro-cracks. If these cracks are not detected, then the component or product leads to catastrophic failure. In other words, the catastrophic failure that occurs in a component when exposed to fatigue stresses for an extended period. Generally the crack formed on the surface is then developed in the component will be in the perpendicular direction to the center tensile axis.

The concepts of mechanism of fatigue fracture have been developed to determine the safety of product or components containing cracks. One of the initial damage mechanisms of structural components was identified as fatigue cracking (Ritchie 1999). The fatigue life has indicated as the number of cycles required to initiate a crack and to propagating the crack to critical size (Ranganathan et al. 2016). Three stages of fatigue failures occur in the components i.e. (i) crack initiation, (ii) stable and continuous crack growth and (iii) rapid fracture (Mallick 1997). In composite, the failure structure is associated with crack initiation and propagation, fiber damages and breakage, delamination/debonding at the fiber matrix interface, and pullout fiber (Santecchia et al. 2016).

In case of bio-composites, fatigue behavior and mechanical properties depend on both modulus of fibre and ductility of the matrix interface (Mitra 2014). The extent of stress transfer between the fiber and matrix interfaces plays a prominent role in determining the fatigue failure.

In general, the fatigue loads are classified as shown in Fig. 2, based on the applied loading modes, commonly three different modes of cyclic loading as shown in Fig. 3, are being provided as detailed below,

1. Tension–Tension/Tension–compression fatigue tests: To evaluate the fatigue strength

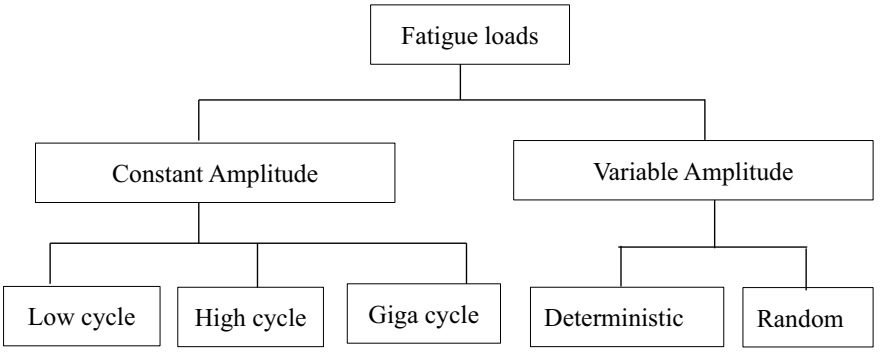


Fig. 2 Classification of fatigue loads

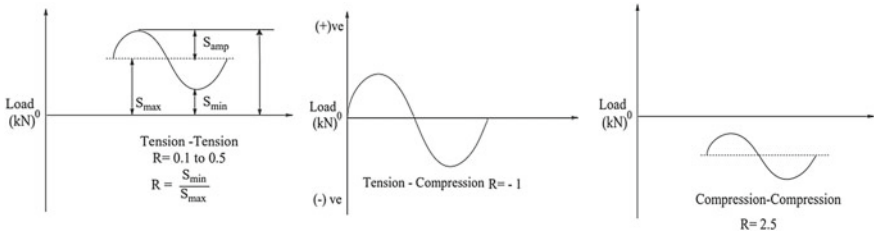


Fig. 3 Three different modes of cyclic loading; **a** Tension–tension; **b** Tension–compression; **c** Compression–compression

- High Cycle fatigue Test: Frequencies ranging approximately from 1 to 5000 Hz
- Low Cycle fatigue test: Frequencies of less than about 10 Hz
- Giga-cycle fatigue test: 1×10^9 cycles or more applied in a short time

2. Plane bending fatigue testing machine
3. Torsional fatigue testing machine.

The static and dynamic loads exerted on composites over a long term cause catastrophic damage at different service periods. The structural durability of bio-composites can sustain deformation under constant cyclic stresses. The fatigue properties are determined by the application of continuous and repetitive loads, these loads are applied in different waveforms namely sine, triangular, square, saw tooth and random with their R-value (Movahedi-Rad et al. 2018, 2019; Burhan and Kim 2018). The R-value is the ratio of minimum and maximum stress applied during fatigue test shown in Eq. (1).

$$R = \sigma_{min}/\sigma_{max} \tag{1}$$

The indications of different modes of fatigue loads and stress ratio (R-values) such as static load ($R = 1$), tension–tension load ($0 < R < 1$), tension–compression load ($-1 < R < 0$), reversed tension–compression ($R = -1$), tension-unload ($R = 0$) respectively. The fatigue performance results are plotted as S–N curve from the obtained values of fatigue stresses and number of cycles to failure. The maximum stress that a material withstands without any failure for infinite number of cycles is termed as endurance limit (Hwang and Han 1986; Wicaksono and Chai 2013; Zhou and Wu 2019). The fatigue life cycle is normally plotted with S–N curves, where S defines fatigue stress, and N defines number of cycle and the endurance determined from the exerted results (Manjunatha et al. 2010; Evans et al. 1996; Schijve 2001).

In S–N curve the value of stress is plotted as alternating stress, maximum stress or minimum stress Versus Number of cycles. Based on fatigue damage formulation the S–N curve models were derived. The S–N curves models directly characterizes the fatigue damage when a material or components were subjected to constant amplitude of loading at a constant stress ratio (R). S–N curve model had been intuitively formulated based on the Basquin Model, as shown in Eq. (2).

$$\sigma_{max} = \sigma_f(N_f)\beta \tag{2}$$

where the fatigue strength coefficient (FSC), σ_{max} = applied peak stress, β = mfatigue strength exponent (FSE) and N_f = number of cycle at failure.

In a linear order, the number of cycles increases with decreasing their fatigue stress. The fatigue behavior is represented as two types of curves one as Wohler curve for constant amplitude loading and other one is Gassner curve for variable amplitude loading, as shown in Fig. 4.

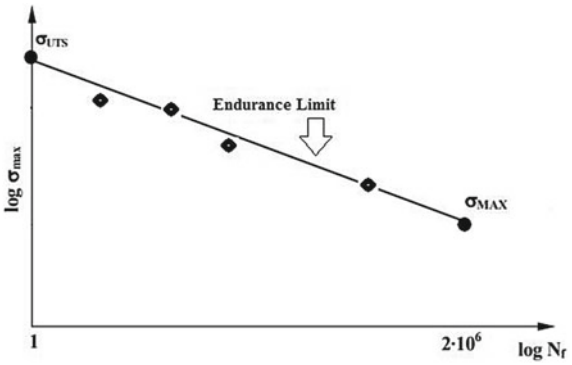


Fig. 4 Schematic representation of S–N curve

Dissimilar polymer exhibits different kind of fatigue life (Schijve 2001). Generally, the test variables influence the fatigue strength of polymeric material containing number of cycles, thermal effects, stress concentration and other environmental conditions and aging etc. There is only limited studies available related to fatigue and creep on bio-based polymers and bio-based composites.

Katogi et al. (2012) studied the fatigue performance of jute fiber reinforced PLA composites. Their study described that due to brittle nature of PLA, the composites exhibited limited fatigue properties. To enhance the fatigue life of natural fiber reinforced PLA composites, the ductile biopolymer namely the Polybutylene succinate (PBS) were reinforced. In the previous study, the author determined the fatigue life of impact modified jute reinforced thermoplastic composites. Table 2 summarizes the fatigue performance of different biocomposites.

Liber-Knec et al. (2015) experimentally investigated the fatigue performance of flax fiber thermoplastic starch (TPS) and polylactic acid (PLA) composites. They resulted that TPS filled flax fibers shown a lower fatigue strength and short life cycle, due to inefficient adhesion between the matrix and reinforcement. The crack initiation and propagation occurs under both static and dynamic loading. The PLA reinforced flax composite found to have slightly increased the fatigue strength compare to TPS reinforced flax composites.

Thew and Liao investigate the biocomposites after one million cycles of fatigue load; the unreinforced polypropylene had a longer fatigue life than bamboo fiber/polypropylene composites and bamboo fiber/glass fiber/polypropylene hybrid biocomposites. Hybrid biocomposites shows better fatigue resistance than the bamboo fiber/polypropylene composites (Thwe and Liao 2003). Similarly, the comparison study of hemp fiber and hemp/glass fiber biocomposites resulted as the fatigue strength of hemp fiber/glass hybrid composites are higher than the hemp fiber composites (Shahzad 2011). Vasconcellos et al. (2014) and Haggui et al. (2019) investigate the fatigue behaviour of biocomposites with complete damage analysis can be monitored by using different instrumentation. Fatigue damage mechanism of hemp fiber/epoxy and flax fiber biocomposites using the acoustic emission, infrared and X-ray tomography techniques.

Table 2 Analysis of fatigue performance of different biocomposites

Refs.	Biocomposites	Mode of fatigue test	Process method adapted	Remarks
Ranganathan (2016)	Jute/viscose/polypropylene	Uniaxial tension–tension fatigue test	Long fibre thermoplastics (LFT) composites ASTM D3479	Viscose fiber modified hybrid composite shown thrice higher fatigue strength than jute reinforced thermoplastic biocomposite. The modification of interfacial strength has enhanced the fatigue behavior of the composites
Shah et al. (2013)	Flax/UP, Jute/UP, Hemp/UP, GF/UP	Tension–tension	Vacuum infusion technique	Fatigue performance of glass fiber composites found to have excellent performance compared to natural fiber composites
Shahzad (2011)	Hemp/epoxy	Tension–tension	Woven fabric composite laminate	±45° orientation laminates exhibited good fatigue strength than ±90° layups Crack propagation was successfully investigated and reported in their study using infrared camera and micro-CT

(continued)

Table 2 (continued)

Refs.	Biocomposites	Mode of fatigue test	Process method adapted	Remarks
de Vasconcellos et al. (2014)	Flax/elium	Tension–tension	Liquid Infusion method ASTM D3479	The biocomposites found to have better fatigue performance in unidirectional configurations
Haggui et al. (2019)	Kenaf/GF/polyester	Uniaxial tension–tension test	Woven composite laminate	Kenaf/GF hybrid composites showed better fatigue strength than individual composites. On constant stress the composites has lowered stiffness due to surface heat generation
Sharba et al. (2016a)	Kenaf/GF/polyester	Tension–compression	Sandwich composites	Fibre orientation strongly affects the fatigue strength of the hybrid biocomposites. The study reported that, the unidirectional kenaf fibers had higher fatigue degradation
Sharba et al. (2016b)	Flax/epoxy	Tension–tension	Resin transfer molding (RTM)	The better alignment of fibers found to have significant effect on the fatigue behavior of the composites

UP—Unsaturated polyester, GF—glass fibre

4 Classification of Environmental Aging on Bio-composites

The environmental aging of polymers is classified into physical and chemical aging processes (Bensadoun et al. 2016; Moritzer et al. 2019). The physical aging is nothing but change in the molecular state of order occurs due to temperature and humidity, whereas the chemical aging process involves the alteration of molecular structure or molecular size, which includes molecular chain scission, oxidation, reduction and hydrolysis (Ehrenstein and Pongratz 2007).

4.1 Physical Aging

The physical aging processes occurs due to physical factors namely heat, light radiation, and high energy radiation. For example, the physical aging occur a result of absorption of medium, especially in fiber reinforced composite. The temperature and humidity breaks up the fiber-matrix interface and deteriorates the properties as a result of change in the molecular state of order (or) changes in crystalline structure.

4.2 Chemical Aging

The chemical aging process involves specific chemical reaction of the polymer/composites with the fluid such as acids, alkalis, salts and oxygen. The common mode of failure of composites of chemical aging is hydrolysis by water, acids and alkalis. The composite surfaces are interacting with surfactants or detergents in nature; it has led to environmental stress cracking. It was one type of failure observed in composite materials and chemical ageing is also irreversible in nature.

5 Fatigue Life of Bio-composites Upon Different Stresses

Last few decades, the composites are performing their unique role in technological world. During their service application the composites might be subjected to different dynamic and static stresses such as Corrosive stresses, Mechanical stresses, Electric Stress, Thermal stress, Photo stress etc.

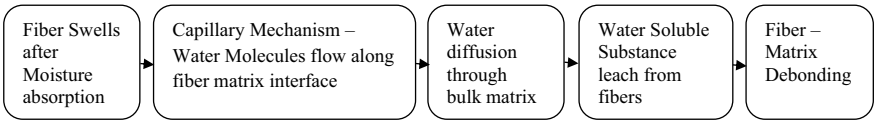


Fig. 5 Schematic representation of natural fibre based biocomposite interface mechanisms

5.1 Corrosive Stress

Corrosive stress can also be termed as Environmental stress cracking (ESC) is one of the key cause of failure in polymers. Understanding the phenomenon of failure is complex, as various aspects such as liquid diffusion, chemical compatibility, craze formation and crack development are playing vital roles. The corrosion or crazing always occurs on the composite surface with their presence of chemical reactant; and it needs adequate activation energy to form the corrosion. Under acidic medium, the cracking occurs very rapidly and may result in catastrophic failure.

Biocomposites, generally suffer from environmental conditions such as moisture and humidity due to the presence of hydroxyl groups. The bio-composites absorbs moisture under humid environments, which causes cyclic swelling stress on to the composites and result in reduction of mechanical performance as described in Fig. 5 (Requile et al.; Pandian et al. 2014). The rate of diffusion of water molecules into composites depends on various factors such as measure of fibre content, fiber orientation, immersion temperature, and surface area exposed to water (Masoodi and Pillai 2012).

The general Eq. (3) given below to calculate the water absorption percentage of the biocomposites (Farah et al. 2016)

$$\text{Water absorption}(\%) = \mathrm{W}_1 - \mathrm{W}_0/\mathrm{W}_0 \times 100\% \tag{3}$$

Based on the rate of diffusion, the deterioration in mechanical properties occurs, which in turn results in reduction of service life of composites. Fotouh et al. experimentally investigated the fatigue behavior of hemp fiber/HDPE composites under wet and dry condition; his results stated that after moisture absorption, fatigue strength was lower on both unreinforced polymer matrix and the hemp/HDPE composites. The reduction in fatigue strength was associated to the hydrophilic form of the natural fibers which resulted in a reduction of interfacial strength between the fibers and the matrix (Ramakrishnan et al. 2019).

5.2 Mechanical Stress

Mechanical aging of composites occurs when it is subjected to constant dynamic and static loads. Commonly, physical changes in color are observed as an effect of

material aging. Furthermore, the brittleness after aging occurs due to chains scissioing and crosslinking, thereby the rise of the mechanical modulus occurs. One of the constant mechanical stresses is creep, i.e. the "plastic deformation of a material over specified duration. The effect of creep on composites does not solely depend only on amount of stress or duration but also greatly depend on the type of composition (Fotouh et al. 2014).

Asim et al. determined the fatigue characteristics on hemp/glass fibers biocomposites. The impact strength and the fatigue characteristics were determined for the development of the biocomposites (Batra 2009). The author revealed that the composites flexural strength is inversely proportional to the applied fatigue stress (Ramakrishnan et al. 1989). When compare to the short fibers/discontinuous fibers, the long fibers significantly increase the fatigue strength with higher fraction of load (Goel et al. 2007). Ranganathan et al. study also stated that the fatigue performance of composites are affected by the toughness; impact modified thermoplastic composites have good fatigue resistance when compared to the unmodified one (Ranganathan et al. 2016).

5.3 Electric Stress

Electrical stresses occur only in electrically operated components; this type of aging depends on the electric field, voltage and the duration of exposure. The development of 20 microns ultrathin nanocellulose diaphragm has the advantage of generating sound velocity same as like aluminum/titanium diaphragm (Kalia et al. 2011). In day-today life, the cellulose has received much importance in electronic sector, majorly for displaying the information. Researchers have also showed more attention to find dynamic display technology (electronic paper). In such electrical/electronic devices the electrical stress developed plays an imperative task in determining the life of the composites (Shah and Brown 2005).

Few researchers reported the fatigue behavior of polymeric biocomposites under electric stress, Pietro et al., analysed the effect of graphene nanoplatelets (GNPs) in polyhydroxyalkanoate (PHA) biopolyester. His study reported that GNPs increased the thermal conductivity; it means that the electrical conductivity of the biocomposites is based on the thermal activation energy (Cataldi et al. 2020). Kreit et al., study stated that Vinyl resin/ Microcrystallince cellulose composites had pronounced thermal activation at the temperature above the glass transition point (Kreit et al. 2019).

5.4 Photo and High-Energy Radiation Stress

The fatigue durability of natural fiber reinforced composites is largely affected by weathering condition mainly UV radiation (Chang et al. 2020). The energy of UV

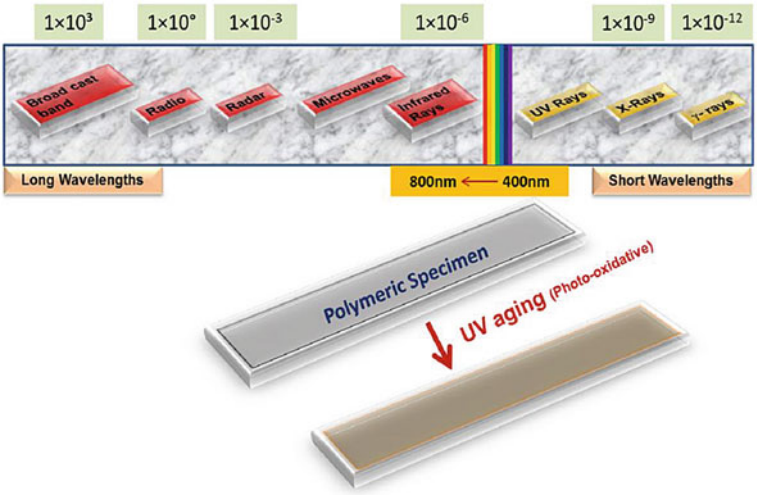


Fig. 6 Wavelength of irradiation waves and UV aging of polymer biocomposites

irradiation can resulted in drastic changes in the physical and chemical properties, and therefore the selection of materials is very important (Mehta et al. 2006; Matuana et al. 2001). UV aging is predominantly caused by solar radiation and, less frequently, by artificially produced UV light. In composites UV irradiation can cause surface discoloration and induce aging at the molecular level, based on the reactions they are termed as photolysis, photo-oxidation and photo-catalysis. Photo-aging declines the mechanical performance of composites due to the chain scission of the material after prolonged exposure to radiation. In such cases, UV stabilizers are often added during manufacturing to enhance the service life of composites. The wavelength of UV irradiation and photo oxidative aging on polymer biocomposites are described in Fig. 6.

Mingwei et al., studied the performance of UV light aging on fatigue properties of asphalt, the penetration and ductility of the asphalt became very poor after suffering the ultraviolet aging. Due to the hardening of asphalt, the fatigue life span of asphalt decreased caused extremely due to ultraviolet light aging (Yi et al. 2014). The effect of photo stabilized HDPE/wood flour composites were investigated by Stark and Matuana (2003) by exposing the composites to 2000 h. The author observed that the flexural strength remained same with photo stabilized HDPE/wood composites whereas found dropped with neat HDPE after 2000 h of weathering exposure. The mechanical properties are determined by retention rate after photo-aging has related using the Eq. (4). After weathering exposure, the retention rate of biocomposites in real life applications should not be lower than 50%.

$$\text{Retention rate} = \frac{\text{SV after aging}}{\text{SV before aging}} \times 100\% \tag{4}$$

where,

SV—Strength Value (strength of tensile/flexural/impact test).

5.5 Thermal Stress

The thermal durability studies were performed in a controlled climatic chamber by varying the heating–cooling cycles. After subjecting the composites to such environmental conditions, they experience deterioration in mechanical performance due to chain scissioning, reduction in molecular weight, embrittlement etc. (Chang et al. 2020). The type of resin, fiber and its content compete the affect of fatigue performance of composites. Miyano et al. analyzed the strong connection between time and temperature in composite fatigue performance to frame a sped up testing methodology (Miyano et al. 2008). Thermal aging affects the arrangement of molecular chains, filler–matrix interfacial adhesion, activation energy, degree of crystallinity, and enthalpic relaxation. Gassan and Bledzki (2001) study also revealed that the conditioning of natural fibers to higher temperature for a specific period of time has slight influence in their tenacity. Chan et al., investigated the long-term indoor stability of nucleating agent (talc and boron nitride) incorporated pine wood flour and PHBV biocomposites. Their study found that the interfaces between the wood flour/PHBV bio-composites were reduced after a period of one year, due to its aging under environmental condition. It also lead to secondary crystallization and stress localization of wood talc. The stiffness enhancement with the presence of talc in the wood flour/PHBV biocomposites was offset after one year of indoor aging (Chan et al. 2018).

6 Conclusions

Biocomposites are most prominently used for biodegradable and lightweight purposes which disburse for many structural applications. To determine the long term degradation behavior and service lifetime of polymer composites under weathering exposure of different environmental conditions is very crucial. In this chapter reviewed and reported the effect of fatigue behavior of natural fiber reinforced biocomposites under different environmental stresses. The various methods involved in determining the fatigue properties of the natural fiber biocomposites were discussed in detail. In addition, the major groups of bio-composites and its environmental aging mechanisms were classified and shown. Furthermore, the chapter highlighted different stresses that composites are subjected during its service application namely corrosive stresses, mechanical stresses, electric stress, thermal stress, photo stress, UV stress, etc. were discussed.

References

Apicella A, Migliaresi C, Nicolais L, Iaccarino L, Roccotelli S (1983) The water ageing of unsaturated polyester-based composites: influence of resin chemical structure. Composites 14(4):387–392

Batra S (2009) Creep rupture and life prediction of polymer composites

Bazli M, Ashrafi H, Jafari A, Zhao XL, Gholipour H, Oskouei AV (2019) Effect of thickness and reinforcement configuration on flexural and impact behaviour of GFRP laminates after exposure to elevated temperatures. Compos B Eng 157:76–99

Beg MDH, Pickering KL (2008) Reprocessing of wood fibre reinforced polypropylene composites. Part I: effects on physical and mechanical properties. Compos Part A Appl Sci Manuf 39(7):1091–1100

Bensadoun F, Vallons KAM, Lessard LB, Verpoest I, Van Vuure AW (2016) Fatigue behaviour assessment of flax–epoxy composites. Compos A Appl Sci Manuf 82:253–266

Brebu M (2020) Environmental degradation of plastic composites with natural fillers—a review. Polymers 12(1):166

Burhan I, Kim HS (2018) SN curve models for composite materials characterisation: an evaluative review. J Compos Sci 2(3):38

Cataldi P, Steiner P, Raine T, Lin K, Kocabas C, Young RJ, et al (2020) Multifunctional biocomposites based on polyhydroxyalkanoate and graphene/carbon-nanofiber hybrids for electrical and thermal applications. Preprint at arXiv:2005.08525

Chan CM, Vandi LJ, Pratt S, Halley P, Richardson D, Werker A, Laycock B (2018) Mechanical properties of poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/wood flour composites: effect of interface modifiers. J Appl Polym Sci 135(43):46828

Chang BP, Mohanty AK, Misra M (2020) Studies on durability of sustainable biobased composites: a review. RSC Adv 10(31):17955–17999

de Vasconcellos DS, Touchard F, Chocinski-Arnault L (2014) Tension–tension fatigue behaviour of woven hemp fibre reinforced epoxy composite: a multi-instrumented damage analysis. Int J Fatigue 59:159–169

Degrieck J, Van Paepegem W (2001) Fatigue damage modeling of fibre-reinforced composite materials. Appl Mech Rev 54(4):279–300

Dhaliwal JS (2019) Natural fibers: applications. In: Generation, development and modifications of natural fibers. IntechOpen

Ehrenstein GW, Pongratz S (2007) Beständigkeit von Kunststoffen. Hanser, München

Evans WJ, Isaac DH, Saib KS (1996) The effect of short carbon fibre reinforcement on fatigue crack growth in PEEK. Compos A Appl Sci Manuf 27(7):547–554

Farah S, Anderson DG, Langer R (2016) Physical and mechanical properties of PLA, and their functions in widespread applications—a comprehensive review. Adv Drug Deliv Rev 107:367–392

Fotouh A, Wolodko JD, Lipsett MG (2014) Fatigue of natural fiber thermoplastic composites. Compos B Eng 62:175–182

Gassan J, Bledzki AK (2001) Thermal degradation of flax and jute fibers. J Appl Polym Sci 82(6):1417–1422

GhaffarianHoseini A, Dahlan ND, Berardi U, GhaffarianHoseini A, Makaremi N, GhaffarianHoseini M (2013) Sustainable energy performances of green buildings: a review of current theories, implementations and challenges. Renew Sustain Energy Rev 25:1–17

Goel A, Chawla KK, Vaidya UK, Chawla N (2007) Fatigue behavior of long fiber reinforced thermoplastic (LFT) composites. In: SAMPE'07: M and P-from coast to coast and around the world

Gurunathan T, Mohanty S, Nayak SK (2015) A review of the recent developments in biocomposites based on natural fibres and their application perspectives. Compos A Appl Sci Manuf 77:1–25

Haggui M, El Mahi A, Jendli Z, Akrout A, Haddar M (2019) Static and fatigue characterization of flax fiber reinforced thermoplastic composites by acoustic emission. Appl Acoust 147:100–110

Hassan T, Jamshaid H, Mishra R, Khan MQ, Petru M, Novak J, Hromasova M (2020) Acoustic, mechanical and thermal properties of green composites reinforced with natural fibers waste. Polymers 12(3):654

Huda MS, Drzal LT, Ray D, Mohanty AK, Mishra M (2008) Natural-fiber composites in the automotive sector. In: Properties and performance of natural-fibre composites. Woodhead Publishing, pp 221–268

Hwang W, Han KS (1986) Fatigue of composites—fatigue modulus concept and life prediction. J Compos Mater 20:154–165

Kalia S, Dufresne A, Cherian BM, Kaith BS, Avérous L, Njuguna J, Nassiopoulos E (2011) Cellulose-based bio-and nanocomposites: a review. Int J Polym Sci

Katogi H, Shimamura Y, Tohgo K, Fujii T (2012) Fatigue behavior of unidirectional jute spun yarn reinforced PLA. Adv Compos Mater 21(1):1–10

Koronis G, Silva A, Fontul M (2013) Green composites: a review of adequate materials for automotive applications. Compos B Eng 44(1):120–127

Kozlowski R, Wladyka-Przybylak M (2004) Uses of natural fiber reinforced plastics. In: Natural fibers, plastics and composites. Springer, Boston, MA, pp 249–274

Kreit L, Bouknaitir I, Zyane A, Hasnaoui ME, Achour ME, Costa LC, Belfkira A (2019) Electrical conductivity and dielectric relaxation studies of biocomposites based on green microcrystalline cellulose-reinforced vinyl resin matrix. J Compos Mater 53(20):2801–2808

Liber-Knéc A, Kúzniar P, Kuciel S (2015) J Polym Environ 23:400–406

Liu T, Liu X, Feng P (2020) A comprehensive review on mechanical properties of pultruded FRP composites subjected to long-term environmental effects. Compos Part B Eng 107958

Mahato KK, Shukla MJ, Kumar DS, Ray BC (2014) In-service performance of fiber reinforced polymer composite in different environmental conditions: a review

Mallick PK (ed) (1997) Composites engineering handbook. CRC Press

Manjunatha CM, Taylor AC, Kinloch AJ, Sprenger S (2010) The tensile fatigue behaviour of a silica nanoparticle-modified glass fibre reinforced epoxy composite. Compos Sci Technol 70(1):193–199

Masoodi R, Pillai KM (2012) A study on moisture absorption and swelling in bio-based jute-epoxy composites. J Reinf Plast Compos 31(5):285–294

Matuana LM, Kamdem DP, Zhang J (2001) Photoaging and stabilization of rigid PVC/wood-fiber composites. J Appl Polym Sci 80(11):1943–1950

Mehta G, Mohanty AK, Drzal LT, Kamdem DP, Misra M (2006) Effect of accelerated weathering on biocomposites processed by SMC and compression molding. J Polym Environ 14(4):359–368

Miller SA (2018) Natural fiber textile reinforced bio-based composites: mechanical properties, creep, and environmental impacts. J Clean Prod 198:612–623

Mitra BC (2014) Environment friendly composite materials: biocomposites and green composites. Def Sci J 64(3):244

Miyano Y, Nakada M, Cai H (2008) Formulation of long-term creep and fatigue strengths of polymer composites based on accelerated testing methodology. J Compos Mater 42(18):1897–1919

Mohammed L, Ansari MN, Pua G, Jawaid M, Islam MS (2015) A review on natural fiber reinforced polymer composite and its applications. Int J Polym Sci

Mohanty AK, Misra M, Drzal LT (2001) Surface modifications of natural fibers and performance of the resulting biocomposites: an overview. Compos Interfaces 8(5):313–343

Mohanty AK, Misra M, Drzal LT (2002) Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. J Polym Environ 10(1–2):19–26

Mohanty AK, Vivekanandhan S, Pin JM, Misra M (2018) Composites from renewable and sustainable resources: challenges and innovations. Science 362(6414):536–542

Moritzer E, Hüttner M, Wächter J (2019) The influence of environmental aging on the material properties of back-molded composite sheets. In: AIP conference proceedings, vol 2065, no. 1. AIP Publishing LLC, p 030024

Moudood A, Rahman A, Khanlou HM, Hall W, Öchsner A, Francucci G (2019) Environmental effects on the durability and the mechanical performance of flax fiber/bio-epoxy composites. Compos B Eng 171:284–293

Movahedi-Rad AV, Keller T, Vassilopoulos AP (2018) Fatigue damage in angle-ply GFRP laminates under tension-tension fatigue. Int J Fatigue 109:60–69

Movahedi-Rad AV, Keller T, Vassilopoulos AP (2019) Stress ratio effect on tension-tension fatigue behavior of angle-ply GFRP laminates. Int J Fatigue 126:103–111

Nakamura T, Singh RP, Vaddadi P (2006) Effects of environmental degradation on flexural failure strength of fiber reinforced composites. Exp Mech 46(2):257–268

Netravali AN, Chabba S (2003) Composites Get Greener. Mater Today 4(6):22–29

Pandian A, Vairavan M, Jebbas Thangaiah WJ, Uthayakumar M (2014) Effect of moisture absorption behavior on mechanical properties of basalt fibre reinforced polymer matrix composites. J Compos

Ramakrishnan V, Wu GY, Hosalli G (1989) Flexural fatigue strength, endurance limit and impact strength of fiber reinforced concretes. Transp Res Rec 1226:17–24

Ramakrishnan S, Krishnamurthy K, Rajasekar R, Rajeshkumar G (2019) An experimental study on the effect of nano-clay addition on mechanical and water absorption behaviour of jute fibre reinforced epoxy composites. J Ind Text 49(5):597–620

Ranganathan N, Oksman K, Nayak SK, Sain M (2016) Structure property relation of hybrid biocomposites based on jute, viscose and polypropylene: the effect of the fibre content and the length on the fracture toughness and the fatigue properties. Compos A Appl Sci Manuf 83:169–175

Requile S, Le Duigou A, Bourmaud A, Baley C Moisture induced hygroscopic and mechanical properties of hemp reinforced biocomposite

Ritchie RO (1999) Mechanisms of fatigue-crack propagation in ductile and brittle solids. Int J Fract 100(1):55–83

Sadh PK, Duhan S, Duhan JS (2018) Agro-industrial wastes and their utilization using solid state fermentation: a review. Bioresour Bioprocess 5(1):1

Santecchia E, Hamouda AMS, Musharavati F, Zalnezhad E, Cabibbo M, El Mehtedi M, Spigarelli S (2016) A review on fatigue life prediction methods for metals. Adv Mater Sci Eng

Schijve J (2001) Fatigue crack growth under variable-amplitude loading. Fatigue Struct Mater 274–309

Shah J, Brown RM (2005) Towards electronic paper displays made from microbial cellulose. Appl Microbiol Biotechnol 66(4):352–355

Shah DU, Schubel PJ, Clifford MJ, Licence P (2013) Fatigue life evaluation of aligned plant fibre composites through S-N curves and constant-life diagrams. Compos Sci Technol 74:139–149

Shahzad A (2011) Impact and fatigue properties of hemp–glass fiber hybrid biocomposites. J Reinf Plast Compos 30(16):1389–1398

Sharba MJ, Leman Z, Sultan MT, Ishak MR, Hanim MA (2016a) Partial replacement of glass fiber by woven kenaf in hybrid composites and its effect on monotonic and fatigue properties. BioResources 11(1):2665–2683

Sharba MJ, Leman Z, Sultan MT, Ishak MR, Hanim MAA (2016b) Effects of kenaf fiber orientation on mechanical properties and fatigue life of glass/kenaf hybrid composites. BioResources 11(1):1448–1465

Shesan OJ, Stephen AC, Chioma AG, Neerish R, Rotimi SE (2019) Improving the mechanical properties of natural fiber composites for structural and biomedical applications. In: Renewable and sustainable composites. IntechOpen

Stark NM, Matuana LM (2003) Ultraviolet weathering of photostabilized wood-flour-filled high-density polyethylene composites. J Appl Polym Sci 90(10):2609–2617

Tang X, Yan X (2017) Acoustic energy absorption properties of fibrous materials: a review. Compos A Appl Sci Manuf 101:360–380

Thwe MM, Liao K (2003) Compos Sci Technol 63:375–387

Wicaksono S, Chai GB (2013) A review of advances in fatigue and life prediction of fiber-reinforced composites. Proc Inst Mech Eng Part l J Mater Des Appl 227(3):179–195

Yates MR, Barlow CY (2013) Life cycle assessments of biodegradable, commercial biopolymers—a critical review. Resour Conserv Recycl 78:54–66
Yi MW, Wang JC, Feng XD (2014) Effect of ultraviolet light aging on fatigue properties of asphalt. In: Key engineering materials, vol 599. Trans Tech Publications Ltd., pp 125–129
Zhou S, Wu X (2019) Fatigue life prediction of composite laminates by fatigue master curves. J Mater Res Technol 8(6):6094–6105

Effect of Moisture Absorption on Interfacial Shear Properties of the Bio-Composites

Dheeraj Kumar, Ranjan Kumar Mitra, Trilok Chouhan, Md Farrukh, and Nadeem Faisal

Abstract Composites are having a massive and extraordinary impact on modern society. Composite manufacturing has witnessed a considerable growth in several areas, including aerospace, structural, and vehicle manufacture. Fibre reinforced polymer composites have become popular throughout the last decade. More recently, researchers have begun paying attention to natural fibre reinforced polymer composites and bio-composites, which are both sustainable and mechanical comparable to synthetics. Also is not only vital in sectors like aircraft and autos, but it becomes critical in civil and structural sectors. This chapter might be useful when it comes to discussing the moisture absorption parameter and qualities for bio-composites. bamboo-based, flax-based, and others bio composites are examined in this chapter. The chapter also describes the impact of moisture content on bio-composites, parameters influencing the effectiveness of moisture absorption treatments used for natural composites, treatment of composites of natural origin, water absorption behaviour, and its effect on mechanical properties of natural fibre reinforced composites. Also, the chapter highlights the environmental impact on the durability and mechanical performance of bio-composites.

Keywords Moisture absorption · Bamboo · Flax · Acetylation · Benzoylation · Alkalization · Bamboo-vinyl ester

D. Kumar · R. K. Mitra
National Institute of Technology, Durgapur, India

T. Chouhan
ITM University, Gwalior, India

M. Farrukh
Netaji Subhas Institute of Technology, Patna, India

N. Faisal (✉)
Central Institute of Petrochemicals Engineering and Technology, Balasore, India

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_13

1 Introduction

The eras of human civilization are indicated by referring to the stages of developing materials under the titles like stone age, bronze, iron, steel, silicon and the silica age. In this direction, current growth of humankind can be referred to as 'composites age'. The ancient Egyptian introduced the most primitive composite materials, namely, straw with mud in brick-making for building walls which are still seen in tomb paintings in the metropolitan museum of art. Also, our roadways are made of either steel-reinforced Portland cement aggregates or asphalt concrete (Evans 1992; Mallick 2007). The fibreglass reinforced composite makes our shower-stand and bath tubs that are closer to our personal hygiene. Also, to improve our domestic living experience imitation granites and cultured marble sinks are widely used. The use of fibre reinforced polymer composites (FRPCs) had seen a constant growth in the aerospace industry from 1969, at that time the F-14 horizontal stabilizers components had boron fibre-reinforced epoxy skins. In the 1970s, carbon fibre reinforced epoxy was used as the primary material components. During 1982, the fighter aircraft with carbon fibre and epoxy composite achieved 25% by weight. Airbus, the first commercial aircraft manufacturer, introduced A310 aircraft in 1987 which had composite components that weighed about 10% of aircraft's total weight. Also, recently, Mercedes-Benz Travego used composites for the engine and transmission exterior components, 20% weight saving was achieved with flax/sisal thermo-set door panels (Mohanty et al. 2005).

Natural fibre reinforced polymer composites (NFRPCs) have witnessed a tremendous growth in the automotive industry since last 25 years as NFRPCs are used to manufacture the automobiles components in light trucks, and heavy trucks. On using NFRPC instead of steel in these components, significant benefits of weight reduction with low tooling cost and more parts integration are achieved. NFRPCs are used in the electronic industry to prepare printed circuit boards, in the power industry for making transformer housing, in the medical field to prepare bone plates for fracture fixation/ implants, in the oil industry to make oil sucker rods for lifting underground oil. It also finds use in many industrial products, like oxygen tanks, step ladders, and transmission shafts (Stevens 2002). Putting NFRPC to actual use requires skilled design practice and suitable process development after gaining little knowledge on their unique mechanical, physical, and thermal characteristics. In 1992 at Aberfeldy, Scotland the first composites bridge for a pedestrian was installed. In 1996, the U.S constructed the first FRP concrete bridge decks at McKinleyville (Robert 2002). These were composite materials consisting of natural fibres of high strength reinforced to a polymer matrix. Both fibre and matrix retain both their physical and chemical identities in order to produce combinational properties that the individual acting constituents cannot achieve. Here, the primary load-carrying members are the natural fibres, while the matrix holds them in the desired position and orientation. Matrix also prevents fibres from damage to the atmosphere when exposed to high temperatures and humidity. Bio-composites are composite materials with natural fibres as reinforcements & petroleum-derived non-biodegradable polymers

like polypropylene, polyester, and epoxies or biopolymers like polylactic acid as matrix. This category also includes composite materials which are derived from biopolymer as matrix & synthetic fibres such as glass/carbon as matrix.

Bio composites are likely more eco-friendly and sometimes termed "green composites". Ecological quality of NFRPCs motivates the researcher to investigate on these cost-effective composites. The natural fibres are available plenty and the ease of manufacture as composites makes researchers focus on these inexpensive fibres to study their feasibility for reinforcement in polymer composite with numerous applications (Nickel and Riedel 2003). Polymer composites usually exist with synthetic fibre and thermoset matrices, that limits the environmental benefits. It can be prepared as bio composite when reinforced with natural fibres instead of synthetic fibres. The stiffness and strength lack of bio composites makes the material less usable for high strength application. The better arrangement in placing the fibres at specific locations and suitable configuration can tackle these problems. There are many natural fibres in India, many of which comes from the forest and farming. Palm fibres belong to such natural fibre resource mainly used for handicrafts and whose capability as reinforcement in composite polymer materials has not been thoroughly explored until now.

Naturally-available palm fibres form as aggregates with polymer matrix during processing and also their poor resistances to moisture reduce the potential of using natural fibres as reinforcement in the polymer matrix. Fibre pre-treatments can reduce this overall incompatibility, conversion of long fibres into a short one, and reinforcement of fibres in the form of mats. In a study it has been found an increased ultimate strength and Modulus of Elasticity (MOE) using Electron Beam (EB) treatment on polyethylene-based wood plastic composite (Palm et al. 2015). Average ultimate strength increased by 10% results from 250 kgf doses. Xu et al., studied the tensile and in-planar shear properties of 3-dimensional needled textile reinforcement on ceramic matrix composite (3DN CMC) (Xu et al. 2015). Omrani et al. (2016), investigated the tribological behavior of NFRPCs. Result showed improvement in tribological properties, better friction and wear behavior obtained by treated and normal oriented fibres Navas et al., studied the agro-industrial wastes (olive wet husk, grape stalks and olive pits) for reinforcement in polymer matrix composite and found that olive wet husk has high moisture, less volatile and fixed carbon characterized by physicochemical and morphological analysis that favors polar polymer matrix compatibility (Navas et al. 2015). Dhawan et al. (2013) studied the mechanical properties of glass fibre reinforced polymer (GFRP) and found that polyester composite provided better result. The result showed more accuracy by the modification of Euler formula studied by Zhu et al. (2015). Accordingly, the improvement of interfacial shear strength on sisal fibre using polyester composite was investigated by Belaadi et al. (2014). Its length and diameter measurement depends on optical light microscope. The tensile & flexural behavior of sisal fibre reinforced polyester bio composites, are determined by testing machine. Wang et al., investigated the mechanical behavior of bamboo fibre on quasi-static tensile loading. The tensile and the fractured test were obtained using WDW3050 universal testing machine (Wang et al. 2015). Misri et al. (2015) investigated behavior of kenaf fibre reinforced polyester composite and

the result showed the capacity of torsion affected by changing the winding angle. Ihueze et al. (2015) examined the characteristics such as mechanical and physical plantain fibre reinforced polyester (PFRP) composites. ASTM standard for tensile test was followed while modeling was carried out using ANSYS. The result showed transverse arrangement of fibres as not effective. Ikpambese et al. (2016), noted that from palm kernel fibres (PKFs), automatic brake pads can be developed. Elemental composition of PKFs, wear rate as 27.7 m/s, coefficient friction as speed varies from 5.56 to 27.78 m/s and values change from 0.16–0.4, porosity 16% to 32%, hardness 5.6–21 h, moisture effects 1.02–2.4%, noise level 40 dB, temperature 102–735 °C, stopping time 5.56 to 27.78 m/s. Balakrishna et al. (2013) studied the tensile properties of fibre-reinforced composite alkali-treated short and randomly oriented borassus flabellifer (palm fruit) and also carried out a quadratic response surface model using ANOVA technique. The max value of tensile strength obtained was 27 MPa. Zhang et al., (2015) investigated the effect of loading frequency of fatigue behavior on GFRP, which depends on developing phenomenological models for the prediction of fatigue life with various stress ratios and loading frequencies.

Mishra et al. (2019) carried out a detailed study on natural fibres in direction of improving its mechanical strength with polymeric matrix reinforced composite materials. Ferreira et al. (2019) did their comprehensive study on modifications of natural cellulose fibres for various applications. Various surface treatments and biological treatments have been included in the article. Asim et al. (2020) did a thermogravimetric study related to isothermal and non-isothermal processes. Thermal behavior on the natural behaviors have been reviewed and effect on temperature on the adhesive property also be included. Mayandi et al. (2019) performed their study on mechanism of capillary flow at the time of absorption. It has been also included the detailed study of factors influencing the mechanical strength. For increasing the durability & mechanical strength of FRP materials also been disserted in this study. An elaborative study carried out by Verma and Senal (2019) for giving a rise in the automobile sector by improving the mechanical strength to the naturally reinforced fibre composites. Many of the investigators studied the mechanical and tri-biological behavior of graphite fillers addition on date palm fibre reinforced polymer composite. Filler addition obtained high interfacial adhesion of the fibre with matrix. Also, performance of the composites increased on adding 3 wt.% of graphite was investigated by Shalwan and Yousif (2014), Savage and Evans (2014). They studied the mechanical properties of reinforced polyester composites made from hybrid banana/kenaf fibres, which were prepared using hand-lay method. Maximum tensile strength as 110 MPa, flexural strength as 150 MPa and impact strength as 28 kJ/m^2 achieved. Scanning electron microscope as well as the FTIR analysis was performed as confirmatory tests to analyze and study the de-bonding of fibre/matrix adhesion. Guessasma et al. (2015), studied the elastic behavior of hemp fibre/starch biopolymer composite by thermo-molding. Major effects like variation in hemp fibre content, filler content, arrangement was studied both numerically and experimentally. The study concluded that the processing of thermo-molding is not appropriate for fibre volume content anything above 10%.

2 Significant Effect of Moisture Absorption on the Interfacial Strength of Bamboo/vinyl Ester Composites

The absorption of moisture in structural composites is an essential consideration for natural fibres used for the reinforcement. This article reports a thorough analysis of bamboo strips' moisture absorption and their influence on the bamboo/vinyl ester interfacial shear strength (IFSS). The bamboo/vinyl ester composite interface also can be damaged after production due to moisture exposure. The bamboo stripes provide a moisture reservoir that spreads further into the interface area and prevents vinyl ester composite hardening Ray et al. (2005)

Bamboo in its natural state is a one-directional, reinforced composite composed of long parallel cellulose (vascular stacks) fibres embedded in a linear matrix (ground tissues). The density values of bamboo plants vary according to their radial location in the cross-section and their length. The outer skin seems to have a significantly greater fibre density than the inner skin. Often referred to as a functional gradient, Ray et al. (2004). Lo et al. (2008) Bamboo's compressive strength is highly correlated with the section's mean fibre density. Bamboo may be utilised in a variety of ways to support the whole bamboo Ghavami (2005), bamboo Nugroho and Ando (2001) parts, bamboo Jain et al. (1992), and bamboo Das et al. (2006) parts. The purpose of this research was to examine bamboo strips that can be created manually or by bamboo culm splitting.

Numerous research groups have investigated polymer composites reinforced with bamboo strips. Shin et al. Deshpande et al. (2000) discovered that bamboo strip reinforced composites had a greater tensile strength than glass fibre reinforced epoxy composites. The bamboo compound was shown to be more sustainable than the bamboo alone Okubo et al. (2004). Bamboo absorbs moisture due to its composition and structure when exposed to damp environments or submerged in water. Bamboo's mechanical properties may alter dramatically as a result of moisture absorption, depending on the type and diagnosis conditions.

Fibres plant (such as flax, hemp, and sisal) When exposed to dampness, reinforced composites may degrade dramatically. FG Shin et al (1989). Water absorption and interface attack are exacerbated by the fissures. The absorbed water starts to form a molar hydrogen bond with the fibres, lowering the matrix and interface conductivity of the fibres and initiating the draining of water-soluble material.

Numerous fibre technologies have the potential to mitigate the harmful effects of humidity on the natural fibre-resin functioning. The incompatibility of hydrophilic natural fibres with the hydrophobic polymer matrix is the primary reason of the poor interface. Moisture present during manufacture might worsen this issue, resulting in a composite's inability to be processed and a poor surface performance.

The influence of moisture on the interface shear strength was investigated in this research using bamboo strips and vinyl ester resin (IFSS). Due to their enormous size and consistent sectional structure, bamboo strips are ideal for pull-out testing. The purpose of this research was to determine how pre-manufacturing moisture exposure

influences matrix hardening behaviour and to create a relative value for pre- and post-manufacturing moisture exposure.

2.1 The Effect of Moisture Content on the Tensile Properties of Bamboo Slits

Moisture absorption also resulted in a modest improvement in the tensile strength of the bamboo strips. As shown by the constant rise in breaking stress and reduction in elastic modulus, moisture absorption influences a natural sweetener on the bamboo stream.

Bamboo is a hydrophilic substance that absorbs a lot of moisture at typical humidity levels. Bamboo strips exhibit moisture sorption hysteresis comparable to that of other natural fibres such as flax and hemp. When moisture is absorbed, they are also anisotropically enlarged. The efficacy testing was done twice as much as a radial expansion on the bamboo peak circumference. The length growth was insignificant. Humidity absorption changed the bamboo strips, resulting in increased extendibility and degradation in stretchy modules, but no effect on tensile strength.

2.2 Effect of Moisture Content on Bamboo/vinyl Ester Composites

Interfacial shear strength (IFSS) was investigated using the pull-out test. In composites, the relative humidity of the composite specimen had a severe impact on the IFSS. In standard room environments, the IFSS (20 °C, 60% RH) was just one half the dry condition. The interfacial strength of composites produced at a high relative humidity level (80% and 90%) is virtually nil. Exposure to high humidity throughout the storage and carbon fibre manufacturing process can be much more damaging for the finished composite materials' interface strength than after moisture exposure.

3 Influences of Parameters on the Effectiveness of Moisture Absorption Treatments for Natural Composites

Natural composites may be created by reinforcing hydrophilic synthetic fibres with natively generated or bio-based polymers. Natural hydrophilic fibres may be used to reinforce biopolymers due to their high compatibility, resulting in ultimate moisture absorption resistance at the fiber-matrix interface. However, biomaterials' expenses are several times greater than that of their plastic fibres, which impedes their propagation in different industries. Synthetic resins are commonly strengthened with

hydrophilic fibres to produce cost-effective natural composites, which improves compatibility issues such as void creation and moisture absorption at fibre-matrix interfaces Dunne et al. (2017).

In various industries, synthetic fibre composite materials have various applications. Because they are excellent thermal isolators and sound absorbers, they could also be used as humidity level controls for construction by using natural polymer composites and layers in the interior walls' structure. Natural composites' characteristics mainly depend on the reinforcing fibre characteristics and the conductivity between the matrix and even the fibre Putra et al. (2018). Several disadvantages need to be addressed to promote natural composites' introduction in different industries, such as insufficient adhesion between hydrophobic compounds, hosting of the mixture and unprocessed fibres, low non-polar plastic wettability, and high-water levels.

The synthetic fibres are made of cellulose, lignin, pectin, wax, hemicellulose, additives, water-soluble, and chubby. Cellulose is considered to be the primary structural component of the structure with fibre. It provides fibre stiffness, strength, and structural stability.

The significant components of plant fibres that soak up the excess fibre supply are hemicellulose and cellulose, and lignin. About moisture. Lignin provides excellent hemicellulose/cellulose protection against adverse climatic conditions. For temperature and humidity conditions, Kong et al. (2016) two main models can be used to describe the absorption actions of moisture:

(i) Pseudo-Fickian conduct in which, after take-off, the weight gain of water did not reach equilibrium; And (ii) Fickian linear conduct, whereby water weight gains have progressively achieved balance. Following the short time frame take-off. The more excellent absorption of moisture facilitates the microorganism's attack, leading to the microbial attack. A procedure known as biodegradation is involved. It is possible to transport humidity levels inside the composite materials. They are facilitated through various mechanisms, including the evaporation of solutes between micro gaps within the micro gaps. The chains of the polymeric materials in natural composites, the water absorbed is categorized into bound and free water. The bound water is water molecules that are dispersed and bound to the polar groups of water. Polymers, whereas the free water molecules, are capable of transporting independently through splinters and defects. The molecules of water diffuse, whenever the natural composite materials are subjected to humidity into the matrix and attach natural fibres to hydrophilicity, creating an intermolecular hydrogen bonding with the natural fibres at the fibre interface/matrix, mitigates interfacial bonding Malkapuram et al. (2009). The deterioration of the application of organic composites takes place when the cellulose swell. In the interfacial regions, stress is generated, leading to the micro-cracking mechanism in the matrix close to the swollen fibres, which, through micro-cracks, emphasize transport and capillarity. With the Excessive water absorption, while the water content declines, the water molecules increase. Liquid solution materials start to liquefy from the fibre and ultimately lead to the matrix and fibre being ultimately debonded. The mechanism mentioned above of diffusion of molecules of water into the natural concrete materials Elanchezhian et al. (2018).

Moisture absorption results in a three-dimensional growth in the laminated composite. However, the increase in composite thickness is far more than the rise in width. Water intake affects duration and length in two ways: I the swelling of the water fibre itself; and (ii) the change in fibre density caused by the absorbed moisture's weight. Water containing polar and hydroxyl groups is present in natural fibres and is attributable to the intake of natural composites.

Moisture absorption results in hydrolysis (segmentation of the polymer chain) and swelling. Debonding, delamination of laminated composites, and delamination of the physical composition of fibres are all examples of how damage to the polymeric matrix accelerates the mechanical and thermal deterioration of natural materials Célino et al. (2014).

However, the modest swelling of natural fibres is beneficial because it highlights the interfacial adhesion of natural composites between the fibre and matrix and its influence on the mechanical characteristics of natural composites Lau et al. (2018). Water absorption increases the mobility of side and molecule chains, resulting in reversible plasticization of the polymer Fernandes et al. (2016). The matrix plasticization process both strengthens and weakens the fracture. Resistance, stiffness, exhaustion, and the inherent periodicity of the natural composite are all characteristics of the natural composite. When sisal polypropylene (PP) composites are submerged in hot water at 900 °C, tensile polypropylene (PP) composites are submerged in hot water at 90 °C. As the duration spent immersed in water increases, the strength and module decrease, but the impact decreases. At initially, strength rises in direct proportion to immersion time. The behavioural distinction between the fibre strengthening swelling action and plasticization may help to explain the tensile properties.

The matrix's contact with the fibre Kabir et al (2012). The migration of water molecules into some kinds of polymer films may drastically affect the intermolecular interaction. It contributes to increased heat capacity and hence decreases thermal insulation. The water absorption behaviour of natural composites is largely determined by a variety of variables. Chemical and physical treatments of natural fibres, fibre loading, fibre distribution, fibre size shapes and forms, linear mass density of natural yarn, fibre permeability, resin hosting crystallinity, and the hydrophilicity of each composite are all influenced by the fiber-matrix interfaces, the duration of exposure to humid environments, and the manufacturing method. The hydrophilicity of natural surface fibres is reduced by treatments. Natural fibres and significant variations in the surface form.

The amount of moisture absorbed by natural filaments is influenced by the fabric's pattern. Mechanical performance of twill weave materials, for example, is excellent even after absorption. In terms of moisture resistance, the natural reinforcing yarns' reduced linear mass density provides the composite with higher humidity resistance while maintaining excellent mechanical properties throughout the moisture exposure phase. Others include Van de Weyenberg et al. (2006). Moisture absorption is caused by composites, which is governed by the fibre arrangement inside the composite structure. The nonwoven structure of a hemp-fibre-reinforced polylactic acid (PLA) composite, for example, absorbs more moisture than an aligned fibre structure. This is because the intricacy of the matrix flow during the manufacturing

process causes higher porosity Azwa et al. (2013). Bio-based chemical treatments, additives, nanocoating, and coatings may improve the hydrophobicity of natural surface fibres, according to Pan and Zhong (2014). Water molecules may be scattered by 50% when the coating is applied appropriately and the material characteristics of the coating are appropriately selected.

The coating is often only good for short- to medium-term moisture protection Nabi Saheb and Jog (1999). Natural composites with more vacuum absorb more moisture than those that do not. In order to minimise the vacuum content that may form during the manufacturing process, it is necessary to manage the production environment for natural composites in order to maintain a vacuum and low humidity level.

Drying natural fibres is often essential to remove excess moisture. Moisture absorption is inversely proportional to the kind of natural moisture fibre used. For example, in the material production process, flax and hemp fibres absorb less moisture than ramie and cotton fibres Akil et al. (2009). Natural fibres are hybridised with other synthetic or natural fibres that have a low moisture absorption propensity.

A realistic strategy for minimising the moisture absorption of natural composites is deemed sufficient. The ambient HR has a direct effect on the composite's moisture content and accumulation average Lai et al (2012). Additionally, it was shown that when temperatures increased, the diffusion activation, moisture absorption via equilibrium, and water diffusion rate all varied.

However, the literature revealed that in certain circumstances, when water molecules bond to the surface of the fibres, the diffusion coefficient rises with lowering temperatures. The porous fibrous substances aid in the absorption of water. The durability of the material under different weather conditions must be considered as a matter of urgency. The life cycle impacts the design stage during composite conditions (temperature, rain, air, solar, and oxygen radiation) Trache et al. (2016).

The water absorption and swelling behavior of composites based on natural fibres should be studied thoroughly to assess the composite performance.

The swelling coefficient can be calculated using the following equation (Eq. 1):

$$T\% = \frac{T_2 - T_1}{T_2} \times 100\% \tag{1}$$

When the initial and final thicknesses for T_1 and T_2 are used, the water is composite, and acceptance can be measured through the following relationship (Eq. 2):

$$W\% = \frac{W_2 - W_1}{W_1} \times 100\% \tag{2}$$

The process can be explained by the diffusivity or diffusion coefficient that describes water molecular transportation rate within the composite and regulates the required duration. (ii) The moisture level of equilibrium regulates the time necessary to attain the moisture level of equilibrium; The composite affinity to water is

described, and (iii) the transient duration directly affected by the composite thickness Furtado et al. (2018). None of the studies have been examined in the best possible way. This review's critical factors regulate composite materials' efficacy for moisture absorption, enhancing the properties, toxin, and mechanical treatment options Chow et al. (2007).

The study focused on the effects and implementation of these variables' chemical and/or chemical characteristics. Physical therapy can increase or decrease the feasibility of the prognosis used. Therefore, this study contributes significantly to the literature review by outlining the factors affecting the more common natural fibre-based composites' moisture absorption treatments.

4 Treatment of Natural Composites

Non-cellulosic substances comprise natural fibre (lignin, hemicellulose, pectin) surfaces and waxes that prevent the fibre from adequately adhering to the host matrix. It is recommended that natural fibres be manufactured to increase the natural fibres' hydrophobicity to composite materials with enhanced mechanical, tribological, and moisture absorption characteristics. This can be achieved by introducing natural fibre surface physical contaminant and chemical treatment Alkbir et al. (2016).

The physical and chemical treatment of natural fibres removes hydrophilic elements from the surface of the fibre. Thus, lignin content increases, and the fibre hygroscopic behavior is likely to decrease substantially Alomayri et al. (2014). Different therapy types' effects to increase the composite materials' water absorption behavior for various types with natural composites can be improved. Certain types of therapies can harm the development of specific composites (jute fibre/UP and kenaf fibre/starch), which are treated respectively for water uptake using hot water and alkalization technology.

This reduction can be linked directly to removing the structure of the treated fibre of hydrophobic components such as lignin, which causes the microstructure to absorb a compound. A higher amount of moisture, depending on its capacity to alter the chemical structure and composition of natural composites, is classified as physical and chemical treatments for moisture absorption. Physical and chemical therapies are widely used to improve various natural composite materials for humidity absorption Dhakal et al. (2007).

4.1 Acetylation

The use of acetic anhydride treatment to several kinds of natural fibres has been shown to boost the moisture resistance of natural composites. This enhancement is related to the elimination of lignin and hemicellulose components from the treated fibres.

4.2 Benzoylation

The fibres are first treated with an alkaline solution containing a particular quantity of sodium hydroxide, followed by treatment with benzoyl chloride.

4.3 Peroxide Treatment

Peroxide treatment entails grafting PE on the surface of natural fibres. Peroxide treatment procedures include pre-treatment of the fibres with alkali.

4.4 Isocyanate Treatment

The chemical link formed by isocyanate creates a strong covalent binding between the matrix (particularly thermoplastic matrixes) and the fibre. Additionally, moisture on the surface of the fibre combines with isocyanate to generate urea, which combines more readily with the cellulose hydroxyl groups.

4.5 Acidic Treatments

Various acids may be employed in this procedure to further enhance the hydrophilicity of synthetic materials such as stearic, hydrochloric, and acrylic acids.

4.6 Alkalization

This is the most viable way for efficiently emphasising the interfacial adhesion between the fibre and matrix, resulting in a considerable increase in the treated composite's water uptake capabilities.

4.7 Treatments for Physical Use

Natural fibre's chemical composition is not altered by physical techniques such as hybrid yarn manufacturing, calendarization, thermal treatment, and stretching. Physical treatments alter the fibre's surface and structural properties and influence the mechanical bonding with the fibre matrix for hosting.

5 Water Absorption Behavior of Natural Fibre Reinforced Composites and Its Effect on Mechanical Properties

The test for the absorption of moisture is maintained following either ASTM D570 or BS EN ISO 62:1999. The specimens are dried at 50 °C in the oven Shen and Springer (1976) cooled in desiccators leading up to immersion in water and immediately weighed. This method is repeated until a constant value is measured. The specimen's mass obtains it. Water absorption is expressed as increasing weight as in terms of percentage (Eq. 13.3).

$$\text{Percentwaterabsorption} = \left[\frac{\text{Wetweight} - \text{Dryweight}}{\text{Dryweight}}\right] \times 100 \quad (13.3)$$

Water absorption promotes fibre swelling, void formation, and microcracks at the fiber-matrix interface. All of these variables contribute to the deterioration of composites' mechanical characteristics and dimensional stability. The effect of water absorption on reinforced geopolymer composites of cotton fabric (CF) was investigated, and it was observed that the composites' flexural strength reduced as a result of the water absorption significantly from 4.51, 6.24, and 8.32 wt% of CF, to decrease substantially from 15.87, 19.78 and 28.13 MPa to 9.39, 13.47 and 21.45 MPa. It has also been established that the hardness of all samples, the composites declined in wet conditions.

The water content and the free water stay in this instance, when water absorption attains saturation level, as a storage tank in the composite. As a result, the fibres become softer and weaker. Mechanical characteristics are degraded as a result of fibre matrix adherence. According to a study on JF/CF-HDPE (Jute fibre (JF) reinforced condition that may yield high-density polyethylene), the tensile modulus of wet 10/90, 20/80, and 30/70 (% fibre/% matrix) composites decreased by 5% fiber/% matrix. Tensile strength decreased by 5.1%, 6.3%, and 9.5%, respectively, compared to 5.3%, 6.5%, and 9.7%, and tensile strength decreased by 8.5% and 22%. At two different temperatures, 25.7 °C, and 50.5 °C, respectively, kenaf fibres' water absorption behavior has been investigated in reinforced polyester resins Muñoz and García-Manrique (2015).

The bending strength was 69.67 MPa and 4.24 GPa, respectively, and a dry composite modulus of 20.70% fibre wt. The flexural strength for exposure to water immersion was reduced to 25.17 MPa at 25 °C and 50.7 °C to 16.48 MPa. At 25.3 °C and with 1.69 GPa and 1.16 GPa, the flexural modulus also followed the same trend at 50.7 °C, respectively. Due to the increased water movement with increasing ambient temperature, the moisture uptake of the composites increases.

Another study Liu et al. (2012) on hemp-reinforced unsaturated polyester composites showed that for five-layer hemp, the %age of weight gain (0.28 volume fraction fibre) reinforced composites are approximately 24% higher than at room temperature at the moisture saturation point at boiling temperature. In this study, moisture uptake results demonstrate Fickian's behavior at room temperature and not Fickian's

at boiling temperature. This is due to the humid environment, high temperatures, and the micro-cracks created on the surface.

Because of the degradation of the interface of the fibre-matrix, the exposure of natural fibres. A significant decrease in mechanical properties results from fibre-reinforced moisture composites. Treatment of chemical fibres, skin protection, use of nanofillers, and use of nanofillers. It has been shown that the use of coupling agents reduces water absorption, thereby working to improve mechanical characteristics.

6 Investigating the Effect of Interfacial Interactions on the Characteristics of Polymer Nanocomposites

Due to the fact that the matrix's superior reinforcing wettability is crucial for achieving excellent filler-matrix adhesion, the wettability of the filler must be evaluated. Wettability is determined using the contact-angle and surface-tension procedures. The contact angle concept postulated that the contact angle of a liquid drop on a flat surface was determined by the mechanical balance of three surface stresses. This concept is important because the angle of the equilibrium state of the liquid drop reflects the liquid's ability to moisten and spread over a flat surface. A contact angle less than 90° is considered acceptable wettability, whereas a contact angle more than 90° is considered undesirable wettability (o).

A contact angle greater than 90° also results in decreased wettability and dispersion. This implies that a lower angle indicates higher wettability, whilst a larger angle indicates maximal wettability. Touch angle measurements for PNCs have been acquired at both the microscopic and macroscopic levels. While wettability measures are suggested as a methodology for determining interfacial adherence, we also identify substantially varied results for a given content. As a result, researchers have expanded their analysis of wettability by using surface stress assessment.

Recent years have seen the development of novel interfacial substrates with exceptional wettability. They have sparked considerable attention in material science. Panacea may be used to describe the extraordinary surface behaviours and interfaces of materials developed through biomimetic processes as a consequence of repetitive environmental stressors. Interfacial substrates with exceptional wettability have been used in a variety of applications, including natural adhesion relief, anti-fogging glass, atmospheric corrosion protection, water collecting, oil/water separation processes, chemical resistance, self-cleaning textiles, and anti-icing.

Additionally, to these applications, they facilitate scientific discovery and technological improvements, such as the development of novel materials with greater wettability. For instance, these materials have enabled the development of intelligent microfluidic devices with unprecedented nanoparticle prototype frictional control, which facilitates the patterning and accuracy of liquid reprography. Interfacial processes such as cell separation, adsorption, biological fouling, corrosion,

interfacial transformation, and catalytic surface reactions are critical in a variety of ecological processes Kota et al. (2012).

Given that wettability is one of the most critical surface attributes, the ability to optimise surface wetting will open up enormous prospects for innovation and enhancement of environmental systems that are governed or highly impacted by interfacial phenomena Zhai et al (2006).

7 Effects of the Environment on the Durability and Mechanical Properties of Flax Fibre/bio Epoxy Composites

To improve the usage of bio composite materials in diverse engineering applications, a thorough knowledge of their service efficiency is required. The material qualities of biomass composites may be influenced by severe environmental circumstances, as such as warm, moist, and cold settings, when subjected to poor climatic circumstances. Furthermore, the usage of these composites in underwater applications might reduce their life cycle. This experiment evaluated the durability and mechanical properties of flax/bio-epoxy composites (wines and flexure). Various circumstances were selected to mimic variables that may impact the toughness of these materials in the real world: water, heat, water, and freezing temperatures.

The temperature, humidity and consistency of the fibres used for the composites influence bio-composites' moisture content and their moisture behaviour. The molecules of water are distributed within the composites through the diffusion of humidity within the matrix. In general, like Fickian, pseudo-Fickian and non-Fichian, the diffusion behavior differs from polymer composites. According to Assarar et al. (2011), Fickian absorbed water at ambient temperature and 13.5% moisture in flax fibre water. Numerous research Dhakal et al. (2007) have shown that three primary processes aid in water circulation. Second, diffusion occurs between the micro gaps and pores as a result of matrix defects such as cracks, pores, and water molecules. The capillary movement of water molecules and the fibre-matrix contact are responsible for water diffusion.

Finally, the microcracks are transported into the matrix by the expansion of the fibres. Numerous studies have been conducted on the ability of natural fibre composites to absorb moisture. For example, when compared to jute fibre composites, flax fibre composites absorbed more moisture (MC) than jute fibre composites. At room temperature, after 40 days of water immersion, saturated flax had a moisture content of 9.61% while jute organic composites had a moisture content of 14.41% Berges et al (2016).

They are critical for the durability of natural fibre-reinforced composites used in relevant technical applications. In practical applications, flax fibre reinforced composites may be exposed to a variety of severe environments, including humidity, simple solutions, acids, alkalis, temperature, thermal cycling, freezing, and ultraviolet

radiation. Thus, in reality, flax fibre reinforced composites must be investigated for toughness and consistency in order to determine their suitability for installation. The purpose of this article is to investigate the physical and mechanical characteristics of flax/bio epoxide composites, including their impact on water saturation (WS), moisture saturation (HS), and freezing (F/T). A sample of water saturated, completely dried, and water saturated (WSD) and freeze–thaw (WSF/T) bio-composites was created and tested to determine their suitability for application in various settings. Finally, the deterioration of bio-composites with increasing exposure durations is explored. Additionally, the techniques are incompatible with the composites formed (AM).

Plant fibres are primarily composed of cellulose, hemicellulose, pectin, and lignin. Cellulose is the primary component of flax fibre. Cellulose makes up more than 75% of the total fibre weight. Cellulose is a collection of hydroxyls (OHs) that enables the formation of stronger hydrogen bonds in order to absorb moisture or water. Cellulose's water absorption capacity is dependent on its crystallinity. Nakamura et al. observed a reduction in the bound water volume of cellulose and the spread of moisture, notably during the amorphous phase Chilali et al. (2018). Hemicellulose and lignin are the primary constituents of the amorphous process and are critical for absorption and moisture conservation. Pectin is found in the lamella and fibre layer S2's middle structure. Pectin is made up of extremely polar carboxylic (COOH) molecules that include water molecules capable of forming hydrogen bonds.

On the contrary, these fibres are very porous and have large replaceable surfaces. When the fibres are placed in a moist environment, humidity may be absorbed and kept inside the structure's free volume. Dripping water and moisture content (MC) reveals a bio-epoxy matrix and flax/bio-epoxy composites subjected to a variety of environmental conditions.

The purpose of this research was to determine the flax/bioepoxy composite's use in structural engineering under a variety of environmental circumstances. The primary motivation for this investigation was to determine the viability of organic composites. This research may aid in assessing the flax/bio epoxy composite's environmental degradation issue by estimating the effect of exposure duration on their attributes. Flax/bio-epoxy composites have been subjected to a variety of environment conditions, including immersion in water, high humidity, and freezing/thawing periods. The overall performance of bio-composites was evaluated using water and moisture absorption characteristics, dimensioning and mechanical characterisation, as well as detrimental consequences from different exposure circumstances (flexural and tensile). The water absorption pattern of the samples submerged in water at room temperature was partially Fickian, with the most damaged and decaying sample being the most impacted. When the composites were subjected to a hot, moist environment, the mechanical characteristics of the bio-composites deteriorated somewhat. There were essentially no adverse impacts found on the performance of bio-composites during freeze/thaw cycles.

The findings of this research indicate that flax/bio-epoxy composites may be utilised in the majority of environmental circumstances, with the exception of subsea applications that significantly degrade material qualities. If the bending strength and

module of this kind of material are accidentally soaked in water over an extended period of time, the composites may be virtually completely restored by drying them for up to three days.

8 Conclusion

From the various studies discussed in the chapter, it is pretty clear that bio-composites are nonetheless when it comes to moisture absorption parameter and they can be used in various industrial application and industries ranging from avionics to structural. Physical therapy can increase or decrease the feasibility of the prognosis. The interfacial strength of composites produced at a high relative humidity level (80% and 90%) is virtually nil. Certain types of therapies can harm the development of specific composites (jute fibre/UP and kenaf fibre/starch), which are treated respectively for water uptake using hot water and alkalization technology. This reduction can be linked directly to removing the structure of the treated fibre of hydrophobic components such as lignin, which causes the microstructure to absorb a compound. Physical and chemical therapies are widely used to improve various natural composite materials for humidity absorption such as acetylation, benzoylation, treatment using peroxide, the isocyanate treatment, treatments with acidic, alkalization, etc. A significant decrease in mechanical properties results from fibre-reinforced moisture composites. Treatment of chemical fibres, skin protection, use of nanofillers, and use of nanofillers. It has been shown that the use of coupling agents reduces water absorption, thereby working to improve mechanical characteristics. When exposed to adverse climatic conditions, the material characteristics of biomass composites can be affected by serious environmental conditions as well as by warm, damp and frozen environments.

9 Future Scope of Work

Apart from flax and bamboo-based bio-composites which are found suitable for their moisture absorption properties other bio composites can be tested and their results can be analysed. Other important moisture parameters and tests can be conducted apart from the conventional ones to test the efficiency of these bio-composites with regards to their effectiveness in moisture absorption properties. Moreover, real life-based test of these composites and their study and analysis can help in understanding the performance of these bio-composites in the long run.

References

Akil HM, Cheng LW, Mohd Ishak ZA, Abu Bakar A, Abd Rahman MA (2009) Water absorption study on pultruded jute fibre reinforced unsaturated polyester composites. Compos Sci Technol. https://doi.org/10.1016/j.compscitech.2009.04.014

Alkbir MFM, Sapuan SM, Nuraini AA, Ishak MR (2016) Fibre properties and crashworthiness parameters of natural fibre-reinforced composite structure: a literature review. Compos Struct 148:59–73. https://doi.org/10.1016/j.compstruct.2016.01.098

Alomayri T, Assaedi H, Shaikh FUA, Low IM (2014) Effect of water absorption on the mechanical properties of cotton fabric-reinforced geopolymer composites. J Asian Ceram Soc 2:223–230. https://doi.org/10.1016/j.jascer.2014.05.005

Asim M, Paridah MT, Chandrasekar M et al (2020) (2020) Thermal stability of natural fibres and their polymer composites. Iran Polym J 29:625–648. https://doi.org/10.1007/s13726-020-00824-6

Assarar M, Scida D, El Mahi A, Poilâne C, Ayad R (2011) Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: flax-fibres and glass-fibres. Mater Des. https://doi.org/10.1016/j.matdes.2010.07.024

Azwa ZN, Yousif BF, Manalo AC, Karunasena W (2013) A review on the degradability of polymeric composites based on natural fibres. Mater Des 47:424–442. https://doi.org/10.1016/j.matdes.2012.11.025

Balakrishna A, Rao DN, Rakesh AS (2013) Characterization and modeling of process parameters on tensile strength of short and randomly oriented Borassus Flabellifer (Asian Palmyra) fibre reinforced composite. Compos B Eng 55:479–485. https://doi.org/10.1016/j.compositesb.2013.07.006

Belaadi A, Bezazi A, Maache M, Scarpa F (2014) Fatigue in sisal fibre reinforced polyester composites: hysteresis and energy dissipation. Procedia Eng 74:325–328. https://doi.org/10.1016/j.proeng.2014.06.272

Berges M, Léger R, Placet V, Person V, Corn S, Gabrion X, Rousseau J, Ramasso E, Ienny P, Fontaine S (2016) Influence of moisture uptake on the static, cyclic and dynamic behaviour of unidirectional flax fibre-reinforced epoxy laminates. Compos Part A Appl Sci Manuf 88:165–177. https://doi.org/10.1016/j.compositesa.2016.05.029

Célino A, Gonçalves O, Jacquemin F, Fréour S (2014) Qualitative and quantitative assessment of water sorption in natural fibres using ATR-FTIR spectroscopy. Carbohydr Polym 101:163–170. https://doi.org/10.1016/j.carbpol.2013.09.023

Chilali A, Zouari W, Assarar M, Kebir H, Ayad R (2018) Effect of water ageing on the load-unload cyclic behaviour of flax fibre-reinforced thermoplastic and thermosetting composites. Compos Struct 183:309–319. https://doi.org/10.1016/j.compstruct.2017.03.077

Chow C, Xing X, Li R (2007) Moisture absorption studies of sisal fibre reinforced polypropylene composites. Compos Sci Technol 67:306–313. https://doi.org/10.1016/j.compscitech.2006.08.005

Das M, Pal A, Chakraborty D (2006) Effects of mercerization of bamboo strips on mechanical properties of unidirectional bamboo–novolac composites. J Appl Polym Sci 100:238–244. https://doi.org/10.1002/app.23028

Deshpande AP, Bhaskar Rao M, Lakshmana Rao C (2000) Extraction of bamboo fibres and their use as reinforcement in polymeric composites. J Appl Polym Sci. https://doi.org/10.1002/(SICI)1097-4628(20000404)76:1%3c83::AID-APP11%3e3.0.CO;2-L

Dhakal H, Zhang Z, Richardson M (2007) Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. Compos Sci Technol 67:1674–1683. https://doi.org/10.1016/j.compscitech.2006.06.019

Dhawan V, Singh S, Singh I (2013) Effect of natural fillers on mechanical properties of GFRP composites. J Compos. https://doi.org/10.1155/2013/792620

Dunne R, Desai D, Sadiku R (2017) Material characterization of blended sisal-kenaf composites with an ABS matrix. Appl Acoust 125:184–193. https://doi.org/10.1016/j.apacoust.2017.03.022

Elanchezhian C, Ramnath BV, Ramakrishnan G, Rajendrakumar M, Naveenkumar V, Saravanakumar MK (2018) Review on mechanical properties of natural fibre composites. Mater Today Proc 5:1785–1790. https://doi.org/10.1016/j.matpr.2017.11.276

Evans JT (1992) Analysis and performance of fibre composites (second edition). Mater Sci Eng A 151:115. https://doi.org/10.1016/0921-5093(92)90189-8

Fernandes RL, de Moura MFSF, Moreira RDF (2016) Effect of moisture on pure mode I and II fracture behaviour of composite bonded joints. Int J Adhes Adhes 68:30–38. https://doi.org/10.1016/j.ijadhadh.2016.01.010

Ferreira DP, Cruz J, Fangueiro R (2019) Surface modification of natural fibres in polymer composites. In: Green composites for automotive applications. Woodhead Publishing, pp 3–41. https://doi.org/10.1016/B978-0-08-102177-4.00001

Furtado SCR, Araújo AL, Silva A (2018) Inverse characterization of vegetable fibre-reinforced composites exposed to environmental degradation. Compos Struct. https://doi.org/10.1016/j.compstruct.2018.01.092

Ghavami K (2005) Bamboo as reinforcement in structural concrete elements. Cem Concr Compos 27:637–649. https://doi.org/10.1016/j.cemconcomp.2004.06.002

Guessasma S, Bassir D, Hedjazi L (2015) Influence of interphase properties on the effective behaviour of a starch-hemp composite. Mater Des 65:1053–1063. https://doi.org/10.1016/j.matdes.2014.10.031

Ihueze CC, Okafor CE, Okoye CI (2015) Natural fibre composite design and characterization for limit stress prediction in multiaxial stress state. J King Saud Univ Eng Sci 27:193–206. https://doi.org/10.1016/j.jksues.2013.08.002

Ikpambese KK, Gundu DT, Tuleun LT (2016) Evaluation of palm kernel fibres (PKFs) for production of asbestos-free automotive brake pads. J King Saud Univ Eng Sci 28:110–118. https://doi.org/10.1016/j.jksues.2014.02.001

Jain S, Kumar R, Jindal UC (1992) Mechanical behaviour of bamboo and bamboo composite. J Mater Sci 27:4598–4604. https://doi.org/10.1007/BF01165993

Kabir MM, Wang H, Lau KT, Cardona F (2012) Chemical treatments on plant-based natural fibre reinforced polymer composites: an overview. Compos Part B Eng 43:2883–2892. https://doi.org/10.1016/j.compositesb.2012.04.053

Kong C, Lee H, Park H (2016) Design and manufacturing of automobile hood using natural composite structure. Compos Part B Eng 91:18–26. https://doi.org/10.1016/j.compositesb.2015.12.033

Kota AK, Li Y, Mabry JM, Tuteja A (2012) Hierarchically structured superoleophobic surfaces with ultralow contact angle hysteresis. Adv Mater. https://doi.org/10.1002/adma.201202554

Lai M, Botsis J, Cugnoni J, Coric D (2012) An experimental–numerical study of moisture absorption in an epoxy. Compos Part A Appl Sci Manuf 43:1053–1060. https://doi.org/10.1016/j.compositesa.2012.01.027

Lau K, Hung P, Zhu M-H, Hui D (2018) Properties of natural fibre composites for structural engineering applications. Compos Part B Eng 136:222–233. https://doi.org/10.1016/j.compositesb.2017.10.038

Liu K, Du J, Wu J, Jiang L (2012) Superhydrophobic gecko feet with high adhesive forces towards water and their bio-inspired materials. Nanoscale. https://doi.org/10.1039/c1nr11369k

Lo TY, Cui HZ, Tang PWC, Leung HC (2008) Strength analysis of bamboo by microscopic investigation of bamboo fibre. Construct Build Mater 22:1532–1535. https://doi.org/10.1016/j.conbuildmat.2007.03.031

Malkapuram R, Kumar V, Negi YS (2009) Recent development in natural fibre reinforced polypropylene composites. J Reinf Plast Compos 28:1169–1189. https://doi.org/10.1177/0731684407087759

Mallick PK (2007) Fibre-reinforced composites: Materials, manufacturing, and design, 3rd edn. CRC Press, pp 1–621

Mayandi K, Rajini N, Manojprabhakar M, Siengchin S, Ayrilmis N (2019) Recent studies on durability of natural/synthetic fibre reinforced hybrid polymer composites. In: Durability and

life prediction in biocomposites, fibre-reinforced composites and hybrid composites. Woodhead Publishing, pp 1–13. https://doi.org/10.1016/B978-0-08-102290-0.00001-5
Mishra S, Dubey A, Prasad E, Agarwal S (2019) Mechanical characterization of natural fibre based polymer matrix composite-a review. Res Develop Mater Sci 11(3):1186–1189. https://doi.org/10.31031/RDMS.2019.11.000765
Misri S, Sapuan SM, Leman Z, Ishak MR (2015) Torsional behaviour of filament wound kenaf yarn fibre reinforced unsaturated polyester composite hollow shafts. Mater Des 65:953–960. https://doi.org/10.1016/j.matdes.2014.09.073
Mohanty AK, Misra M, Drzal LT (2005) Natural fibre, biopolymer, and biocomposites. Taylor & Francis Group, Boca Raton, p 896
Muñoz E, García-Manrique JA (2015) Water absorption behaviour and its effect on the mechanical properties of flax fibre reinforced bioepoxy composites. Int J Polym Sci 2015:1–10. https://doi.org/10.1155/2015/390275
Nabi Saheb D, Jog JP (1999) Natural fibre polymer composites: a review. Adv Polym Technol. https://doi.org/10.1002/(SICI)1098-2329(199924)18:4%3c351::AID-ADV6%3e3.0.CO;2-X
Navas CS, Reboredo MM, Granados DL (2015) Comparative study of agroindustrial wastes for their use in polymer matrix composites. Procedia Mater Sci 8:778–785. https://doi.org/10.1016/j.mspro.2015.04.135
Nickel J, Riedel U (2003) Activities in biocomposites. Mater Today 6(4):44–48
Nugroho N, Ando N (2001) Development of structural composite products made from bamboo II: fundamental properties of laminated bamboo lumber. J Wood Sci 47:237–242. https://doi.org/10.1007/BF01171228
Okubo K, Fujii T, Yamamoto Y (2004) Development of bamboo-based polymer composites and their mechanical properties. Compos Part A Appl Sci Manuf 35:377–383. https://doi.org/10.1016/j.compositesa.2003.09.017
Omrani E, Menezes PL, Rohatgi PK (2016) State of the art on tribological behavior of polymer matrix composites reinforced with natural fibres in the green materials world. Eng Sci Technol an Int J 19:717–736. https://doi.org/10.1016/j.jestch.2015.10.007
Palm A, Smith J, Driscoll M, Smith L, Larsen LS (2015) Influence of ionizing radiation on the mechanical properties of a wood-plastic composite. Phys Procedia. https://doi.org/10.1016/j.phpro.2015.05.079
Pan Y, Zhong Z (2014) A nonlinear constitutive model of unidirectional natural fibre reinforced composites considering moisture absorption. J Mech Phys Solids 69:132–142. https://doi.org/10.1016/j.jmps.2014.04.007
Putra A, Or KH, Selamat MZ, Nor MJM, Hassan MH, Prasetiyo I (2018) Sound absorption of extracted pineapple-leaf fibres. Appl Acoust 136:9–15. https://doi.org/10.1016/j.apacoust.2018.01.029
Ray AK, Das SK, Mondal S, Ramachandra Rao P (2004) Microstructural characterization of bamboo. J Mater Sci 39:1055–1060. https://doi.org/10.1023/B:JMSC.0000012943.27090.8f
Ray AK, Mondal S, Das SK, Ramachandra Rao P (2005) Bamboo—a functionally graded composite-correlation between microstructure and mechanical strength. J Mater Sci 40:5249–5253. https://doi.org/10.1007/s10853-005-4419-9
Savage L, Evans K (2014) The importance of the mesostructure in toughening cellulosic short fibre composites. Compos Sci Technol. https://doi.org/10.1016/j.compscitech.2014.01.003
Shalwan A, Yousif BF (2014) Influence of date palm fibre and graphite filler on mechanical and wear characteristics of epoxy composites. Mater Des. https://doi.org/10.1016/j.matdes.2014.02.066
Shen CH, Springer GS (1976) Moisture absorption and desorption of composite materials. J Compos Mater. https://doi.org/10.1177/002199837601000101
Shin FG, Xian XJ, Zheng WP, Yipp MW (1989) Analyses of the mechanical properties and microstructure of bamboo-epoxy composites. J Mater Sci 24:3483–3490. https://doi.org/10.1007/BF02385729
Stevens ES (2002) Green plastics: an introduction to the new science of biodegradable plastics. J Chem Educ Am Chem Soc. https://doi.org/10.1021/ed079p1072.1

Trache D, Hussin MH, Chuin TD, Hussin MH, Hui Chuin CT, Sabar S, Fazita MRN, Taiwo OFA, Hassan TM, Haafiz MKM (2016) Microcrystalline cellulose: isolation, characterization and bio-composites application—a review. Int J Biol Macromol 93:789–804. https://doi.org/10.1016/j.ijbiomac.2016.09.056

Van de Weyenberg I, Chi Truong T, Vangrimde B, Verpoest I (2006) Improving the properties of UD flax fibre reinforced composites by applying an alkaline fibre treatment. Compos Part A Appl Sci Manuf 37:1368–1376. https://doi.org/10.1016/j.compositesa.2005.08.016

Verma D, Senal I (2019) Natural fibre-reinforced polymer composites. In: Biomass, biopolymer-based materials, and bioenergy: construction, biomedical, and other industrial applications. Elsevier, pp 103–122. https://doi.org/10.1016/B978-0-08-102426-3.00006-0

Wang F, Shao J, Keer LM, Li L, Zhang J (2015) The effect of elementary fibre variability on bamboo fibre strength. Mater Des 75:136–142. https://doi.org/10.1016/j.matdes.2015.03.019

Xu H, Zhang L, Cheng L (2015) The yarn size dependence of tensile and in-plane shear properties of three-dimensional needled textile reinforced ceramic matrix composites. Mater Des. https://doi.org/10.1016/j.matdes.2014.11.061

Zhai L, Berg MC, Cebeci FÇ, Kim Y, Milwid JM, Rubner MF, Cohen RE (2006) Patterned superhydrophobic surfaces: toward a synthetic mimic of the namib desert beetle. Nano Lett. https://doi.org/10.1021/nl060644q

Zhang W, Zhou Z, Zhang B, Zhao S (2015) A phenomenological fatigue life prediction model of glass fibre reinforced polymer composites. Mater Des 66:77–81. https://doi.org/10.1016/j.matdes.2014.10.036

Zhu X, He R, Lu X, Ling X, Zhu L, Liu B (2015) A optimization technique for the composite strut using genetic algorithms. Mater Des 65:482–488. https://doi.org/10.1016/j.matdes.2014.09.039

Hygrothermal Aging, Kinetics of Moisture Absorption, Degradation Mechanism and Their Influence on Performance of the Natural Fibre Reinforced Composites

M. Ramesh, M. Tamil Selvan, and K. Niranjana

Abstract The reduction of synthetic fibre usage in the various industries has grabbed attention of the researchers towards natural fibres. Since petroleum-based polymers and fibres are harming eco-system constantly by exhausting poisonous gases. Natural fibres are considered to be a potential replacement of synthetic fibres by means of eco-friendly, bio-degradability, recyclability, sustainability and innumerable other unique characteristics. It directly contributes towards circular economy of the local market. Hydrophilic nature plays vital role in impacting performance of the natural fibre, hence it becomes a sensitive towards humidity in working condition of the fabricated parts. The parts reinforced with natural fibre are subjected to hygrothermal ageing which directly influence the physical and chemical characteristics. The diffusion coefficient a property which defines the rate at which water molecules diffuses through material. By using Arrhenius equation and Fickian model optimize the modelling of a hygrothermal ageing of natural fibre reinforced polymer composites.

Keywords Modelling · Hygrothermal aging · Natural fibres · Bio-composites · Circular economy

1 Introduction

Fibres obtained naturally from plants are usually termed as natural fibres, since they are extracted from plant parts such as bark stem, petals, roots and fruits. Several plants such as jute, flax, sisal, hemp, kenaf, bamboo, bagasse, ramie, cotton, kapok, sisal, pineapple leaf, coconut/coir, rye, oat, corn, rice, etc., are used as the reinforcements in composites (Sahu and Rath 2019; Asrofi et al. 2021; Vimal et al. 2015; Ramesh et al. 2019, 2021). Natural fibres are intended to provide a distinctive blend

M. Ramesh (✉) · M. Tamil Selvan
Department of Mechanical Engineering, KIT-Kalaignarkarunanidhi Institute of Technology, Coimbatore, Tamil Nadu, India

K. Niranjana
Department of Aeronautical Engineering, KIT-Kalaignarkarunanidhi Institute of Technology, Coimbatore, Tamil Nadu, India

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_14

of distinguished performance, high flexibility, weight less, recyclability, high quality, bio-degradable in nature and cost advantages for production. In recent years, with growing environmental concerns, scientists have amplified their interest in analysing bio-based materials (Balaji et al. 2021; Tian et al. 2018; Rocha et al. 2019; Kollia et al. 2020; Sakthi et al. 2020; Retegi et al. 2006). The practices of natural fibres manufactured from plants are used as reinforcements to replace artificial fibres in composites for the need of sustainable engineering and industrial growth. Natural fibres have particular qualities like lower density, economical, renewable and bio-degradable nature compared with synthetic fibres like glass and carbon. In the fields of automotive, aerospace and construction, fibre incorporated polymer composites have a broad range of applications. This is due to their excellent mechanical behaviour, corrosion resistance and durability (Xiao et al. 2011; Wang et al. 2019; Mejri et al. 2018; Wang et al. 2021).

The researchers are unfamiliarised about hydrophilic nature and its effect of hygrothermal aging influencing the physical property of natural fibre composites. Hence discovery of bio-degradable fibre composites is still under research status and not implemented in any application (Mejri et al. 2018). Research shows the exposure to plant fibre composites in a moist condition leads to reduce the mechanical strengths of material as the water spreads throughout the layer. This deficit of strengths due to water absorption has been observed in different composites with sisal, bamboo, jute, hemp and flax fibres (Scida et al. 2013). However, bio-composites have a high sensitivity to moisture, resulting in high water uptake when exposed in a wet climate, causing distension of natural fibres, interfacial cracks between fibres and polymer been observed, and reduction in mechanical strengths. Therefore, in order to surge the use of plant fibre reinforced composites in outdoor applications, a fair definition and a reliable estimate of water penetration effects on physical properties of the composites (Islam et al. 2010; Nour et al. 2018; Tian and Zhong 2019).

1.1 Application of Natural Fibre Composites

In the recent past, industrial applications of plant-based fibre composites has increased in several fields such as construction, packaging, sports, automobile, textile industry, biological fields and many other applications. Besides having low cost, it is extremely environmentally friendly materials, many natural fibres provide a sufficient range of mechanical, thermal, and other physical properties. These properties are accompanied by several inherent limitations such as affinity to moisture and climatic temperatures on the performance which directly limiting the utilisation to other unfamiliar applications (Bhowmick et al. 2012; Kamboj et al. 2020). From ancient period plant fibres are used as structural materials for urban civilisation by mankind and are formally referred to lingo-cellulosic. Current era, people throughout the globe begin to use materials extracted from natural resources. This majorly due to global warming, energy usage and need to industrialised goods from sustainable sources.

Floras are certainly a true gift of god as a material perspective because products derived from them have attractive unique properties. Since they are obtainable abundantly, renewable and requires least fossil fuel energy for industrialisation. Few of the plant fibres are gained attention related to synthetic fibre (Khalil et al. 2000). Even investigation and technology of fibre reinforced composites has been increasing day by day. They play a key role in various structural elements in various fields such as aerospace vehicles, naval structural bodies and several other engineering fields for their high qualities like strength, specific rigidity, incredible durability and design tailoring capability (Balakrishnan et al. 2011). The wide range of applications ranging from space frame, staircase rails, aeroplanes, automotive doors, rocket engine cases, oxygen tanks, printed circuit boards and tennis rackets (Ishak et al. 2001).

The fibre reinforced polymer composites when placed in the increased temperature and humid condition, elastic modulus and internal stresses are decreased simultaneously. This will have a direct effect of safety and integrity of constructed parts. The renowned example is the temperature gradients experienced by aircraft during takeoff, climb, cruise and descent condition. Therefore, study of difference in stresses seems to be perilous concern as external surface temperature has a good relationship with characteristics of materials. The resulting sustainable composites are commonly referred to as eco-composites or bio-composites and have many commercial applications (Dhakal et al. 2007; Thwe and Liao 2002; Stamboulis et al. 2001). In order to promote people's awareness, the government regulations have been positioned around the world to resolve problems dealing with plastic waste by placing stringent limits on use of plastic and encouraging eco-friendly solutions, additionally facilitating the use of bio-composites. Various demerits of natural fibre stackled properly like effect of ecosystem influence towards mechanical properties of the material (Ma et al. 2018; Stamboulis et al. 2000).

1.2 Influences on Natural Fibre Composites

In some scopes, natural fibre composites have materialized as practicable alternative to glass fibre reinforced composites since early 1990s. Due to economical advantages and lower density attributes, natural fibre impregnated composites, flax fibre with polypropylene (PP) and Chinese reed fibre with PP are particularly beneficial material to the automotive industries. Comparative study showed advantages of natural fibre composites are better than glass fibre composites (Scida et al. 2013; Joshi et al. 2004; Chen et al. 2009b; Assarar et al. 2011; Arbelaiz et al. 2005). A substantial impact on use of natural fibres as a proxy to E-glass fibres for their low density, high specific mechanical properties, lower environmental impact, renewability, sustainability, and biodegradability. This has fostered significant public demand, which has risen in particular over the last couple of decades and has been influenced by local or contextual factors, such as availability and high-performance textile products (Arbelaiz et al. 2005; Chunhong et al. 2016; Chow 2007). The fibres used in the textile

industries require flexural characteristics, since natural fibres have a greater flexural strength it can replace synthetic fibres (Le Duigou et al. 2009). This gives a slightly optimizable solution but variety of problems have been posed are considerable concern as well. In fact, natural fibres have been used in composites to primarily enhance properties and reduce costs instead of strengthening mechanical characteristics. However, the ecological issues associated with the manufacture and usage of synthetic fibres has changed the situation. Natural fibres used as reinforcing material for all types of matrices in the earlier decade. Natural fibres have enhanced properties for the most part, but progress in tensile strength has been minimal (Alix et al. 2011; Pan and Zhong 2015; Li and Xue 2016; Wang et al. 2016; Standard test method for moisture absorption properties and equilibrium conditioning of polymer matrix composite materials).

2 Hygrothermal Ageing

Each component's hygrothermal ageing behavior, such as the fibre, matrix, and interface, was explored (Standard test method for moisture absorption properties and equilibrium conditioning of polymer matrix composite materials; Kablov et al. 2011; Bledzki and Gassan 1999; Chen et al. 2009a). Hygrothermal ageing was subjected to specimens from each batch material prepared for tensile property. They were installed in a test chamber with a relative humidity of 90% at varying temperatures after being dried for 24 h at an average temperature of 30 °C. To increase the diffusion process, composites were not covered on the edge. Specimens were regularly taken out of the chamber during ageing experiment and at particular times. The weight of the specimen was ceased when the weight gain was maintained constantly or when the weight gain reached saturation point. The water absorption was evaluated over time using the relative uptake of weight specified by M_t according to Scida et al. (2013).

$$M_t(\%) = \frac{W_t - W_0}{W_0} \times 100 \tag{1}$$

The consumption of by-products or even waste from manufacturing system of natural fibres has been geared to global movement towards a circular economy (Santulli 2019). In most cases, degradation activity of vegetable fibre composites subjected to meteorological changes like humidity that characterised by a water uptake phenomenon. Many factors influence water absorption behaviour of the material. There have a quite lot of possibilities of water ooze into reinforcement (Sivasankaraiah and Lokavarapu 2021; Alix et al. 2011; Tao et al. 2020; Yongbo et al. 2013). Water transportation can be evaluated by diffusion within resin structure, occurrence of defects within microstructure of the matrix like micro-space, pores, or cracks formed during compounding process, or capillary action along interfaces with defects between reinforcement and matrix system. Even if these mechanisms are all involved at same time, guessing global activity with diffusion mechanism may be

inadequate. The form of the sorption curve (as Fickian or Non-Fickian) will potentially differentiate different types of diffusion activity (as Fickian or Non-Fickian) represented by Scida et al. (2013):

$$\frac{M_t}{M_m} = k \cdot t^n \tag{2}$$

where k & n = diffusion parameters, M_t = moisture uptake, M_m = maximum moisture uptake. The mode of diffusion is indicated by the diffusion exponent n (Scida et al. 2013).

In natural fibre reinforced composites, moisture absorption typically follows a Fickian pattern. Fick's law shows water absorption increases linearly with square root of mean time in a one-dimensional approach. For values M_t/M_m less than 0.6, the initial part of the curve can be related by Scida et al. (2013):

$$\frac{M_t}{M_m} = \frac{4}{h}\sqrt{\frac{D \cdot t}{\pi}} \tag{3}$$

where D denotes diffusion coefficient; h denotes the specimen thickness.

For M_t/M_m greater than 0.6, use the following approximation for the second half-sorption (Scida et al. 2013):

$$\frac{M_t}{M_m} = 1 - \exp\left[-7.3\left(\frac{D \cdot t}{h^2}\right)^{0.75}\right] \tag{4}$$

In the case where values M_t are less than 60% of the equilibrium value M_m, D, is calculated using the following Eq. (5)

$$D = \frac{\pi}{(4M_m)^2}\left(\frac{M_t h}{\sqrt{t}}\right)^2 = \pi\left(\frac{k}{4M_m}\right)^2 \tag{5}$$

where h = thickness of the specimen and k is the linear component of the curve's slope (Scida et al. 2013).

$$Mt = f\left(\frac{\sqrt{t}}{h}\right) \tag{6}$$

Cured specimens have to be placed in the degradation chamber with a temperature of −100 to −600 °C. Ageing of the sample is carried out as per the requirements of CSN EN ISO9142. The temperature standards for the composite are set at 70 and −40 °C, and the humidity varies from 50 to 90%. With 90% humidity and −40 °C for 3 h, the temperature within the chamber is kept at 70 °C for 16 h and the temperature is again raised to 70 °C and maintained at 50% humidity for 5 h. The

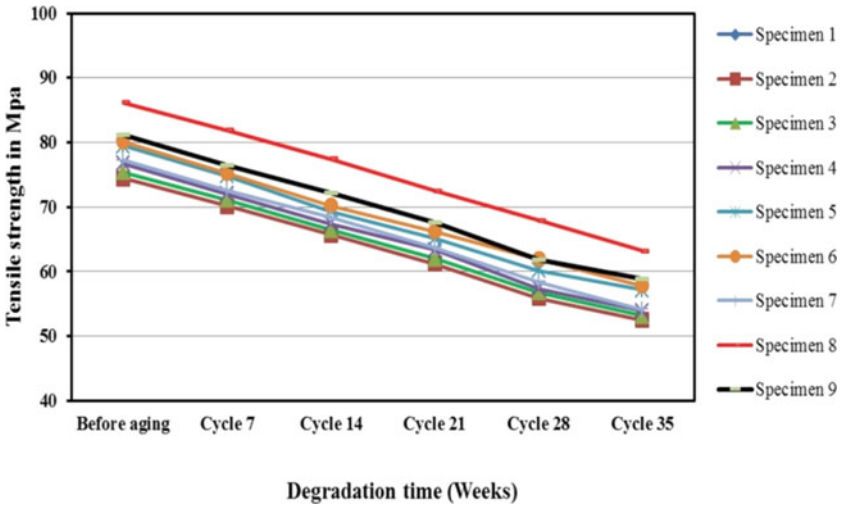


Fig. 1 Ageing influence on the tensile property of the material (Sakthi et al. 2020)

procedure is carried out for 24 h, during which one cycle is completed. After seven cycles, the specimens are removed from the chamber, kept in laboratory conditions for 24 h, and then mechanically examined. The above mechanism continues for a total of 35 cycles (35 cycles $\times$ 24 h $=$ 840 h) in-between which the test was carried out at the end of the seventh cycle. In order to choose the most suitable properties of fibre and filler and chemical treatment ensures superior mechanical properties, a total of five test results have been obtained. It is obvious from the Fig. 1 that as ageing increases, the tensile strength and other properties appear to decrease. Finally, the sample range's tensile strength was about 50–60 MPa. The significant reduction in tensile strength due to ageing indicates that the fibres from the matrix and a natural plant fibre are debonded, the level of degradation will be slightly higher to other manmade fibres. The outcome revealed that the effect of palm kernel seed powder does not contribute to the composites' tensile strength. The alkaline modification of the fibres leads to increase the bonding effect, but with regard to time, ageing has reduced the strength. The extremely influential factor which impacts mechanical properties of the composites can be assessed by creating regression analysis (Sakthi et al. 2020; Yongbo et al. 2013; Jianze et al. 2021; Rajaram et al. 2020).

2.1 Water Uptake

For discussion, water absorption curves of reinforced polymer specimens of basalt fibres soaked in water or alkaline solutions at varying temperatures. Some noteworthy singularity shown can be noticed and analyzed from the Fig. 2 (Xiao et al. 2011).

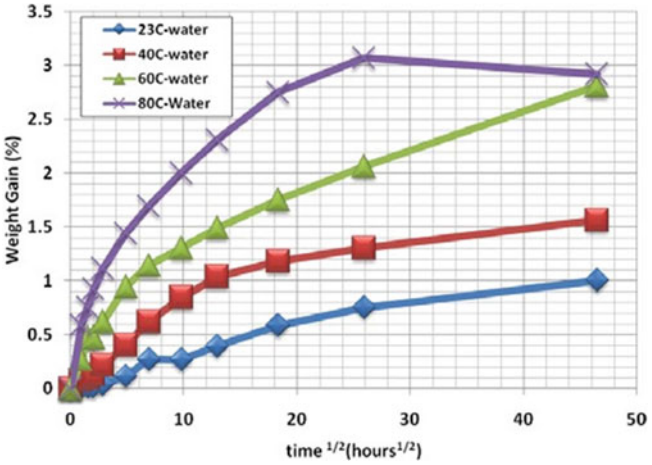


Fig. 2 Water absorption curves (Xiao et al. 2011)

The water absorption in the specimen is considered for same duration is also increased with increased submerged temperature due to thermal activation of the water diffusion mechanism. The higher immersion temperature, swifter the water diffusion rate. Hence it is been observed that immersion temperature is proportional to water diffusion rate. The sample submerged in water has a water absorption ratio at the same immersion temperature (except for 80 °C) relative to the sample immersed in an alkaline solution. This property implies that in alkaline solutions, basalt fibre reinforced polymer (BFRP) appears to become more deteriorated. The specimen immersed in water shows a higher water uptake ratio than specimen immersed in alkaline solution at the very same immersion temperature of 80 °C. This suggests that the alkaline solutions, BFRP has found to greater degradation of the material.

When (M_t/M_m) 0:6, Fick's law's diffusivity coefficient D is calculated by

$$D = \frac{\pi}{t}\left(\frac{hM_t}{4M_m}\right)^2 \tag{7}$$

where M_m = maximum relative water absorption, and h = thickness of the specimen.

To project BFRP's water uptake

$$\frac{M_t}{M_m} = \begin{cases} \frac{4}{h}\sqrt{\frac{Dt}{\pi}}\frac{M_t}{M_m} < 0.6 \\ 1 - exp\left[-7.3\left(D_w^i \frac{t}{s^2}\right)^{0.75}\right]\frac{M_t}{M_m} \geq 0.6 \end{cases} \tag{8}$$

M_t rises exponentially with hygrothermal ageing time at first, then gradually plateaus, revealing typical Fickian behaviour as defined by Eq. (8). The water absorption of treated specimens is slightly lower than that of untreated specimens, with the

acetylated group having the lowest uptake. The diffusion coefficient D, as determined by Eq. (7). After alkalization, salinization, and acetylation treatment, D of the given specimen decreases by 30.09%, 43.57%, and 47.32%, respectively, as compared to the untreated one. FRP water absorption is reduced by heavy fibre-matrix interfacial adhesion (Alix et al. 2011; Pan and Zhong 2015). The treated fibres have a greater fibre-matrix adhesion due to their lower water uptake. The colour of the specimens has clearly changed after hygrothermal ageing. With the passing of time, the distinction between matrix and fibre becomes increasingly apparent (Wang et al. 2019).

2.2 Moisture Absorption

The measurements of moisture absorption were performed following the ASTM D5229/D5229M standards. It must be remembered at this stage; specimens were placed in specially built holding trays to reveal aqueous atmosphere to all the surfaces of the material. The distilled water has been refreshed or changed on a weekly basis, so it is possible to classify the pH difference as insignificant. Periodic weighting measured the amounts at which water was consumed. Gravimetric measurement was measured by taking sample out of the water and cleaned with tissue cloth to get rid of excess moisture and weighed in digital balance. Throughout the method, a constant measurement technique was followed (Kollia et al. 2020). The relative mass uptake was calculated using the method defined and is expressed by:

$$Mt = Mm\left[1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{e^{\left[(2n+1)^2\pi^2\left(-\frac{Dt}{h^2}\right)\right]}}{(2n+1)^2}\right] \tag{9}$$

The following are some basic conclusions that can be drawn from the discussed topic: (i) The water absorption of bio-composites is augmented with increase in exposure temperature. At 60 °C, each material system's water uptake at saturation stage is slightly higher. (ii) After 25 h of exposure to 60 °C, saturation level is reached, while after 178 h at 40 °C, the saturation stage is reached, with the exception of the GZ system, where saturation is reached after 45 h. (iii) Bio-composites have virtually similar actions and lower water uptake, despite being made using different preparation methods. (iv) In the case of green epoxy 56 bio-resin, it is clear that the process affects water uptake at both exposure temperatures. Compression moulding prompts a gradual increase in water absorption, which is directly related to the consistency of the prepared bio-composite, since the compression moulding process creates a higher number of micro-voids. (v) Ultimately, as opposed to RSF and SP composites, green epoxy 56 composites consume more water at both exposure temperatures. Furthermore, the rate of water uptake in green epoxy 56 composites is higher (Kollia et al. 2020).

For a total period of 180 days, the water absorption of pure carbon nano-fibre (CNF)/FFRE laminates. It can be assessed that as compared to pure FFRE laminates,

the water intake of laminates with different quantities of CNFs has clearly decreased. From the SEM images, the distribution of CNFs with 1 and 2 wt% content in the epoxy matrix can be observed, showing that 1 wt% CNFs is uniformly distributed in the matrix. However, some studies seem to demonstrate that when the CNF content was increased to 2 wt%, as it appeared. Some defects can cause these aggregates of CNFs to degrade the epoxy matrix's water-resistance. There has also been a related phenomenon found in other research (Wang et al. 2021; Srinivasan et al. 2021; Radha and Ranganathaiah 2008; Ma et al. 2019; Ishak et al. 2001).

2.3 Kinetics of Moisture Sorption

Flax pulps like certain other natural fibres, retain a lot of moisture because of its hydrophilic properties. Water is absorbed mainly due to –OH groups of fibres in their polymeric composites. Microcracks can also stimulate moisture transfer by allowing water to flow and accumulate within the cracks (Ishak et al. 2001; Ma et al. 2020; Wang et al. 2017; Xin et al. 2016; Yang et al. 2019; Liu et al. 2020). The study of the kinetics of diffusion was based on the theory of Fick's principle. The sorption mechanism resembles Fickian behaviour in several respects. The Fickian diffusion circumstance is more apparent in MAPP1, but values deviate slightly from Fickian actions in MAPP2 (Fig. 3). Similar findings for other natural fibre-reinforced items were recorded by other authors (Retegi et al. 2006).

According to Fick's rule, the absorbed mass of water rises linearly with square root of time, then progressively decreases until it reaches an equilibrium plateau. The Fickian mechanism hypothesis was used to explore diffusivity. The diffusion

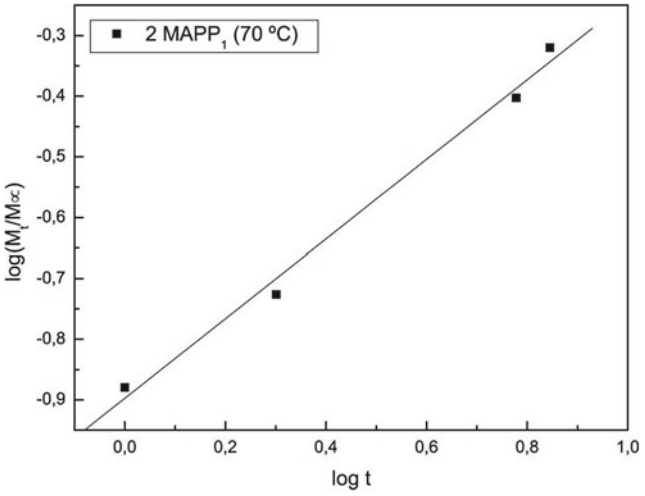


Fig. 3 Diffusion fitting plot for flax pulp/PP adjusted with 2% of MAPP

coefficient was calculated using a one-dimensional method.

$$\mathrm{D} = \pi\left(\frac{\mathrm{d}\theta}{4\Delta \mathrm{W}_{(\infty)}}\right)^2 \tag{10}$$

where d = initial sample thickness, s = sample thickness, and m = mass of sorbed water. However, to account for the sample's finite width w and length h in comparison to its thickness, a correction factor is required (Retegi et al. 2006; Le Duigou et al. 2009).

2.4 Effect of Temperature on Water Uptake

Temperature is a variant that will affect the water absorption percentage of the composites, which are regulated by diffusion. A research was conducted on this report's natural fibre based composites. By applying information to an equation, the rate of diffusion was calculated.

$$M = Bt^{1/2} \tag{11}$$

where B = constant correlated with diffusion coefficient, t = exposure time and M = mass change. The Arrhenius relationship is used to associate the rate of diffusion (D) to temperature when diffusion is Fickian and only a function of temperature. As a result, Fick's law is used to measure the water absorption theoretically.

Fick's law's theoretical equation was shown as an equation.

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\left(\frac{D\times t}{h^2}\right)\pi^2\times(2n+1)^2\right] \tag{12}$$

where h denotes specimen thickness and D denotes diffusivity, a central parameter in the Fickian model.

It is typically governed by linear initial part of the curve, so it can be calculated from the graph. The diffusivity was typically determined using Eq. (13)

$$D = \frac{\pi}{(4M_m)^2}\left(\frac{M_t h}{\sqrt{t}}\right)^2 = \frac{\pi\cdot k'^2}{(4M_m)^2} \tag{13}$$

The slope of the curve is defined by the coefficient k′ (Joshi et al. 2004). Temperature had a major impact on water absorption when $\mathrm{M_m}$ and D at different conditions were compared. This is in line with the findings of other studies. The Arrhenius equation, which stated that temperature influenced reaction rate constants in the same way,

was shown as Eq. (14) (Joshi et al. 2004).

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{14}$$

where, D_0 denotes diffusivity constant, E_a = active energy, R = Universal gas constant, and T as temperature. The diffusion rate was determined by a change of mass against time. In this regard, the linear fashion with such a plot should be stated as no evidence of diffusion, since other mechanisms, such as permeation, also follow such rate legislation (Standard test method for moisture absorption properties and equilibrium conditioning of polymer matrix composite materials; Liu et al. 2020; Zheng et al. 2021; Yazdi et al. 2017; Le Duigou et al. 2009; Ishak and Berry 1994). This can be explained since, with the rise in temperature, the polyester used as the matrix can expand.

2.5 *Effect of Hygrothermal Aging on Tensile Properties*

It can be shown that, with time of exposure, the tensile properties decreased by up to 365 days. The tensile strength of untreated empty fruit bunch fibre and coir composites was identical with no exposure (at 45% fibre loading) to those of acetylated fibres. However, the strengths of untreated samples were significantly reduced after saturation with water. A significant decrease in strength was observed with unmodified composites of empty fruit bunch fibre and coir, even after 3 months of ageing. With an extended ageing period of up to 1 year, the intensity reduction and break elongation increased significantly, but the modulus reduction was very gradual (Fig. 4). As compared to empty fruit bunch fibre composites, coir showed lower losses (Khalil et al. 2000).

2.6 *Effect of Formulation on Water Absorption*

Diffusion and permeation are the two major mechanisms for water uptake. In a capillary network of these dimensions, diffusion is a molecular-scale mechanism that will occur (Fig. 5).

Permeation occurs in micro-cracks or voids with larger dimensions. Processing parameters cause micro cracks in the composite; fibre incorporation may increase the probability of these occurrence. At different temperatures, with or without acetylation (empty fruit bunch fibre and coir), moisture absorption correlates with temperature (Khalil et al. 2000; Chen et al. 2009b). The weight shift is highly affected by the composite composition like temperature, chemical functional group and treatment of the composites. As compared to empty fruit bunch fibre-based composites, coir

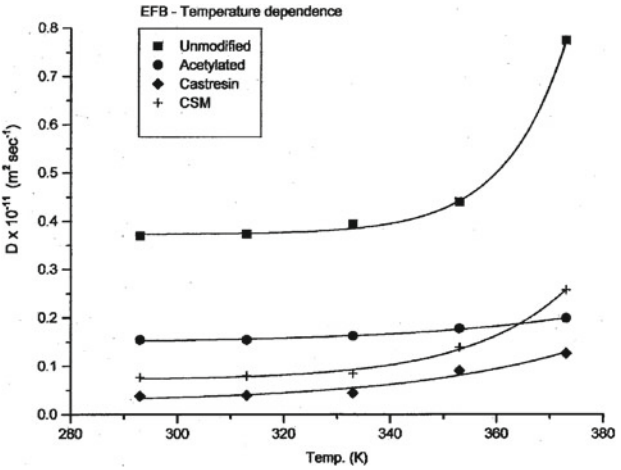


Fig. 4 Diffusion and temperature relations (Khalil et al. 2000)

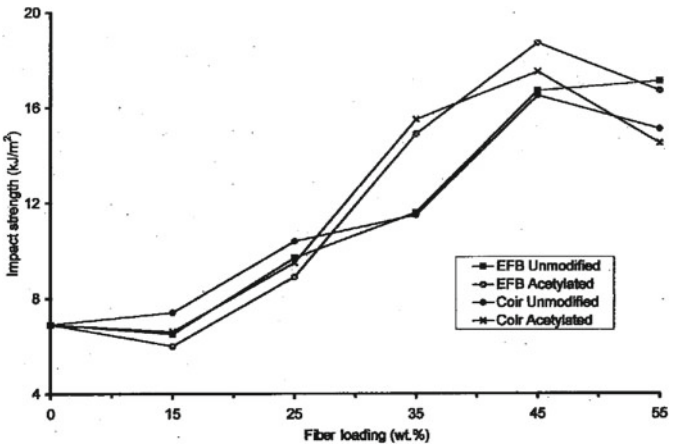


Fig. 5 Effect power of acetylated empty fruit bunch fibre and coir polyester composites relative to unmodified fibers (impact strength vs. fiber loading) (Khalil et al. 2000)

had a marginally inferior rate of uptake. The rate of water absorption rises in all situations (Khalil et al. 2000).

In contrast to the adjusted test samples, the untreated samples showed the highest water uptake at all temperatures and time taken. With exposure time and temperature, fibre swelling tends to increase. As a result of the fibres swelling, cracks can appear in the matrix. This may result in increase in the amount of water entering the composites after prolonged exposure to varying temperatures. The overall moisture absorption of the acetylated fibre composites at 20 °C is just 3.9%. When acetylated fibres were compared to unmodified fibres, they had a 60% lower relative

Table 1 Impact property of empty fruit bunch fibre and coir composites (Khalil et al. 2000)

Reinforcement	Duration	Impact strength (kJ/m^2)	
Fibre	Months	Unmodified	Acetylated
Empty fruit bunch fibre	3	10.7	4.4
	6	20.7	10.7
	12	40.5	12.6
Coir	3	13.6	5.4
	6	18.8	5.8
	12	30.3	10.8

water uptake. The fact that acetylated treated fibre composites absorb less water than unmodified fibres are due to good interfacial communication between fibre and resin. The fact about the treated fibres is high hydrophobic in nature than unmodified plant fibres. When natural fibre reinforced composites are exclusively exposed to water, moisture absorption arises due to the hydrophilic nature of lignin cellulose fibre, capillary action in the matrix and dimensional properties of the samples taken can alter. The maximum water absorption at 100 °C for empty fruit bunch fibre reinforced composites were found to be about 15.8% for untreated) and 5.7% for acetylated, respectively, while for coir, they were calculated to be under 15.9% and 5.9%, respectively. Improved fibre–matrix adhesion may clarify to improvise moisture resistance induced by fibre modification (Kamboj et al. 2020; Khalil et al. 2000).

The moisture uptake in these samples was reduced by acetylation of the hydroxyl groups in the cell-wall membrane of the polymer. This can be due to improved fibre–matrix touch, which reduces or removes void formation in the composite. The influence of different modifications on mechanical properties and decay resistance is associated with adsorption mechanism of moisture uptake. This shows that fibre–matrix adhesion is the primary cause of the process that decides the characteristics of the plant fibre based composites (Ishak and Berry 1994; Barbosa et al. 2015).

2.7 Effect of Hygrothermal Aging on Impact Strength

Table 1 showsthe impact strength deteriorates after three, six, and twelve months in the soil. In general, the improvements seen in both forms of fibre composites followed a similar trend to that seen in tensile properties.

2.8 Hydrothermal Ageing Mechanisms of FFRP

Plant fibres have a higher water content than synthetic fibres which is considered to be a unique nature. Its specific and different microstructures, as well as numerous

other chemical components had a high impact towards the research. In general, an elementary flax fibre was made up of a primary outer cell wall and a secondary inner wall made up of three layers, namely S1, S2, and S3 is shown in Fig. 6 (Li and Xue 2016).

A cavity, also known as a lumen, was present in the middle, resulting in a hollow structure that differed from that of synthetic fibres (Nour et al. 2018). When perceived as a drain, it has the ability to play a significant role in the material's water absorption. The main layer S2, which accounts for around 85% of the total portion, was discovered to be made up of spirally wound vastly cellulose fibrils in an amorphous hemicellulose and pectin. These fibrils developed a 10-degree angle with the fibre axis, known as the micro-fibrillar angle, which has a major impact on the mechanical properties of fibres (Tian and Zhong 2019). The key hemicellulose moieties produced were pectin, low crystallized cellulose, and xyloglucan. Because of their irregular composition and high abundance of hydroxyl groups, the major components of the primary wall bear the major problem for water intake nature (Rocha et al. 2019; Tian and Zhong 2019). Composites reinforced with natural fibres were more susceptible to degradation due to their multiscale structure and hydrophilic constituents. The majority of research work found that exposing plant fibre based composites to a humid environment for an extended period resulted in a loss of mechanical strengths. The reduction percentage in tensile values for flax fibre composites was 3 times higher than synthetic fibre composites after a 10-day immersion in water (Bhowmick et al. 2012). Water-saturated plant fibre reinforced composites displayed a greater reduction in Young's modulus (Kamboj et al. 2020). The shear and frictional strengths decreased rapidly before stabilizing in sense of immersion time increased (Khalil et al. 2000). The key harm mechanism for natural fibre composites during

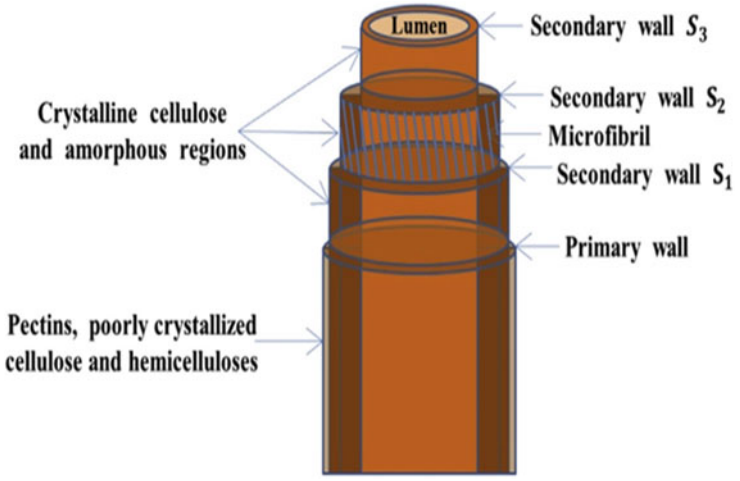


Fig. 6 Microstructural layers of flax fibre (Li and Xue 2016)

hygrothermal ageing, according to most experts, is the weakening of the matrix interface.

The Fig. 7 demonstrates the ageing processes of flax fibre composites in a hygrothermal climate, water enters composites by diffusion into the matrix, capillarity at the fibre-matrix interface, absorption of hydrophilic materials, and movement of lumens in the fibres. Found to have a expansion of lumen and interaction of cellulose with water particles, flax fibres appeared to swell. Matrix fractured around the swollen fibres are increased in size. Meanwhile, the absorption processes with water caused micro-fibril angle to shift due to the components and multi-stack structures of flax fibres. Pectins, hemicelluloses, and some badly crystallized celluloses within flax fibres gradually decayed as they aged, resulting in ultimate fibre/matrix interfacial bonding, as shown in Fig. 7 shows swelling behaviors of cell-wall layer caused the fibres to break and peel.

The three stages of FFRP's hydrothermal ageing processes can be follows:

- First stage is regulated by the mechanism, which involves material plasticization and swelling nature, as well as a reversible behavior.
- Next stage is the propagation of micro-structural damage to fibres as well as matrix, which is referred to as the damage mechanism stage.
- Third stage is the chemical process became involved as hydrolysis and leaching of constituents in the primary cell-wall of flax fibres. Usually, products with irreversible mechanical characteristics are administered by the ageing processes of the second and third levels.

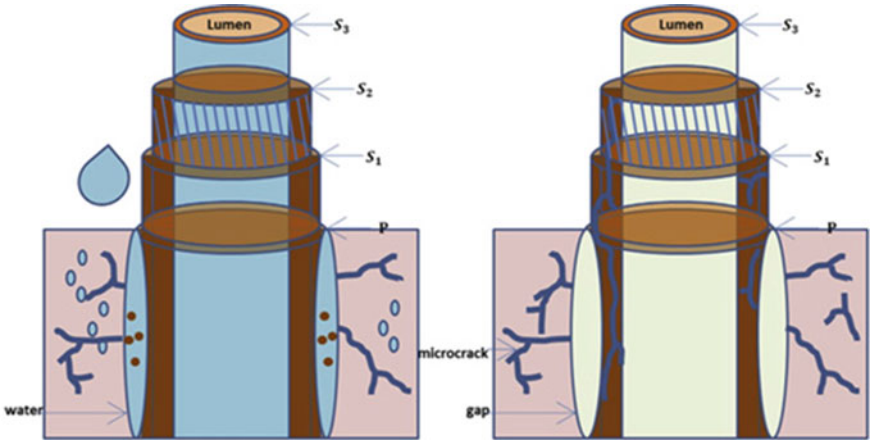


Fig. 7 Hygrothermal ageing mechanism representation of fibre reinforced composites (Li and Xue 2016)

2.9 Liquid Water Sorption in Matrix and in Composites

The water absorption of composites reinforced with unmodified flax fibres increased significantly after 300 h. The water absorption was in the range of 5–6% in composites made of treated fibres moisture resistance was increased. Similarly, moisture absorption increased fibre volume percentage due to increased voids and polysaccharide contents in composites made of an unsaturated polyester matrix, with messaging varying from 3–11% for fibre contents of 10–26% (Alix et al. 2011). The difference of the water absorption of the composites versus the time in order to disregard the effect of the film thickness. The diffusivity of water in the composite is illustrated by this representational lowered. The water diffusivity was decreased due to the presence of fibres. Water molecules have been trapped in micro and macro-voids of bundle fibres and within single fibre, resulting in water tank results (lumen). When the fibres were alkaline treated, delay effect was more noticeable, particularly with styrene. The minimal sorption obtained with treated fibres is consistent with this finding (Stamboulis et al. 2001). This phenomenon was caused by an increase in the interface fibre/matrix consistency in (Si) treated fibres. Water permeation measurements were determined to validate these preliminary findings. The evolving patterns of water uptake revealed that it is increased linearly with time in the beginning, then became slower after some time, as predicted by the model (Tao et al. 2020; Zhou and Lucas 1999, b; Abdelmalek et al. 2009; Patel et al. 2002). The parameters can be determined by using the following Eq.

$$M(t) = M_{\infty}\left(1 + k\sqrt{t}\right)\left\{1 - \frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{\exp\left[-(2j+1)^2 n^2\left(\frac{Dt}{h^2}\right)\right]}{(2j+1)^2}\right\} \tag{15}$$

where M(t) = water uptake at fixed time intervals, M_{∞} = efficient equilibrium water uptake. Equation is used to measure the water diffusion coefficient, which is a property defining the rate at which water molecules in the composite travel (Chunhong et al. 2016).

$$D = \pi\left(\frac{Kh}{4M_{\infty}}\right)^2 \tag{16}$$

where k = initial slope of a M(t) versus $t^{1/2}$ plot, M1 = maximum weight gain, and h = composite thickness (Chunhong et al. 2016).

3 Conclusion

The factor affecting the natural fibre composites are hygrometric rate, fibre fraction, fibre nature, porosity, fibre geometry and matrix form. According to Fick's law it has been found water absorption increases is linearly proportional to time in one dimensional approach. The water absorption is increases simultaneously with the temperature of the material. The fabrication techniques also play a role in the absorption such as hand layup and compression moulding eventually produces much voids compare to resin transfer moulding and autoclave. The voids are more prompt to increase in the water absorption rate. The kinetics of moisture sorption due to hydroxyl functional group of fibre in polymeric composites. The Arrhenius equation and Fickian model for water absorption has been discussed for its reaction rate constant. In Arrhenius equation, temperature is directly proportional to reaction rate constant whereas Fick's law showing water absorption rate has a higher value up to the ratio between water absorption at a time to the maximum water absorption should be around 0.6. Therefore water absorption rate should be maintained at a saturation point under equilibrium state for each different fibre.

References

Abdelmalek A, Bouazza M, Zidour M, Benseddiq N (2019) Hygrothermal effects on the free vibration behavior of composite plate using nth-order shear deformation theory: micromechanical approach. Iran J Sci Technol Trans Mech Eng. https://doi.org/10.1007/s40997-017-0140-y

Alix S, Lebrun L, Morvan C, Marais S (2011) Study of water behaviour of chemically treated flax fibres-based composites: a way to approach the hydric interface. Compos Sci Technol. https://doi.org/10.1016/j.compscitech.2011.02.004

Arbelaiz A, Fernandez B, Ramos JA, Retegi A, Llano-Ponte R, Mondragon I (2005) Mechanical properties of short flax fibre bundle/polypropylene composites: Influence of matrix/fibre modification, fibre content, water uptake and recycling. Compos Sci Technol. https://doi.org/10.1016/j.compscitech.2005.01.008

Asrofi M, Sapuan SM, Ilyas RA, Ramesh M (2021) Characteristic of composite bioplastics from tapioca starch and sugarcane bagasse fiber: effect of time duration of ultrasonication (Bath-Type). Mater Today: Proceed. https://doi.org/10.1016/j.matpr.2020.07

Assarar M, Scida D, El Mahi A, Poilâne C, Ayad R (2011) Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: Flax–fibres and glass–fibres. Mater Des. https://doi.org/10.1016/j.matdes.2010.07.024

Balaji D, Ramesh M, Kannan T, Deepan S, Bhuvaneswari V, Rajeshkumar L (2021) Experimental investigation on mechanical properties of banana/snake grass fiber reinforced hybrid composites. Mater Today: Proceed. https://doi.org/10.1016/j.matpr.2020.09

Balakrishnan H, Hassan A, Imran M, Wahit MU (2011) Aging of toughened polylactic acid nanocomposites: water absorption, hygrothermal degradation and soil burial analysis. Enhanced Polym Res. https://doi.org/10.1007/s10924-011-0338-9

Barbosa AQ, da Silva LFM, Öchsner A (2015) Hygrothermal aging of an adhesive reinforced with microparticles of cork. Adhes Sci Technol. https://doi.org/10.1080/01694243.2015.1041358.

Bhowmick M, Mukhopadhyay S, Alagirusamy R (2012) Mechanical properties of natural fibre reinforced composites. Text Prog. https://doi.org/10.1080/00405167.2012.676800

Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. Prog Polym Sci 24:221–274

Chen H, Miao M, Ding X (2009a) Influence of moisture absorption on the interfacial strength of bamboo/vinyl ester composites. Mater Sci Eng. https://doi.org/10.1016/j.compositesa.2009.09.003

Chen H, Miao M, Ding X (2009b) Influence of moisture absorption on the interfacial strength of bamboo/vinyl ester composites. Compos: Part A. https://doi.org/10.1016/j.compositesa.2009.09.003

Chow CPL, Xing XS, Li RKY (2007) Moisture absorption studies of sisal fibre reinforced polypropylene composites. Compos Sci Technol. https://doi.org/10.1016/j.compscitech.2006.08.005

Chunhong W, Shengkai L, Zhanglong Y (2016) Mechanical, hygrothermal ageing and moisture absorption properties of bamboo fibres reinforced with polypropylene composites. J Reinf Plast Compos. https://doi.org/10.1177/0731684416637681

Dhakal HN, Zhang ZY, Richardson MOW (2007) Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. Adv Poly Compos https://doi.org/10.1016/j.compscitech.2006.06.019

Le Duigou A, Davies P, Baley C (2009) Seawater ageing of flax/poly(lactic acid) biocomposites. Polym Degrad Stab. https://doi.org/10.1016/j.polymdegradstab.2009.03.025

Islam MS, Pickering KL, Foreman NJ (2010) Influence of hygrothermal ageing on the physico-mechanical properties of alkali treated industrial hemp fibre reinforce polylactic acid composites. Mater Sci Eng. https://doi.org/10.1007/s10924-010-0225-9

Ishak ZAM, Yow BN, Ng BL, Khalil HPSA, Rozman HD (2001) Hygrothermal aging and tensile behavior of injection-molded rice husk-filled polypropylene composites. J Appl Polym Sci https://doi.org/10.1002/app.1491

Ishak ZAM, Berry JP (1994) Hygrothermal aging studies of short carbon fibre reinforced nylon 6.6. J Appl Polym Sci. https://doi.org/10.1002/app.1994.070511306

Ishak ZAM, Ariffin A, Senawi R (2001) Effects of hygrothermal aging and a silane coupling agent on the tensile properties of injection molded short glass fibre reinforced poly(butylene terephthalate) composites. Eur Polym J. https://doi.org/10.1016/S0014-3057(01)00033-7

Jianze L, Jingxin N, Wei T, Wenlong M, Guangbin W, Yuan G (2021) Comparative study on mechanical properties of aluminum alloy and BFRP single lap joints with hygrothermal aging. J Adhes. https://doi.org/10.1080/00218464.2020.1712656

Joshi SV, Drzal LT, Mohanty AK, Arora S (2004) Are natural fibre composites environmentally superior to glass fibre reinforced composites. Compos: Part A. https://doi.org/10.1016/j.compositesa.2003.09.016

Khalil HPSA, Rozman HD, Ahmad MN, Ismail H (2000) Acetylated plant-fibre-reinforced polyester composites: a study of mechanical, hygrothermal, and aging characteristics. Polym-Plast Technol Eng. https://doi.org/10.1081/PPT-100100057

Kablov EN, Startsev OV, Krotov AS, Kirillov VN (2011) Climatic aging of composite aviation materials: I. aging mechanisms. Promising Mater Technol. https://doi.org/10.1134/S0036029511100065

Kamboj I, Jain R, Jain D, Bera TK (2020) Effect of fibre pre-treatment methods on hygrothermal aging behavior of agave fibre reinforced polymer composites. J Nat Fibres. https://doi.org/10.1080/15440478.2020.1838398

Kollia E, Saridaki X, Karagiannis D, Kostopoulos V (2020) Effect of water aging on the mechanical properties of flax fibre/bio-based resin composites. J Appl Polym Sci. https://doi.org/10.1002/app.48787

Li Y, Xue B (2016) Hydrothermal ageing mechanisms of unidirectional flax fabric reinforced epoxy composites. Polym Degrad Stab. https://doi.org/10.1016/j.polymdegradstab.2016.02.004

Liu L, Zhao Z, Chen W, Xue M, Shuang C (2020) Interlaminar shear property and high-velocity impact resistance of CFRP laminates after cyclic. Int J Crashworthiness. https://doi.org/10.1080/13588265.2019.1590905

Ma B, Feng Y, He Y, Zhang T, Zhang S, Zhang T (2019) Effect of hygrothermal environment on the tension–tension fatigue performance and reliable fatigue life of T700/MTM46 composite laminates. Appl Phys Eng. https://doi.org/10.1631/jzus.A1900081

Ma G, Yan L, Shen W, Zhu D, Huang L, Kasal B (2018) Effects of water, alkali solution and temperature ageing on water absorption, morphology and mechanical properties of natural FRP composites: plant-based jute versus mineral-based basalt. Compos Part B. https://doi.org/10.1016/j.compositesb.2018.09.015

Ma S, He Y, Hui L, Xu L (2020) Effects of hygrothermal and thermal aging on the low-velocity impact properties of carbon fibre composites. Adv Compos Mater. https://doi.org/10.1080/09243046.2019.1630054

Mejri M, Toubal L, Cuillière JC, François V (2018) Hygrothermal aging effects on mechanical and fatigue behaviors of a short natural-fibre-reinforced composite. J Fatigue. https://doi.org/10.1016/j.ijfatigue.2017.11.004

Nour A, Mechakra H, Benkoussas B, Tawfiq I, Settet AT, Renane R (2018) Modeling composite reinforced with short Alfa fibres to determine its fatigue and structural homogenization. Mech Compos Mater. https://doi.org/10.1007/s11029-018-9758-0

Pan Y, Zhong Z (2015) The effect of hybridization on moisture absorption and mechanical degradation of natural fibre composites: an analytical approach. Compos Sci Technol. https://doi.org/10.1016/j.compscitech.2015

Patel BP, Ganapathi M, Makhecha DP (2002) Hygrothermal effects on the structural behaviour of thick composite laminates using higher-order theory. Compos Struct. https://doi.org/10.1016/j.compscitech.2006.08.005

Radha JC, Ranganathaiah C (2008) Effect of hygrothermal aging on the diffusion of seawater in epoxy/glass composites studied by positron lifetime spectroscopy. Polym Compos. https://doi.org/10.1002/pc.20391

Rajaram AN, Boay CG, Srikanth N (2020) Effect of curing on the hygrothermal behaviour of epoxy and its carbon composite material. Compos Commun. https://doi.org/10.1016/j.coco.2020.100507

Ramesh M, Bhoopathi R, Deepa C, Sasikala G (2019) Experimental investigation on morphological, physical and shear properties of hybrid composite laminates reinforced with flax and carbon fibers. J Chin Adv Mater Soc 6(4):640–654

Ramesh M, Deepa C, Tamil Selvan M, Rajeshkumar L, Balaji D, Bhuvaneswari V (2021) Mechanical and water absorption properties of Calotropis gigantea plant fibers reinforced polymer composites. Mater Today: Proceed. https://doi.org/10.1016/j.matpr.2020.11.480

Retegi A, Arbelaiz A, Alvarez P, Llano-Ponte R, Labidi J, Mondragon I (2006) Effects of hygrothermal ageing on mechanical properties of flax pulps and their polypropylene matrix composites. J Appl Polym Sci. https://doi.org/10.1002/app.24331

Rocha IBCM, van der Meer FP, Raijmaekers S, Lahuerta F, Nijssen RPL, Mikkelsen LP, Sluys LJ (2019) A combined experimental/numerical investigation on hygrothermal aging of fibre-reinforced composites. Knowl Centre WMC. https://doi.org/10.1016/j.euromechsol.2018.10.003

Standard test method for moisture absorption properties and equilibrium conditioning of polymer matrix composite materials

Sahu SK, Rath MK (2019) Hygrothermal aging behavior of fibre-reinforced composites. Process Green Compos. https://doi.org/10.1007/978-981-13-6019-0_4

Sakthi BG, Ravichandran M, Santhosh Kumar V (2020) Study of ageing effect on mechanical properties of prosopisjuliflora fibre reinforced palm seed powder filled polymer composite. Aust J Mech Eng. https://doi.org/10.1080/14484846.2020.1806194

Santulli C (2019) Natural fibre-reinforced composites: recent developments and prospective utilization in railway industries for sleeper manufacturing, Biopolym-Based Mater. https://doi.org/10.1016/B978-0-08-102426-3.00012-6

Scida D, Assarar M, Poilâne C, Ayad R (2013) Influence of hygrothermal ageing on the damage mechanisms of flax-fibre reinforced epoxy composite. Compos: Part B. https://doi.org/10.1016/j.compositesb.2012.12.010

Sivasankaraiah T, Lokavarapu BR (2021) Strength degradation of glass epoxy composites under hygrothermal environment. Mater Today Proceed. https://doi.org/10.1016/j.matpr.2020.08.778
Srinivasan T, Suresh G, Ramu P, Vignesh R, Vijay Harshan A, Vignesh KP (2021) Effect of hygrothermal ageing on the compressive behavior of glass fibre reinforced IPN composite pipes. Mater Today Proceed. https://doi.org/10.1016/j.matpr.2020.06.102
Stamboulis A, Baillie CA, Garkhail SK, Van melick HGH (2000) Environmental durability of flax fibres and their composites based on polypropylene matrix. Appl Compos Mater. https://doi.org/10.1023/A:1026581922221
Stamboulis A, Baillie CA, Peijs T (2001) Effects of environmental conditions on mechanical and physical properties of flax fibers. Compos Part A: Appl Sci Manuf 32(8):1105–1115
Tao L, Min W, Qi L, Cheng C, Song T, Yu ZSM (2020) The hygrothermal aging process and mechanism of CFRP papered by prepreg that may be stored at room temperature. Polym Degrad Stab. https://doi.org/10.1016/j.polymdegradstab.2020.109395
Thwe MM, Liao K (2002) Effects of environmental aging on the mechanical properties of bamboo–glass fiber reinforced polymer matrix hybrid composites. Compos Part A: Appl Sci Manuf 33(1):43–52
Tian F, Zhong Z (2019) Modeling of load responses for natural fibre reinforced composites under water absorption. Compos: Part A. https://doi.org/10.1016/j.compositesa.2019.105564
Tian F, Zhong Z, Pan Y (2018) Modeling of natural fibre reinforced composites under hygrothermal ageing. Compos Struct. https://doi.org/10.1016/j.compstruct.2018.05.083
Vimal R, Subramanian KHH, Aswin C, Logeswaran V, Ramesh M (2015) Comparisonal study of succinylation and phthalicylation of jute fibres: study of mechanical properties of modified fibre reinforced epoxy composites. Mater Today: Proceed 2:2918–2927
Wang B, Li J, Gao Y (2017) Enhancing hygrothermal resistance of aeronautical carbon fabric/epoxy composites via air plasma processing. Adhes Sci Technol. https://doi.org/10.1080/01694243.2016.1218314
Wang X, Petru M, Yu H (2019) The effect of surface treatment on the creep behavior of flax fibre reinforced composites under hygrothermal aging conditions. Adv Technol Innov. https://doi.org/10.1016/j.conbuildmat.2019.03.001
Wang Y, Zhu W, Wan B, Meng Z, Han B (2021) Hygrothermal ageing behavior and mechanism of carbon nanofibres modified flax fibre-reinforced epoxy laminates. Compos: Part A. https://doi.org/10.1016/j.compositesa.2020.106142
Wang J, GangaRao H, Liang R, Liu W (2016) Durability and prediction models of fibre-reinforced polymer composites under various environmental conditions: a critical review durability and prediction models of fibre-reinforced polymer composites under various environmental conditions: a critical review. J Reinf Plast Compos. https://doi.org/10.1177/0731684415610920
Xiao B, Li H, Xian G (2011) Hygrothermal ageing of basalt fibre reinforced epoxy composites. In: Ye L, Feng P, Yue Q (eds) Advances in FRP composites in civil engineering. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-17487-2_77
Xin H, Liu Y, Mosallam A, Zhang Y, Wang C (2016) Hygrothermal aging effects on flexural behavior of pultruded glass fibre reinforced polymer laminates in bridge applications. Construct Build Mater. https://doi.org/10.1016/j.conbuildmat.2016.09.151
Yongbo Z, Huimin F, Zhihua W, Xiaobin M (2013) An experimental investigation into the damage mechanisms in notched CCF300/QY8911 and T300/qy8911composites subjected to hygrothermal environment condition. Appl Compos Mater. https://doi.org/10.1007/s10443-013-9323-x
Yang S, Liu W, Fang Y, Huo R (2019) Influence of hygrothermal aging on the durability and interfacial performance of pultruded glass fibre reinforced polymer composites. J Mater Sci. https://doi.org/10.1007/s10853-018-2944-6
Zheng G, He Z, Wang K, Liu X, Luo Q, Li Q (2021) On failure mechanisms in CFRP/Al adhesive joints after hygrothermal. Thin-Walled Struct. https://doi.org/10.1016/j.tws.2020.107184

Yazdi MH, Sullivan PL, Moallemi A (2017) Specific heat capacity of polycarbonate/acrylonitrile–butadiene–styrene (PC/ABS) blend after hygrothermal aging. Hygrotherm Condition. https://doi.org/10.1007/s10973-017-6559-y

Zhou J, Lucas JP (1999a) Hygrothermal effects of epoxy resin. Part I: the nature of water in epoxy. Polymer. https://doi.org/10.1016/S0032-3861(98)00790-3

Zhou J, Lucas JP (1999b) Hygrothermal effects of epoxy resin. Part II: variations of glass transition temperature. Polymer. https://doi.org/10.1016/S0032-3861(98)00791-5

Performance of Natural Fiber Based Nanocomposites Under Environmental Aging Conditions

Atanu Kumar Das, Md Nazrul Islam, Afroza Akter Liza, and Ahsan Rajib Promie

Abstract Nanocomposites are suitable for advanced engineering applications, i.e., automotive, aeronautics, biomedical applications, catalysts, gas-separation membranes, contact lenses, bioactive implant materials, bone applications, and food packaging due to their higher mechanical and thermal resistance properties. Environmental friendly natural fibre-based bionanocomposites are important because of their renewable, biodegradable and compostable nature. Natural fibers both in nano, i.e., cellulose nanocrystal (CNC), microfibrallated cellulose (MFC), microcrystalline (MCC), and macro-sized, i.e., carboxymethyl cellulose (CMC) are used to produce bionanocomposites together with bio or synthetic polymers, i.e., starch, polyurethane (PU), polylactic acid (PLA), using different methods. These composites have already proved to be invaluable gifts to the present and future generations in many different aspects, and thus, thanks go to the modern science and technology. However, in the same way as other composites the physical and mechanical properties are affected severely by different aging conditions like pressure, temperature, humidity and the curing condition. The absorption of water and plasticization of the composites deteriorates the service life, increases the chain mobility and decreases the glass transition temperature. It also reduces the mechanical properties of the composites. Thus, researchers are working on the effect of different aggressive environments on the durability of composites and to understand the changes in the physical and mechanical properties over the period of aging. This chapter deals with the different environmental aging conditions and their impact on the properties of the composites.

Keywords Natural fibers · Nanocellulose · Nanocomposites · Properties · Biodegradation

A. K. Das
Department of Forest Biomaterials and Technology, Swedish University of Agricultural Sciences, SE-90183 Umeå, Sweden

M. N. Islam (✉) · A. A. Liza · A. R. Promie
Forestry and Wood Technology Discipline, Khulna University, Khulna 9208, Bangladesh

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_15

1 Introduction

Nanocomposites consist of materials having at least one of them with the dimension of nano size, i.e., 1–100 nm (Murray et al. 2015; Vercelheze et al. 2013). These nanocomposites possess higher mechanical, thermal, barrier and physicochemical properties in comparison to the traditional composites composed of micro-sized materials (Ferfera-Harrar and Dairi 2014; Murray et al. 2015; Vercelheze et al. 2013). At present, scientists are trying to develop environmentally friendly bio-based nanocomposites with biodegradable and compostable properties maintaining the quality of conventional composites (Fortunati et al. 2013; Kalita et al. 2020; Sanchez-Safont et al. 2016). Natural fibers both nano and macro-sized including nanocellulose, i.e., cellulose nanocrystal (CNC), microfibrillated cellulose (MFC) and microcrystalline cellulose (MCC), and macrofiber, i.e., carboxymethylcellulose (CMC) are used in preparing bionanocomposites for automotive, aeronautics, biomedical, and food packaging applications due to having light in weight and higher strength properties (Das et al. 2020; Ferreira et al. 2018; Yang et al. 2020). These natural fibers are used to produce nanocomposites by incorporating chemicals such as poly(hydroxybutyrate) (PHB), polyurethane (PU) and polylactic acid (PLA) (Alikarami et al. 2013; Maiti et al. 2013; Seoane et al. 2017a). Moreover, natural fibers based nanocomposites can be fabricated by polymerization (Bitinis et al. 2013; Cao et al. 2009; Jardin et al. 2020; Yao et al. 2014), extrusion (Arrieta et al. 2014a, b) and compression (Platnieks et al. 2020) methods.

Natural fibers help to increase the thermal stability and storage modulus of the nanocomposites (Banerjee et al. 2014; Liu et al. 2014; Moran et al. 2013; Pinheiro et al. 2019; Seoane et al. 2019; Tran et al. 2016; Yao et al. 2014). On the other hand, it can increase (Kalita et al. 2020; Liu et al. 2014; Roy et al. 2012; Seoane et al. 2019) or decrease (Kohli et al. 2019; Platnieks et al. 2020; Sanchez-Safont et al. 2016) the biodegradability of the nanocomposites compared to the original polymer materials. Crystallinity behaviour of cellulose improves the properties of natural fiber-based nanocomposites (Matsumura et al. 2000). Due to the hydrophilic nature of cellulose, it shows poor physical and mechanical properties at higher humidity condition (Ferfera-Harrar and Dairi 2014; Kalia et al. 2011). Ultraviolet irradiation from the sun, moisture from rainfall and temperature cycling in the natural environment may have impact on the performance of fibers based nanocomposites (Awad et al. 2019). This chapter deals with the natural fiber-based (nano and macro) nanocomposites and their performance considering environmental aging conditions. It also analyses the information which influence of the natural aging conditions on natural fibers based nanocomposites.

2 Natural Fibers Based Nanocomposites

Modern science and technology has established the biodegradable bionanocomposites as valuable gift to the present and future generations. These are one type of hybrid materials, composed of biopolymers and inorganic solids having nanometer scale dimension at least in one dimension (Arora et al. 2018). In this section, bionanocomposites obtained from natural fibers have been discussed. Natural fibers used in the form of nano or macro for making nanocomposites are the main concern of this section.

Cellulose whisker (CW) obtained from microcrystalline cellulose (MCC) by acid hydrolysis (sulphuric acid) was mixed with furfural alcohol (FA) to produce CW/FA nanocomposites through in situ polymerization (Pranger and Tannenbaum 2008). The dispersion of CW in FA matrix is possible because of the electrostatic stabilization by sulphonic acid groups, and thus, this can form a nanocomposite (Ray and Sain 2016). In another study, cellulose nanocrystal (CNC)/waterborne polyurethane (WPU) composite was prepared following by in situ polymerization (Cao et al. 2009). In this case, CNC was obtained by sulphuric acid hydrolysis followed by solvent exchanging, i.e., water, acetone, N,N-dimethylformamide (DMF) and centrifugation (Cao et al. 2009). Pei et al. (2011) used CNC (0.5, 1 and 5 wt%) for producing hard polyurethane (PU)/CNC nanocomposites by the same method, however, used sonication and freeze-drying before dispersing in DMF. Thermoplastic polyurethane (TPU)/microfibrillated cellulose (MFC) nanocomposite was prepared where MFC was extracted from wood pulp (Yao et al. 2014). WPU grafted CNC-WPU chains obtained through the reaction between hydroxyl group (OH) of CNC and isocyanate of WPU can provide a crystalline structure to form a matrix of CNC/WPU composite (Ray and Sain 2016). CNC can disperse in natural and synthetic rubber latex and produce CNC/rubber latex nanocomposites (Jardin et al. 2020). Bitinis et al. (2013) produced PLA-g-CNC/natural rubber latex nanocomposites and CNC showed a higher affinity with PLA. In another study, CNC mixed with PLA to obtain CNC/PLA nanocomposites (de Paula et al. 2015). CNC and Poly(hydroxybutyrate) (PHB) were used to produce CNC/PHB nanocomposite (Seoane et al. 2017a, b, 2019). TPU and MFC make a matrix following the similar procedure (Yao et al. 2014). CW obtained from esparto (*Alfa tenassissima*) bleached soda pulp was used to prepare CW/poly(styrene-co-hexylacrylate) nanocomposite (Ben Elmabrouk et al 2009). CNC was mixed with glycerol based pre-polymers (glycerol, succinic anhydride and maleic anhydride mixed polymer called poly(glycerol succinate-co-maleate) (poly(GlySAMA)) to make CNC/poly(GlySAMA) nanocomposites (Medeiros et al. 2014). CW enhances the filler-filler and filler-matrix interaction to obtain the nanocomposites (Ray and Sain 2016). MCC/poly(d,l-lactide) (PDLLA) nanocomposite was prepared by dispersing MCC in chloroform followed by mixing with PDLLA. The well dispersion of MCC in PDLLA provided a better MCC/PDLLA nanocomposite (Liu et al. 2014). In another study, MCC was used to prepare MCC/PMMA (poly(methyl methacrylate) nanocomposite. In this case, MCC was converted to amorphous cellulose by dissolving with TFA (trifluoroacetic

acid) which provides a better MCC/PMMA nanocomposite (Tran et al. 2016). CNF obtained from waste brewed tea leaf was used to prepare CNF/WBPE (waterborne polyester) nanocomposite following in situ polymerization technique (Dutta and Karak 2019). Again, CNF obtained from barley husk, polyvinyl alcohol (PVA) and kaolinite clay (KC) were used to fabricate CNF/PVA/KC nanocomposite (Kohli et al. 2019). In another study, PVA was mixed with MFC to produce MFC/PVA nanocomposites (Qiu and Netravali 2013). The surface of cellulose nanofibril (CNF) (obtained from jute fibers) treated by methyl methacrylate (MMA) was used to prepare CNF/polymethyl methacrylate (PMMA) nanocomposite by *in-situ* polymerization referred as MMIPC while it was called as MMEPC when *ex-situ* polymerization technique was applied (Banerjee et al. 2014). Sain et al. (2015) produced CNF/PMMA nanocomposite by in-situ (IPMC) and ex-situ (EPMC) polymerization as well. In another study, Sain et al. (2014) produced CNF/PMMA nanocomposites by in-situ and ex-situ polymerization where CNF was extracted from jute fibers. Micro/nanocrystalline cellulose extracted from jute fibers and PMMA were used to produce MCC/PMMA nanocomposites following in-situ (IPC) and ex-situ (EPC) polymerization Maiti et al. (2013). Surface modified by octadecyl isocyanate CNCs obtained from munguba (*Pseudobombax munguba*) fibers and MCC were used to prepare CNC/PBAT (poly (butylene adipate-co-terephthalate) nanocomposites where octadecyl isocyanate reduces the hydrophilicity and increases the compatibility between CNC and PBT in the matrix (Pinheiro et al. 2019, 2017).

MCC, PLA and polycaprolactone (PCL) was blended and extruded by twin-screw extruder to produce MCC/PLA/PCL nanocomposites (Kalita et al. 2020). CNC obtained from MCC, PLA and poly(hydroxybutyrate) (PHB) were extruded to obtain CNC/PLA/PHB nanocomposites (Arrieta et al. 2014a, b). CNC extracted from waste cotton materials was used to produce a composite of CNC/CB (carbon black)/NR (natural rubber latex) (Li et al. 2018). Poly (butylene succinate) (PBS) and CNF were used to prepare CNF/PBS nanocomposite by compression followed by cooling (Platnieks et al. 2020). Nanocellulose obtained from water hyacinth (*Eichhornia crassipes*) was used to produce nanocelulose/starch nanocomposites where the starch was obtained from bengkuang (*Pachyrhizus erosus*). The used gel was treated with an ultrasonic bath before fabricating the composites (Syafri et al. 2019). CNC and starch derived from sugar palm were also used to manufacture CNC/starch nanocomposites (Ilyas et al. 2018). Another type of nanocomposite, carboxymethyl cellulose-g-polyacrylonitrile (CMC-g-PAN) along with montmorillonite (MMT) were used to obtain CMC-g-PAN/MMT nanocomposite (Sahoo and Jena 2018). In another study, CMC was used to produce nanocomposite (CMC/PCL/SiO_2) incorporation with nano-silica (SiO_2) and poly (ε-Caprolactone (PCL). Different types of natural fiber-based bionanocomposites are presented in Table 1.

Table 1 Natural fibers based bionanocomposites and their properties

Type of natural fibers	Type of nanocomposite	Properties				References
		Biodegradation	Thermal	Strength	Water absorption	
CW	CW/PFA	–	Thermal resistance	–	–	Pranger and Tannenbaum (2008)
CW	CW/poly(styrene-co-hexylacrylate)	–	–	Storage modulus resistance	–	Ben Elmabrouk et al. (2009)
CNC	CNC/poly(GlySAMA)	Biodegradation resistance	Thermal resistance	–	–	Medeiros et al. (2014)
CNC	CNC/WPU	–	Thermal resistance	–	–	Cao et al. (2009))
CNC	CNC/PU	–	–	Storage modulus resistance	–	Pei et al. (2011)
CNC	CNC/rubber latex	–	–	–	Water permeable	Jardin et al. (2020)
CNC	CNC/PBAT	Biodegradable	Thermal resistance	–	–	Pinheiro et al. (2019, 2017)
CNC	PLA-g-CNC/natural rubber latex	Biodegradable	–	–	–	Bitinis et al. (2013)
CNC	CNC/PLA/PHB	Biodegradable	–	–	–	Arrieta et al. (2014a, b)
CNC	CNC/PLA	Biodegradation resistant	–	–	Water resistant	de Paula et al. (2015)
CNC	CNC/starch	Biodegradable	–	–	Water resistant	Ilyas et al. (2018)
CNC	CNC/CB/NR	Biodegradable	Thermal resistance	–	–	Li et al. (2018)

(continued)

Table 1 (continued)

Type of natural fibers	Type of nanocomposite	Properties				References
		Biodegradation	Thermal	Strength	Water absorption	
CNC	CNC/PHB	Biodegradable	Thermal resistance	–	–	Seoane et al. (2017a, b, 2019)
MFC	MFC/TPU	–	–	Storage modulus resistance	–	Yao et al. (2014)
MFC	MFC/PVA	Biodegradation resistant	–	–	–	Qiu and Netravali (2013)
CNF	CNF/ PMMA	–	Thermal resistance	–	Moisture resistance	Banerjee et al. (2014)
CNF	CNF/PMMA	–	Thermal resistance	–	Moisture resistance	Sain et al. (2015)
CNF	CNF/PMMA	Biodegradable	–	–	–	Sain et al. (2014)
CNF	CNF/WBPE	Biodegradable	Thermal resistance	–	–	Dutta and Karak (2019)
CNF	CNF/PVA/KC	Biodegradation resistant	–	–	Water resistant	Kohli et al. (2019)
CNF	CNF/PBS	Biodegradation resistant	–	Storage modulus resistance	–	Platnieks et al. (2020)
MCC	MCC/PMMA	Biodegradable	–	–	–	Maiti et al. (2013)

(continued)

Table 1 (continued)

Type of natural fibers	Type of nanocomposite	Properties				References
		Biodegradation	Thermal	Strength	Water absorption	
–	nanocelulose/starch nanocomposites	–	Thermal resistance	–	Moisture absorb resistant	Syafri et al. (2019)
CMC	CMC-g-PAN/MMT	Biodegradable	Thermal resistance	–	–	Sahoo and Jena (2018)
CMC	CMC/PCL/SiO_2	Biodegradation resistant	–	–	Water resistant	Alikarami et al. (2013)

3 Environmental Aging Conditions

Like other composite materials, bionanocomposites are also affected by different environmental aging conditions like pressure, temperature, humidity and the curing condition.

In case of the natural fiber-based nanocomposites, temperature and moisture influences the most, and these are responsible for biodegradation and strength properties loss. Biodegradation means fragmentation or disintegration of the materials because of the enzymes secreted by microorganisms and loss of mechanical properties (Murray et al. 2015; Paul et al. 2005; Rhim et al. 2013). It occurs through hydrolysis catalyzed by enzymes and oxidation caused by different types of microorganisms, i.e., bacteria, fungi, and algae (Ashaduzzaman et al. 2011; Catia and Franco 2020; Murray et al. 2015; Paul et al. 2005; Qiu and Netravali 2013; Rhim et al. 2013). The suitable conditions important for biodegradations are temperature, pH, relative humidity, moisture and oxygen availability (Murray et al. 2015; Wroblewska-Krepsztul et al. 2018). On the other hand, surface area, hydrophilic or hydrophobic nature, chemical structure, molecular weight, crystallinity, crosslinking and melting temperature of the composite components have also a significant effect on biodegradation (Qiu and Netravali 2013). Cellulose is hydrophilic in nature lead to water absorption and thus, bacterial growth is increased (Lucas et al. 2008; Samal and Sahoo 2009). The decomposition of cellulose causes breaking down the main chain resulting the degradation of composites (Maiti et al. 2013; Sain et al. 2014).

The fragmentation and disintegration happen in two ways—firstly the secreted enzymes by microorganisms cause smaller oligomeric fragments through backbone scission and fractures, and later oligomeric fragments are converted into biomass, minerals and salts, water and gaseous substances, i.e., carbon dioxide and methane (Catia and Franco 2020). Biodegradation causes changes in surface properties since microorganisms' attack on the surface first. Further degradation results in lowering molecular weight through the breaking of backbone chains and thus, it is responsible for reducing the mechanical and thermal properties of the composites (Catia and Franco 2020; Qiu and Netravali 2013). Again, the temperature also influences the weight loss because of the formation of volatile compounds alongside the other environmental factors (Murray et al. 2015). Higher temperature also causes degradation of cellulose and its consequences provide weaker bonding in the matrix resulted in poor strength properties (Pei et al. 2011; Platnieks et al. 2020).

4 Performances Under Environmental Aging Conditions

Nanocellulose is crystalline in nature leading to thermal stability and higher storage of modulus (Pranger and Tannenbaum 2008; Ray and Sain 2016). The hydrophilic nature of cellulose causes water absorption and thus, resulting biodegradation of

cellulose (Jardin et al. 2020). Table 1 shows the aging properties of different types of natural fiber-based bionanocomposites.

4.1 Thermal Resistance

CW/PFA based nanocomposite showed better thermal resistance properties as the degradation started at 80 °C, however, only 5% weight loss until the temperature reached at 323 °C (Pranger and Tannenbaum 2008). CW formed a rigid structure (Ray and Sain 2016) since it had higher crystallinity and elastic modulus due to having strong intermolecular hydrogen bonding. Therefore, it provided better thermal resistance properties (Pranger and Tannenbaum 2008). CNC/WPU composite having 2–10 wt% CNC loading showed better thermal stability as the thermal degradation started at around 250 °C temperature (Cao et al. 2009). Strong interfacial interaction between CNC and WPU, and better dispersion ability enhanced the thermal stability of CNC/WPU composite (Pei et al. 2011; Ray and Sain 2016). MMIPC and IPMC showed better thermal stability due to having better H-bonding between CNF and ester groups of PMMA (Banerjee et al. 2014; Sain et al. 2015). CNF/WBPE based nanocomposites exhibited initial weight loss at 345–355 °C temperature. The cross-linking between glycerol based epoxy and poly(amidoamine) exhibited excellent thermal resistance (Dutta and Karak 2019). Octadecyl isocyanate modified CNC enhanced the thermal resistance of CNC/PBAT nanocomposites which degraded thermally at 340 °C temperature (Pinheiro et al. 2017). Removal of inner layers by surface modification and presence of acid sulphate groups resulted in higher thermal resistance for the surface modified bionanocomposites (Alvarez and Vazquez 2004; Mariano et al. 2016). It was reported that first weight loss for MCC/PMMA nanocomposite happened at 150–200 °C temperature (Fig. 1a, b) (Tran et al. 2016). Nanocel-

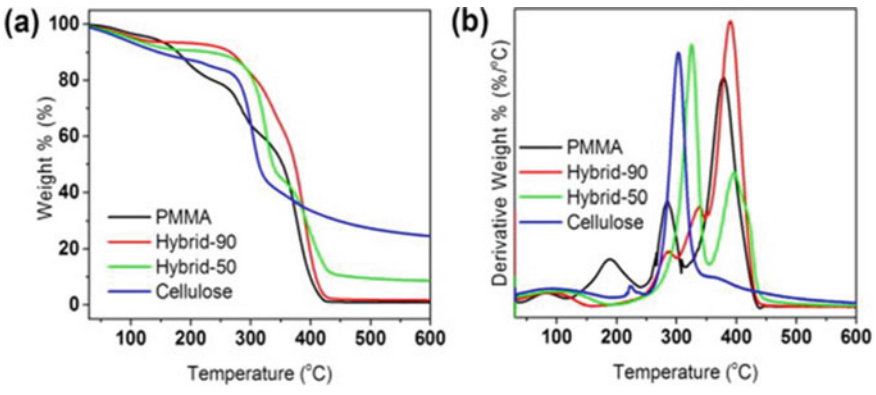


Fig. 1 **a** TGA thermal weight loss plots for pure PMMA, cellulose, Hybrid-50 and Hybrid-90 films, and **b** derivative of the thermograms in (**a**) (Tran et al. 2016)

lulose/starch nanocomposite started losing weight at around 100 °C temperature, and the ultrasonic treatment showed better thermal stability (Syafri et al. 2019). The interfacial adhesion was better for treated composites due to having a less free hydroxyl group (OH) (Abral et al. 2018a, b; Asrofi et al. 2018a) and thus, these composites showed better thermal stability (Syafri et al. 2019). CNC/CB/NR nanocomposites showed higher thermal stability where the weight loss started at 200–300 °C temperature (Li et al. 2018). Scavenging peroxides and free radicals by CB and slower down the diffusion of degradation by NR molecules improved the thermal resistance properties (Li et al. 2018). CNC/poly(GlySAMA) nanocomposites also showed thermal resistance (Medeiros et al. 2014) like CNC/PHB nanocomposites (Seoane et al. 2017a, b, 2019). The adhesion of CNC and matrix in the composites stimulated the thermal stability (Fortunati et al. 2014). Thermal stability of CMC-g-PAN/MMT was better and the weight loss started at 250 °C temperature (Sahoo and Jena 2018) where better dispersion of MMT clay in the matrix increased the thermal stability (Lucas et al. 2008; Shami and Sharifi-Sanjani 2010).

4.2 Strength Properties Resistance

The storage modulus of PU/CNC nanocomposite was stable up to 210–230 °C temperature (Fig. 2b), however, higher temperature degraded cellulose leading lowering the storage modulus of PU/CNC nanocomposites (Pei et al. 2011). TPU/MFC also showed a similar trend for the storage modulus with the variation of the temperature (Fig. 2a) (Yao et al. 2014). The higher content of MFC (5 wt%) showed higher storage of modulus. MFC enhanced the load transfer capability and helped to make a bridge during crack propagation in the matrix due to having a long and elongated structure. Thus, it increased the strength properties of the nanocomposites (Ray and Sain 2016). A similar effect of temperature on storage modulus was observed for CW/poly(styrene-co-hexylacrylate) nanocomposite but

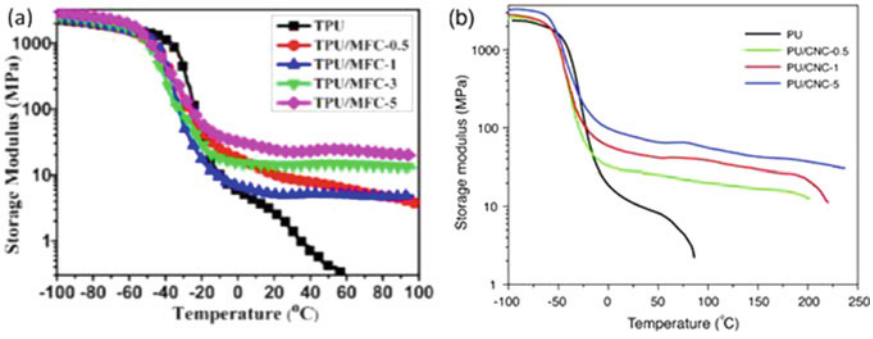


Fig. 2 Storage modulus of **a** neat TPU and the TPU/MFC (Yao et al. 2014), and **b** PU and PU/CNC (Pei et al. 2011) nanocomposites as a function of temperature

5 wt% CW loaded nanocomposite showed stable storage modulus (Ben Elmabrouk et al. 2009). CW provided better bonding in the matrix to obtain a rigid nanocomposite (Ben Mabrouk et al. 2011; Ray and Sain 2016). MCC/PDLLA nanocomposite showed a similar relationship between temperature and storage modulus; higher MCC content composite had a more stable storage of modulus (Liu et al. 2014). CNF/PBS nanocomposite showed higher storage modulus due to having a rigid network in the matrix provided by CNF (Platnieks et al. 2020).

4.3 Moisture Resistance

MMIPC (Banerjee et al. 2014) and IPMC (Sain et al. 2015) showed better moisture resistant properties compared to MMEPC. The *in-situ* polymerization technique allows less free –OH groups compared to ex-situ polymerization. Therefore, the moisture absorption was lower for MMIPC than that of MMEPC (Banerjee et al. 2014; Sain et al. 2015). The higher percentage of CNC enhanced the water absorption and permeability for CNC/rubber latex composites. Hydrophilic CNC caused higher water absorption and permeability of those nanocomposites (Jardin et al. 2020). The higher MCC content in MCC/PDLLA nanocomposite showed higher water absorption properties (Fig. 3a, b) (Liu et al. 2014). Higher hydroxyl group in MCC increased water absorption for higher MCC content composite (Ardizzone et al. 1999). MCC/PMMA nanocomposite showed water absorption resistant property up to 20% of MCC content (Tran et al. 2016). The crystallinity nature of cellulose film for this composite hindered water absorption (Banerjee et al. 2014; Li et al. 2014). Besides, ultrasonic treated nanocelulose/starch nanocomposites showed less water absorption. These treatments enhanced the homogenous distribution of nanocellulose in the starch matrix resulted in a strong hydrogen bond in the matrix. Thus, it

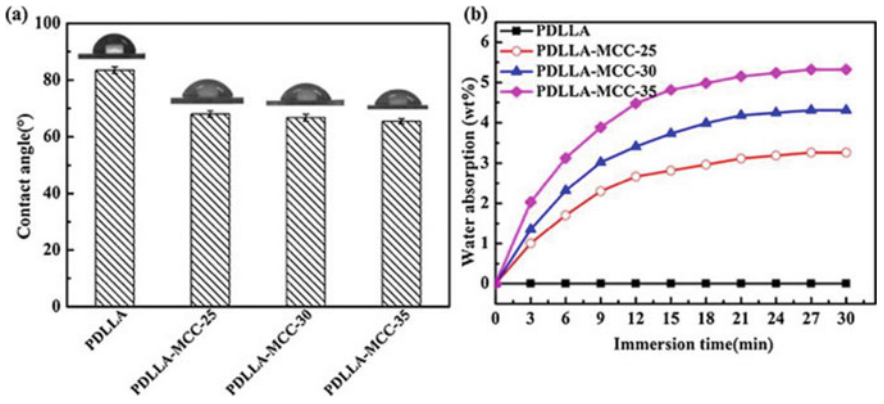


Fig. 3 **a** Water contact angle of the pure PDLLA and PDLLA/MCC composites, and **b** ratio of absorbed water to sample weight versus immersion time (Liu et al. 2014)

caused a barrier of water absorption (Abral et al. 2018b; Asrofi et al. 2018b; Ilyas et al. 2018). Strong hydrogen bonding may allow less free OH group in the matrix leading to provide water resistant properties (Majeed et al. 2013; Minelli et al. 2010). CNC/PLA nanocomposite also showed water resistance as it engulfed the particles. The esterified nanocrystal is hydrophobic and thus, hinders water absorption (de Paula et al. 2015). The higher percentage of CNF content in CNF/PVA/KC composites showed higher water absorption but the use of KC helped to reduce the water absorption (Kohli et al. 2019). The hydrophilicity of CNF enhanced water absorption for CNF based nanocomposites (Hossain et al. 2012). CMC/PCL/SiO_2 nanocomposite showed better water resistant properties; the presence of inorganic compounds hinder to uptaking water in the composite matrix (Alikarami et al. 2013). Therefore, cellulose crystallinity, better compatibility, and inorganic content can influence on water resistant properties of the bionanocomposite although cellulose is hydrophilic in nature.

4.4 Fungal Resistance

For a better understanding of biodegradation, PMMA/MCC nanocomposites samples were buried into the compost. IPC showed higher weight loss, lower molecular weight and higher poly-dispersity indicated biodegradability of the nanocomposites (Fig. 4a) (Maiti et al. 2013). Sain et al. (2014) and Dutta and Karak (2019) observed similar trend in biodegradation for PMMA/CNF and CNF/WBPE nanocomposite prepared by *in-situ* polymerization. Cellulose filler makes a chemical bond with PMMA molecules. Decomposition of cellulose weakens the main chain link point's

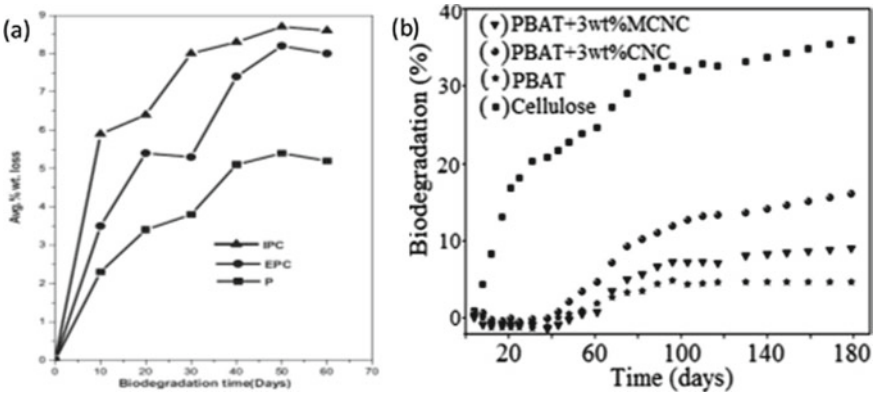


Fig. 4 Biodegradation test of **a** PMMA/MCC nanocomposites (Maiti et al. 2013), and **b** (*filled star*) neat PBAT, nanocomposites with (*filled circle*) 3 wt% CNC, (*filled down-pointing triangle*) 3 wt% MCNC (octadecyl isocyanate modified CNC) and (*filled square*) cellulose (Pinheiro et al. 2017)

leads to break down the long chain and thus, degradation happens for nanocomposites (Maiti et al. 2013; Sain et al. 2014). CNC incorporated CNC/PBAT nanocomposites showed higher biodegradation during soil buried test (Fig. 4b) (Pinheiro et al. 2017, 2019). The consumption of CNC by microorganism during the exposure to the environment reduced the integrity of the composites and increased the porous matrix. Thus, it enhanced biodegradation of CNC based CNC/PBAT nanocomposites (Hassan et al. 2012). The hydrophilicity of CNC, on the other hand, increased the biodegradability of CNC based bionanocomposites (Ferreira et al. 2018; Garcia-Garcia et al. 2018). PLA-g-CNC/natural rubber latex nanocomposites showed better biodegradability (Bitinis et al. 2013). MCC/PLA/PCL based nanocomposites showed 60–90% biodegradability in 100–140 days, and the biodegradation increased with the increase of MCC and PCL content in the nanocomposites (Kalita et al. 2020). Similarly, CNC incorporated CNC/PLA/PHB (Arrieta et al. 2014b) and MCC based MCC/PDLLA nanocomposite (Liu et al. 2014) exhibited biodegradability. The hydrophilicity of MCC enhanced the biodegradability of MCC based nanocomposites (Liu et al. 2014). CNC/PHB nanocomposites containing a higher content of CNC showed higher biodegradation. The hydrophilicity of CNC allows more water absorption leading to hydrolysis of materials and thus, it influences biodegradation (Seoane et al. 2017a, b, 2019). As a bioproduct, the CNC/starch nanocomposites are also biodegradable (Ilyas et al. 2018). Starch absorbs water and enhances the microbial attack resulting quick biodegradability (Kiatkamjornwong et al. 1999; Sahari et al. 2013). The incorporation of CNC improved the biodegradation of CNC/CB/NR nanocomposites (Li et al. 2018). CNC/poly(GlySAMA) nanocomposites lowered biodegradation (Medeiros et al. 2014). In another study, CNC/PLA nanocomposite performed lowering of the biodegradation where esterified CNC hinders the water absorption and thus, it caused less degradation (de Paula et al. 2015). The biodegradability of CNF/PVA/KC nanocomposite decreased when KC was incorporated in the composites (Kohli et al. 2019). KC particles in the composite reduced the diffusion capability in the matrix and thus, it reduced biodegradation of KC incorporated nanocomposites (Fortunati et al. 2012). MFC/PVA nanocomposites showed less biodegradability. Highly crystalline MFC provides crack-bridging ability causing breaking resistance which prevents degradation (Qiu and Netravali 2013). CNF/PBS nanocomposite showed higher resistance against biodegradation. The crystallinity of CNF reduced susceptibility to biodegradation (Platnieks et al. 2020). CMC-g-PAN/MMT nanocomposite had better biodegradable properties (Sahoo and Jena 2018). The hydrophilic nature of MMT increased the water absorption and thus, it increased the growth of bacteria leading to biodegradation (Lucas et al. 2008; Samal and Sahoo 2009). CMC/PCL/SiO_2 nanocomposite showed lower degradation by microbial attacks due to having inorganic SiO_2 in the composite matrix (Alikarami et al. 2013).

5 Conclusions

Natural fibers based bionanocomposites are consisted of nano and macro-sized fibers along with different types of bio and synthetic polymers and other inorganic solids. The used technologies of synthesis of these nanocomposites are ex-situ and in-situ polymerization, and extrusion. These possess higher thermal resistance and storage of modulus properties. The modification of cellulose and presence of inorganic in the matrix can improve the water resistant properties. The incorporation of natural fibers enhances the biodegradation properties of bionanocomposites. The hydrophilic nature of cellulose allows moisture and stimulates the degradation though inorganic content and modified cellulose lower the degradation. The biodegradability nature of bionanocomposites may add a new dimension for utilization them in advanced applications.

References

Abral H, Dalimunthe MH, Hartono J, Efendi RP, Asrofi M, Sugiarti E, Sapuan SM, Park J, Kim H-J (2018a) Characterization of tapioca starch biopolymer composites reinforced with micro scale water hyacinth fibers. Starch-Starke 70:1700287

Abral H, Putra GJ, Asrofi M, Park JW, Kim HJ (2018b) Effect of vibration duration of high ultrasound applied to bio-composite while gelatinized on its properties. Ultrason Sonochem 40(Pt A):697–702

Alikarami M, Abbasi Z, Moradi V (2013) Study of enzymatic degradation and water absorption of composites carboxymethyl cellulose and poly (epsilon-caprolactone) containing SiO2 nanoparticle by cellulase. J Environ Sci Health Part A Toxic/hazardous Substances Environ Eng 48(12):1516–1521

Alvarez VA, Vazquez A (2004) Thermal degradation of cellulose derivatives/starch blends and sisal fibre biocomposites. Polym Degrad Stab 84(1):13–21

Ardizzone S, Dioguardi FS, Mussini T, Mussini PR, Rondinini S, Vercelli B, Vertova A (1999) Microcrystalline cellulose powders: structure, surface features and water sorption capability. Cellulose 6(1):57–69

Arora B, Bhatia R, Attri P (2018) 28-Bionanocomposites: green materials for a sustainable future. In: Hussain CM (ed) New polymer nanocomposites for environmental remediation. Elsevier, A.K. Mishra, pp 699–712

Arrieta MP, Fortunati E, Dominici F, Rayon E, Lopez J, Kenny JM (2014a) Multifunctional PLA-PHB/cellulose nanocrystal films: Processing, structural and thermal properties. Carbohyd Polym 107:16–24

Arrieta MP, Fortunati E, Dominici F, Rayon E, Lopez J, Kenny JM (2014b) PLA-PHB/cellulose based films: mechanical, barrier and disintegration properties. Polym Degrad Stab 107:139–149

Ashaduzzaman M, Das AK, Kayes MI, Shams MI (2011) Natural durability of Akashmoni (*Acacia auriculiformis*) and Sissoo (*Dalbergia sissoo*). Bangladesh J Sci Indus Res 46(2):225–230

Asrofi M, Abral H, Kasim A, Pratoto A, Mahardika M, Hafizulhaq F (2018a) Mechanical properties of a water hyacinth nanofiber cellulose reinforced thermoplastic starch bionanocomposite: effect of ultrasonic vibration during processing. Fibers 6(2)

Asrofi M, Abral H, Putra YK, Sapuan SM, Kim H-J (2018b) Effect of duration of sonication during gelatinization on properties of tapioca starch water hyacinth fiber biocomposite. Int J Biol Macromol 108:167–176

Awad SA, Mahini SS, Tucker SJ, Fellows CM (2019) Evaluation of the performance of microcrystalline cellulose in retarding degradation of two epoxy resin systems. Int J Polym Anal Charact 24(2):150–168

Banerjee M, Sain S, Mukhopadhyay A, Sengupta S, Kar T, Ray D (2014) Surface treatment of cellulose fibers with methylmethacrylate for enhanced properties of in situ polymerized PMMA/cellulose composites. J Appl Polym Sci 131(2)

Ben Elmabrouk A, Thielemans W, Dufresne A, Boufi S (2009) Preparation of poly(styrene-co-hexylacrylate)/cellulose whiskers nanocomposites via miniemulsion polymerization. J Appl Polymer Sci 114(5):2946–2955

Ben Mabrouk A, Magnin A, Belgacem MN, Boufi S (2011) Melt rheology of nanocomposites based on acrylic copolymer and cellulose whiskers. Compos Sci Technol 71(6):818–827

Bitinis N, Fortunati E, Verdejo R, Bras J, Kenny JM, Torre L, Lopez-Manchado MA (2013) Poly(lactic acid)/natural rubber/cellulose nanocrystal bionanocomposites. Part II: properties evaluation. Carbohydrate Polym 96(2):621–627

Cao XD, Habibi Y, Lucia LA (2009) One-pot polymerization, surface grafting, and processing of waterborne polyurethane-cellulose nanocrystal nanocomposites. J Mater Chem 19(38):7137–7145

Catia B, Franco B (2020) General characteristics, processability, industrial applications and market evolution of biodegradable polymers, De Gruyter. Berlin, Boston, pp 147–182

Das AK, Islam MN, Ashaduzzaman M, Nazhad MM (2020) Nanocellulose: its applications, consequences and challenges in papermaking. J Packaging Technol Res

de Paula EL, Mano V, Duek EAR, Pereira FV (2015) Hydrolytic degradation behavior of plla nanocomposites reinforced with modified cellulose nanocrystals. Quim Nova 38(8):1014–1020

Dutta GK, Karak N (2019) Waste brewed tea leaf derived cellulose nanofiber reinforced fully bio-based waterborne polyester nanocomposite as an environmentally benign material. Rsc Adv 9(36):20829–20840

Ferfera-Harrar H, Dairi N (2014) Green nanocomposite films based on cellulose acetate and biopolymer-modified nanoclays: studies on morphology and properties. Iran Polym J 23(12):917–931

Ferreira FV, Dufresne A, Pinheiro IF, Souza DHS, Gouveia RF, Mei LHI, Lona LMF (2018) How do cellulose nanocrystals affect the overall properties of biodegradable polymer nanocomposites: a comprehensive review. Eur Polymer J 108:274–285

Fortunati E, Puglia D, Santulli C, Sarasini F, Kenny JM (2012) Biodegradation of Phormium tenax/poly(lactic acid) composites. J Appl Polym Sci 125:E562–E572

Fortunati E, Puglia D, Kenny JM, Minhaz-Ul Hague M, Pracella M (2013) Effect of ethylene-co-vinyl acetate-glycidylmethacrylate and cellulose microfibers on the thermal, rheological and biodegradation properties of poly(lactic acid) based systems. Polym Degrad Stab 98(12):2742–2751

Fortunati E, Luzi F, Puglia D, Dominici F, Santulli C, Kenny JM, Torre L (2014) Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves. Eur Polym J 56:77–91

Garcia-Garcia D, Lopez-Martinez J, Balart R, Strömberg E, Moriana R (2018) Reinforcing capability of cellulose nanocrystals obtained from pine cones in a biodegradable poly(3-hydroxybutyrate)/poly(ε-caprolactone) (PHB/PCL) thermoplastic blend. Eur Polymer J 104:10–18

Hassan ML, Bras J, Hassan EA, Fadel SM, Dufresne A (2012) Polycaprolactone/modified bagasse whisker nanocomposites with improved moisture-barrier and biodegradability properties. J Appl Polym Sci 125:E10–E19

Hossain KMZ, Ahmed I, Parsons AJ, Scotchford CA, Walker GS, Thielemans W, Rudd CD (2012) Physico-chemical and mechanical properties of nanocomposites prepared using cellulose nanowhiskers and poly(lactic acid). J Mater Sci 47(6):2675–2686

Ilyas RA, Sapuan SM, Ishak MR, Zainudin ES (2018) Sugar palm nanocrystalline cellulose reinforced sugar palm starch composite: degradation and water-barrier properties. In: Jawaid M, Mazlan N (eds) Wood and biofiber international conference, vol 368

Jardin JM, Zhang Z, Hu G, Tam KC, Mekonnen TH (2020) Reinforcement of rubber nanocomposite thin sheets by percolation of pristine cellulose nanocrystals. Int J Biol Macromol 152:428–436

Kalia S, Dufresne A, Cherian BM, Kaith BS, Averous L, Njuguna J, Nassiopoulos E (2011) Cellulose-based bio- and nanocomposites: a review. Int J Polymer Sci 2011

Kalita NK, Bhasney SM, Mudenur C, Kalamdhad A, Katiyar V (2020) End-of-life evaluation and biodegradation of poly(lactic acid) (PLA)/polycaprolactone (PCL)/microcrystalline cellulose (MCC) polyblends under composting conditions. Chemosphere 247

Kiatkamjornwong S, Sonsuk M, Wittayapichet S, Prasassarakich P, Vejjanukroh PC (1999) Degradation of styrene-g-cassava starch filled polystyrene plastics. Polym Degrad Stab 66(3):323–335

Kohli D, Garg S, Jana AK (2019) Physical, mechanical, optical and biodegradability properties of polyvinyl alcohol/cellulose nanofibrils/kaolinite clay-based hybrid composite films. Indian Chem Eng

Li W, Wu YH, Liang WW, Li B, Liu SL (2014) Reduction of the water wettability of cellulose film through controlled heterogeneous modification. ACS Appl Mater Interfaces 6(8):5726–5734

Li CX, Huang F, Wang J, Liang XR, Huang SW, Gu J (2018) Effects of partial replacement of carbon black with nanocrystalline cellulose on properties of natural rubber nanocomposites. J Polym Eng 38(2):137–146

Liu Y, Li Y, Chen HM, Yang G, Zheng XT, Zhou SB (2014) Water-induced shape-memory poly(D, L-lactide)/microcrystalline cellulose composites. Carbohyd Polym 104:101–108

Lucas N, Bienaime C, Belloy C, Queneudec M, Silvestre F, Nava-Saucedo JE (2008) Polymer biodegradation: mechanisms and estimation techniques. Chemosphere 73(4):429–442

Maiti S, Sain S, Ray D, Mitra D (2013) Biodegradation behaviour of PMMA/cellulose nanocomposites prepared by in-situ polymerization and ex-situ dispersion methods. Polym Degrad Stab 98(2):635–642

Majeed K, Jawaid M, Hassan A, Abu Bakar A, Khalil H, Salema AA, Inuwa I (2013) Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. Mater Des 46:391–410

Mariano M, Cercena R, Soldi V (2016) Thermal characterization of cellulose nanocrystals isolated from sisal fibers using acid hydrolysis. Ind Crops Prod 94:454–462

Matsumura H, Sugiyama J, Glasser WG (2000) Cellulosic nanocomposites. I. Thermally deformable cellulose hexanoates from heterogeneous reaction. J Appl Polymer Sci 78(13):2242–2253

Medeiros ES, Offeman RD, Klamczynski AP, Glenn GM, Mattoso LHC, Orts WJ (2014) Synthesis, characterization and nanocomposite formation of poly(glycerol succinate-co-maleate) with nanocrystalline cellulose. J Polym Environ 22(2):219–226

Minelli M, Baschetti MG, Doghieri F, Ankerfors M, Lindstrom T, Siro I, Plackett D (2010) Investigation of mass transport properties of microfibrillated cellulose (MFC) films. J Membr Sci 358(1–2):67–75

Moran JI, Vazquez A, Cyras VP (2013) Bio-nanocomposites based on derivatized potato starch and cellulose, preparation and characterization. J Mater Sci 48(20):7196–7203

Murray KA, Killion JA, Major I, Geever LM (2015) Thermal degradation of bio-nanocomposites. In: Visakh PM, Arao Y (eds) Thermal degradation of polymer blends, composites and nanocomposites, pp 221–245

Paul MA, Delcourt C, Alexandre M, Degee P, Monteverde F, Dubois P (2005) Polylactide/montmorillonite nanocomposites: study of the hydrolytic degradation. Polym Degrad Stab 87(3):535–542

Pei AH, Malho JM, Ruokolainen J, Zhou Q, Berglund LA (2011) Strong nanocomposite reinforcement effects in polyurethane elastomer with low volume fraction of cellulose nanocrystals. Macromolecules 44(11):4422–4427

Pinheiro IF, Ferreira FV, Souza DHS, Gouveia RF, Lona LMF, Morales AR, Mei LHI (2017) Mechanical, rheological and degradation properties of PBAT nanocomposites reinforced by functionalized cellulose nanocrystals. Eur Polymer J 97:356–365

Pinheiro IF, Ferreira FV, Alves GF, Rodolfo A, Morales AR, Mei LHI (2019) Biodegradable PBAT-based nanocomposites reinforced with functionalized cellulose nanocrystals from pseudobombax munguba: rheological, thermal, mechanical and biodegradability properties. J Polym Environ 27(4):757–766

Platnieks O, Gaidukovs S, Barkane A, Sereda A, Gaidukova G, Grase L, Thakur VK, Filipova I, Fridrihsone V, Skute M, Laka M (2020) Bio-based poly(butylene succinate)/microcrystalline cellulose/nanofibrillated cellulose-based sustainable polymer composites: thermo-mechanical and biodegradation studies. Polymers 12(7)

Pranger L, Tannenbaum R (2008) Biobased nanocomposites prepared by in situ polymerization of furfuryl alcohol with cellulose whiskers or montmorillonite clay. Macromolecules 41(22):8682–8687

Qiu KY, Netravali AN (2013) A composting study of membrane-like polyvinyl alcohol based resins and nanocomposites. J Polym Environ 21(3):658–674

Ray D, Sain S (2016) In situ processing of cellulose nanocomposites. Compos A Appl Sci Manuf 83:19–37

Rhim JW, Park HM, Ha CS (2013) Bio-nanocomposites for food packaging applications. Prog Polym Sci 38(10–11):1629–1652

Roy N, Saha N, Kitano T, Saha P (2012) Biodegradation of PVP-CMC hydrogel film: a useful food packaging material. Carbohyd Polym 89(2):346–353

Sahari J, Sapuan SM, Zainudin ES, Maleque MA (2013) Effect of water absorption on mechanical properties of sugar palm fibre reinforced sugar palm starch (SPF/SPS) Biocomposites. J Biobased Mater Bioenergy 7(1):90–94

Sahoo PK, Jena DK (2018) Synthesis and study of mechanical and fire retardant properties of (carboxymethyl cellulose -g-polyacrylonitrile)/montmorillonite biodegradable nanocomposite. J Polymer Res 25(12)

Sain S, Sengupta S, Kar A, Mukhopadhyay A, Sengupta S, Kar T, Ray D (2014) Effect of modified cellulose fibres on the biodegradation behaviour of in-situ formed PMMA/cellulose composites in soil environment: isolation and identification of the composite degrading fungus. Polym Degrad Stab 99:156–165

Sain S, Ray D, Mukhopadhyay A (2015) Improved mechanical and moisture resistance property of in situ polymerized transparent PMMA/cellulose composites. Polym Compos 36(9):1748–1758

Samal R, Sahoo PK (2009) Development of a biodegradable rice straw-g-poly(methyl methacrylate)/sodium silicate composite flame retardant. J Appl Polym Sci 113(6):3710–3715

Sanchez-Safont EL, Gonzalez-Ausejo J, Gamez-Perez J, Lagaron JM, Cabedo L (2016) Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/purified cellulose fiber composites by melt blending: characterization and degradation in composting conditions. J Renew Mater 4(2):123–132

Seoane IT, Cerrutti P, Vazquez A, Manfredi LB, Cyras VP (2017a) Polyhydroxybutyrate-based nanocomposites with cellulose nanocrystals and bacterial cellulose. J Polym Environ 25(3):586–598

Seoane IT, Manfredi LB, Cyras VP, Torre L, Fortunati E, Puglia D (2017b) Effect of cellulose nanocrystals and bacterial cellulose on disintegrability in composting conditions of plasticized PHB nanocomposites. Polymers 9(11)

Seoane IT, Cerrutti P, Vazquez A, Cyras VP, Manfredi LB (2019) Ternary nanocomposites based on plasticized poly(3-hydroxybutyrate) and nanocellulose. Polym Bull 76(2):967–988

Shami Z, Sharifi-Sanjani N (2010) The role of Na-montmorillonite on thermal characteristics and morphology of electrospun PAN nanofibers. Fibers Polym 11(5):695–699

Syafri E, Sudirman M, Yulianti E, Deswita, Asrofi M, Abral H, Sapuan SM, Ilyas RA, Fudholi A (2019) Effect of sonication time on the thermal stability, moisture absorption, and biodegradation of water hyacinth (Eichhornia crassipes) nanocellulose-filled bengkuang (*Pachyrhizus erosus*) starch biocomposites. J Mater Res Technol Jmr&T 8(6):6223–6231

Tran TN, Paul U, Heredia-Guerrero JA, Liakos I, Marras S, Scarpellini A, Ayadi F, Athanassiou A, Bayer IS (2016) Transparent and flexible amorphous cellulose-acrylic hybrids. Chem Eng J 287:196–204

Vercelheze AES, Oliveira ALM, Rezende MI, Muller CMO, Yamashita F, Mali S (2013) Physical properties, photo- and bio-degradation of baked foams based on cassava starch, sugarcane bagasse fibers and montmorillonite. J Polym Environ 21(1):266–274

Wroblewska-Krepsztul J, Rydzkowski T, Borowski G, Szczypinski M, Klepka T, Thakur VK (2018) Recent progress in biodegradable polymers and nanocomposite-based packaging materials for sustainable environment. Int J Polym Anal Charact 23(4):383–395

Yang XP, Biswas SK, Han JQ, Tanpichai S, Li MC, Chen CC, Zhu SL, Das AK, Yano H (2020) Surface and interface engineering for nanocellulosic advanced materials. Adv Mater

Yao XL, Qi XD, He YL, Tan DS, Chen F, Fu Q (2014) Simultaneous reinforcing and toughening of polyurethane via grafting on the surface of microfibrillated cellulose. ACS Appl Mater Interfaces 6(4):2497–2507

Influence of Moisture Absorption on Physico-Chemical Properties of Natural Fiber-Based Hybrid Composites

Md Sarif Sakaeyt Hosen, Md Jaynal Abedin, Md Enamul Hoque, and Md Zillur Rahman

Abstract Natural fiber-based hybrid composites have received the attention of many researchers for their excellent mechanical properties. However, moisture absorption into the hybrid composites affects the properties during their application. Hemicellulose and cellulose of the fiber are mainly accountable to moisture absorption. This chapter discusses the effects of moisture absorption on the mechanical and physical properties of natural fiber-based hybrid composites. Physical properties such as dimensional instability and glass transition temperature (T_g), and mechanical properties (tensile, flexural, fracture, and impact) decrease when the natural fibers absorb the moisture. This is predominantly owing to the reduction in interfacial bonding between the fiber and the matrix. Since water molecules works like a plasticizer, strain to failure decreases, and strain energy release increases. Understanding the moisture absorption of hybrid composites can give insight into increasing their durability and performance.

Keywords Hybrid composite · Moisture absorption · Natural fiber · Synthetic fiber · Mechanical properties · Physical properties

1 Introduction

Natural fiber composites and Hybrid composites have drawn the attention of many researchers and interest in developing them is growing day by day. Hybridization may occur between natural-natural fibers and natural-synthetic fibers. Natural fibers are

M. S. S. Hosen · M. J. Abedin
Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

M. E. Hoque (✉)
Department of Biomedical Engineering, Military Institute of Science and Technology (MIST), Dhaka, Bangladesh

M. Z. Rahman
Department of Mechanical Engineering, Bangabandhu Sheikh Mujibur Rahman Aviation and Aerospace University (BSMRAAU), Dhaka, Bangladesh

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_16

used as a reinforcing material because of their superior properties (Asim et al. 2015; Haniffah et al. 2015; Tshai et al. 2014). Moreover, natural fibers are cheap, biodegradable, reusable, abundant, lightweight, non-abrasive, environmentally friendly, and cheaper than conventional synthetic fibers (Salit et al. 2015). The practice of using hybrid composites is becoming increasingly common because of their higher mechanical properties than single fiber composites. On the contrary, natural fibers have some disadvantages, such as moisture absorptive, less strengthy, and relatively less durable. Natural fibers can be hybridized with natural or synthetic fibers to overcome some of these drawbacks. Many researchers have already studied natural fibers hybridization, for example, kenaf/PET (Dan-mallam et al. 2015), kenaf/glass (Atiqah et al. 2014), jute/glass (Braga and Magalhaes 2015), and orka/glass (Sule et al. 2014). However, the hydrophilic nature of the natural fiber adversely affects the mechanical properties of hybrid composites. Composites absorb moisture through micro holes in the polymer chain, defects at the fiber-matrix interfaces, and cracks. Moisture absorption causes fiber swelling, crack formation, dimensional instability, and weight gain. Therefore, this chapter aims to study the influence and behavior of moisture absorption in hybrid composites used in automobile, aerospace, military, marine and civil engineering applications.

2 Hybrid Composites

Hybrid composite is a promising material for various structural and non-structural applications for its excellent mechanical properties and low production cost. This composite is manufactured by incorporating two or more different types of fibers into a single matrix. If two types of fiber are used to make a hybrid composite, one type of fiber needs to have lower modulus and/or lower cost, for example, glass or kevlar, and another type of fiber need to have higher modulus and/or higher cost, for example, boron or carbon fiber (Safri et al. 2018). The composite made by fibers of a low modulus is more damage resistant and can be produced with low cost. In contrast, another expensive fiber with a higher modulus adds significant load-bearing capability to the composites. As a result, hybrid composites are more economical and have some distinct advantages over other composites. Some traditional composites made of expensive fibers can be replaced by hybrid composites even using nanoparticles. Hybrid composite has superior mechanical properties (high stiffness and strength to weight ratio), impact energy absorption, thermal distortion resistance, durability performance (e.g. corrosion resistance), electrical properties, optical properties (Sagadevan et al. 2017a, b, 2018), and low manufacturing cost (Dong et al. 2016). They can diversely be applied in aircraft, automobile, military, marine, and civil engineering applications.

Hybrid composites can generally be classified into two types: fiber-hybrid composite and matrix-hybrid composite. Matrix-hybrid composite is produced by the curing process in which the thermoplastic fiber dissolves into the thermoset

matrix, whereas when the thermoplastic fiber remains in fiber form, it is referred to as fiber-hybrid composite (Fong et al. 2015).

The energy absorption of hybrid composite loaded with thermoplastic fiber is significantly improved by plastic deformation. Glass fiber-based composites absorbed almost the same amount of energy as matrix hybrid composites. This indicates that the fiber properties affect the total energy absorption of the composite. Notably, different matrices also contribute to the variation in energy absorption of the hybrid composite.

Two kinds of hybrid effects can be seen in the hybrid composite: positive hybrid effect (i.e., a rise in properties over conventional composites) and negative hybrid effect (i.e., a decline in properties over conventional composites). Such effects are typically caused by three major factors, such as the relative volume fraction of two fibers, load configuration, and fiber arrangement (Safri et al. 2018). Natural and synthetic fibers can be used as reinforcement in hybrid composites in three different combinations, including mixing different synthetic fibers, natural fibers, and synthetic and natural fibers, as discussed below.

2.1 Synthetic-Synthetic Fiber-Reinforced Hybrid Composites

Synthetic fiber can generally be utilized for structural purposes due to its lightweight and standard mechanical properties, which can even replace certain metallic materials. When two synthetic fibers, low stiffness glass fibers (inexpensive) and high stiffness carbon/graphite fiber (expensive), are combined to produce hybrid composites, they can offer some excellent mechanical properties at a relatively low cost. For example, the hybrid composite comprised of carbon and glass fibers has a higher ultimate tensile strength compared to carbon fiber composites (Safri et al. 2018). Some synthetic-synthetic fiber-reinforced hybrid composites can be made using Kevlar-carbon-glass fibers, carbon-Kevlar fibers, glass-carbon fibers, and so on.

2.2 Synthetic-Natural Fiber-Reinforced Hybrid Composites

Natural fibers have widely been used due to their renewability, low-cost production, low density, and high stiffness and strength. However, natural fiber has some drawbacks, for example, low durability, lower impact strength, and higher moisture absorption. For addressing these disadvantages, some attempts were made using synthetic-natural fiber-based hybrid composite to enhance the thermo-mechanical properties of the natural fiber based composites. Carbon or glass fiber, for example, has better moisture absorption resistance and higher mechanical properties compared to natural fibers. Thus, composites consisted of synthetic fiber (e.g., glass) and plant

fiber (e.g., flax) can display improved mechanical properties, along with low moisture sensitivity and low production cost. Hybridizing hydrophilic plant fiber with hydrophobic synthetic fiber makes a composite with high moisture absorption resistance, thereby preventing degradation of composite properties. Glass-jute fibers, carbon-flax fibers, and glass-sisal fibers are the synthetic-natural fiber combinations to manufacture hybrid composites.

2.3 Natural-Natural Fiber-Reinforced Hybrid Composites

Although natural fibers have many advantages, their characteristics are highly variable due to differences in their origin. The structural use of natural fiber-based composites, particularly for exterior applications, is less successful because of their hydrophilic nature (Rahman 2021). Different regions of fiber origin and associated environmental conditions, and various retting processes have a great impact on the size, shape, and strength of the fiber. However, plant fiber-reinforced composite can be used effectively in structural applications for its excellent mechanical properties stemmed from higher cellulose content of approximately 70%, where cellulose exhibits tensile stiffness of 138 GPa as well as strength of >2 GPa (Rahman 2021). Hybridization of two different natural fibers also shows good mechanical properties at a low production cost. However, several factors (fiber-matrix, fiber orientation, porosity, and fiber-matrix interface) regulate the performance of Hybrid composites produced from natural fibers.

Several natural-natural fiber-reinforced hybrid composites, including sisal-bamboo-banana-jute fibers, jute-sisal fibers, and oil palm-jute fibers, have been manufactured over the years. Banana or kenaf fiber-reinforced composites have lower mechanical strength than banana-kenaf fibers hybrid composites (Thiruchitrambalam et al. 2009). Also, hybridization of jute fiber and oil palm empty fruit bunches (EFB) fiber in a combination of jute-EFB-jute fibers provides outstanding flexural strength than jute-jute fibers composites (Jawaid et al. 2014).

3 Moisture Absorption Behavior

3.1 Moisture Absorption

Moisture absorption in natural fiber-based hybrid composites has become one of the major concerns due to its adverse effect on changing properties. This can also make limited use of such composites in structural and non-structural applications (Mochane et al. 2019). The main constituents of natural fibers are cellulose, lignin, hemicellulose, and other non-cellulose components. All-natural fiber constituents do not cause moisture absorption; only those with a larger extent of hydroxyl groups (–OH),

such as cellulose and hemicellulose, lead to moisture absorption. Lignin contains a low hydroxyl to carbon ratio and is hydrophobic. In contrast, cellulose is the main constituent of natural fiber, which has a high hydroxyl to carbon ratio; only a limited portion of it is water accessible due to cellulose's semi-crystalline nature. Water molecules are unable to penetrate the crystalline region of the cellulose, but they can access the amorphous portion. Hemicellulose (which is mainly amorphous) is susceptible to water molecules. (Barkoula and Peijs 2011; Mokhothu and John 2015). When natural fibers absorb water molecules, they lead to fiber swelling because of the presence of water molecules into the microfibrils, otherly named as the temporary microcapillary network. Then, the penetrated H_2O molecules can either form a single layer or a multilayer. All water molecules are attracted directly by available hydroxyl groups, but only certain amounts of water molecules can interact intimately with available hydroxyl groups when they form a multilayer. The percentage of moisture absorption of various natural fiber-based hybrid composites increases with the water immersion time, as depicted in Fig. 1 (Venkateshwaran et al. 2011). Other authors also show similar results (Bhagat, Biswas, and Dehury 2014; Wang, Sain, and Cooper 2006).

Moisture absorption into polymer composites which are natural fiber reinforced is influenced by several factors, including fiber volume fraction, degree of crosslinking and crystallinity, fiber type, temperature, diffusivity, and response between polymer and water molecules (Deshpande and Rangaswamy 2016; Zhang et al. 2014). As long fibers have a larger void space, moisture absorption increases with increasing fiber length. As a result, water molecules have more space to penetrate. Increased fiber

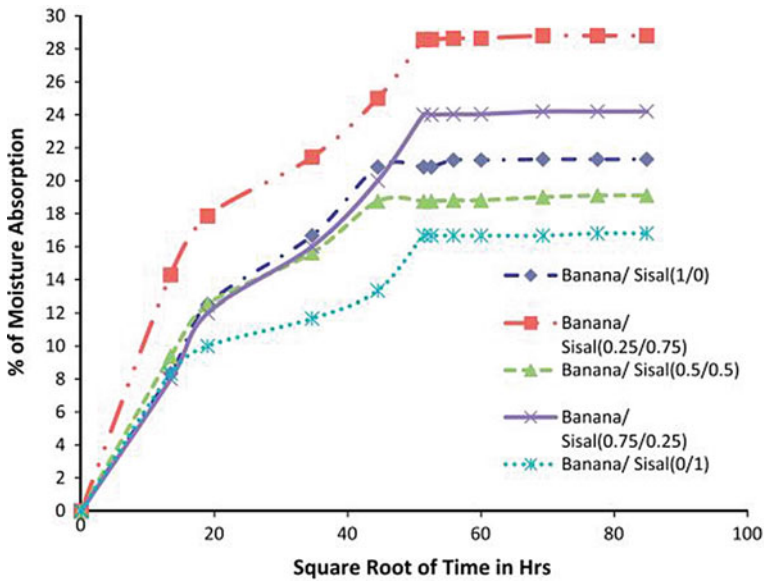


Fig. 1 Moisture absorption behavior of various hybrid composites (Venkateshwaran et al. 2011)

loading also raises moisture absorption. The rate moisture absorption of a composite with a 10 wt% coir fiber loading is higher than that of a composite with a 5 wt% coir fiber loading.

3.2 Moisture Absorption Mechanism

Moisture absorption mainly occurs in the composite materials following the diffusion mechanism. Diffusion is the transportation of substances from a more concentrated portion to a less concentrated portion of the system as a result of random molecular motion. Water molecules diffuse into composite materials in three ways (Akil et al. 2014; Panthapulakkal and Sain 2007; Zhou and Lucas 1995):

1. Water molecules directly enter the micro-sized gaps between the polymer chains.
2. Water molecules transport in the matrix through micro-cracks, formed by fiber swelling.
3. Water molecules enter the interfaces and flow between the fibers and polymers, owing to the poor wetting.

When natural fiber-based hybrid composite materials are exposed to an ambient environment, the high hydroxyl to carbon ratio and the amorphous portion of the fiber cause moisture absorption and then fiber swelling. Fiber swelling causes the bonds at fiber-matrix interfaces to disintegrate, resulting in cracks, as shown in Fig. 2. The leaching of water-soluble substances from the fiber surface induces the formation of osmotic pressure pockets (see Fig. 2) (Ashik et al. 2018; Azwa et al. 2013). Moreover, the penetrated water molecules can act as a plasticizer, reducing load transfer efficiency in various parts of the composites and ultimately resulting in mechanical properties (Alomayri et al. 2014; Mochane et al. 2019).

Moisture absorption tests of composite materials are generally conducted following ASTM D 570-98, and the moisture absorbed into the fiber of the composite is calculated by

$$MB = \left(\frac{M-m}{m}\right) \times 100\% \tag{1}$$

where MB is the moisture absorbed into the fiber in percentage, M is the mass of the composite after absorbing moisture, and m is the initial mass. Fiber thickness varies because of the moisture absorption, and the extent of thickness swelling (TS) or dimensional stability can be estimated by

$$TS = \left(\frac{T_{f-T_i}}{T_i}\right) \times 100\% \tag{2}$$

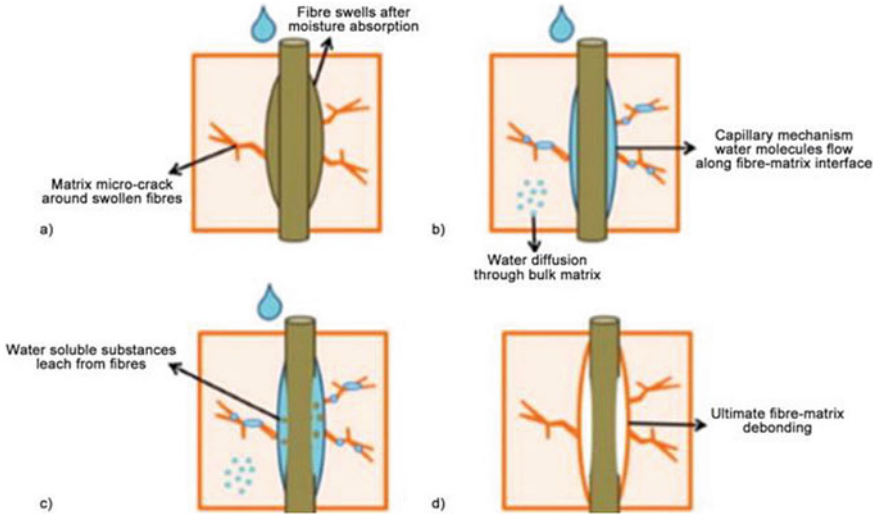


Fig. 2 Moisture absorption effect on fiber-matrix interfaces, **a** micro crack formation as a result of fiber swelling, **b** penetration and transportation of H_2O molecules by the micro-cracks, **c** leaching of water-soluble substance, and **d** bonding disintegration at the fiber-matrix interface (Mochane et al. 2019)

where, TS is the fiber thickness swelling in percentage, T_f is the fiber thickness after absorbing moisture, and T_i is the initial fiber thickness. Moisture absorption in composites materials is occurred by several mechanisms, but the diffusion mechanism is most widely used to model the overall effect. Furthermore, in accordance with Fick's theorem, the moisture absorption process follows the diffusion mechanism and kinetics. The Fickian diffusion coefficient (D) can be utilized for estimating the penetration of H_2O molecules into the composite.

$$D = \left(\frac{TS}{4M_{\max}} \right) \tag{3}$$

where, T refers the initial thickness of the composite, $M_{\max}$ is the maximum moisture absorbed into the composite at equilibrium, and S refers the initial slope of the moisture absorbed in pursuance of the sorption curve (see Fig. 1) that can be expressed as

$$S = \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \tag{4}$$

The efficiency of H_2O molecules movement along the polymer segments can be characterized by the diffusion coefficient. The permeability of H_2O molecules by the composite materials relies on the fiber's moisture absorption in the composite.

Hence, the sorption coefficients of the fiber are related to its equilibrium sorption, which can be determined using Eq. (5).

$$C = \frac{M_{\max}}{M_t} \tag{5}$$

where M_t and $M_{\max}$ are the molar percentages of absorbed moisture after t time and infinity time, respectively. The permeability coefficient (P) can be estimated ny the following equation:

$$P = D \times C. \tag{6}$$

4 Effects of Moisture on Physical Properties

4.1 Glass Transition Temperature

The glass transition temperature (T_g) is related to the maximum service temperature of the hybrid composite (Jankowsky et al. 1994). A study on unidirectional hybrid composites showed that moisture absorption lowers the T_g (Barjasteh and Nutt 2012). A decrease in T_g is observed considering one part of a specimen (capped) and another part of the same specimen (uncapped) in a humid environment for several weeks above saturation (Barjasteh and Nutt 2012), as shown in Fig. 3. When the specimen reaches the saturation point, T_g changing rate reduces because H_2O molecules diffuse into the matrix, retarding Van der Waals and hydrogen bonds and increasing chain

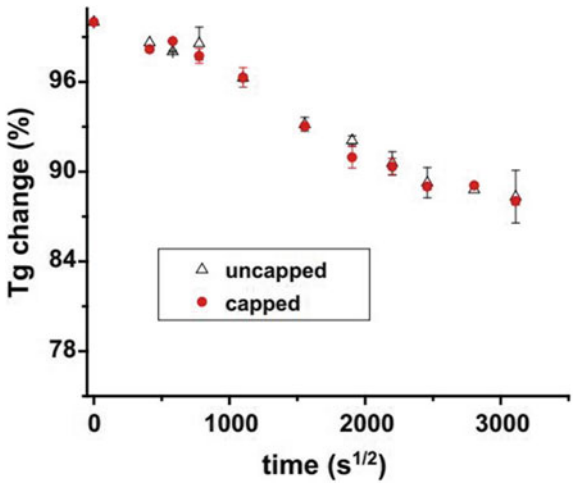


Fig. 3 Variation in the percentage of glass transition temperature with the square root of time (Barjasteh and Nutt 2012)

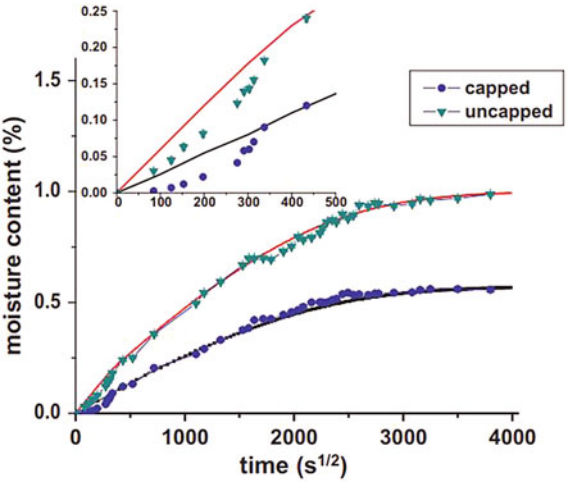


Fig. 4 Moisture content variations for capped and uncapped composite rods as a function of the square root of time (Barjasteh and Nutt 2012)

mobility (Zhou and Lucas 1999). Additionally, the uncapped specimen has a lower moisture diffusion rate than the capped specimen. However, a noticeable decrease in T_g occurs for the capped and uncapped specimens.

4.2 Weight

The weight of the Hybrid composite increases due to moisture absorption. The moisture content rises with exposure time for both capped and uncapped specimens before reaching saturation. Figure 4 depicts the moisture content variation with the time for both capped and uncapped specimens at 60 °C and 80% relative humidity, with the top curve showing moisture content variation for short exposure time. Some Fickian curve deviations happen for short exposure time. The mechanism of the deviation from Fickian behavior is unknown due to the complexity of the process. However, Fickian deviation is negligible under short time exposure, except for the small initial duration and associated data of the curve. Notably, the saturation level of the capped specimen (~0.5%) is less than that of the uncapped specimen (~1%). So, the uncapped specimens absorb more moisture than the capped specimens due to simultaneous longitudinal and radial diffusions of water molecules.

4.3 Dimensional Stability

The presence of more cellulose content in hybrid composite decreases thickness swelling (Edhirej et al. 2017). The dimensional instability of the hybrid composite is occurred by thickness swelling. The percentage of thickness swelling of oil palm

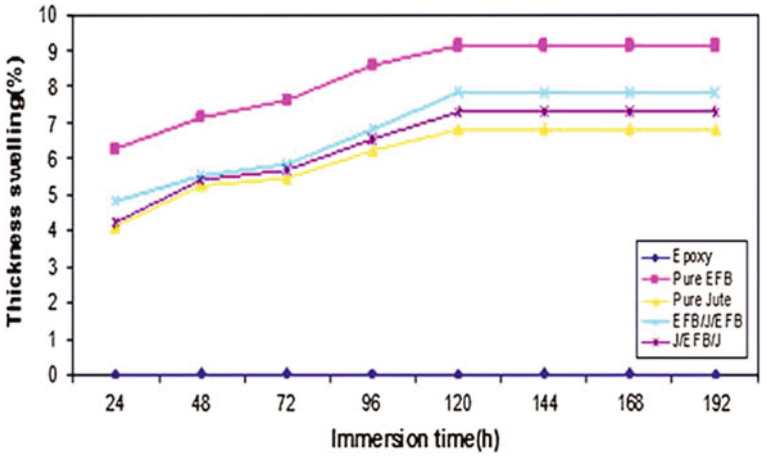


Fig. 5 Thickness swelling of oil palm empty food bunch-jute fiber-reinforced epoxy hybrid composites (Jawaid et al. 2011)

empty food bunch (EFB)-jute fiber-reinforced epoxy hybrid composite is illustrated in Fig. 5. The water absorption (i.e., 21.39%) of pure EFB is higher than epoxy, pure jute, EFB-jute-EFB, and jute-EFB-jute, resulting in the maximum thickness swelling (i.e., 9.12%) of the pure EFB composites. This is because of the presence of high porosity or voids on the surface of pure EFB composites. However, hybridization of EFB-jute-EFB and jute-EFB-jute exhibits moderate dimensional stability, with 11.2 and 6.02% water absorption, respectively. This also demonstrates how layering patterns affect thickness swelling.

5 Effects of Moisture on Mechanical Properties

5.1 Tensile Properties

The absorbed moisture into the Hybrid composites negatively affects its tensile properties. Ahmad et al. (2018) observed the moisture effect on the tensile properties of woven hemp composites (HH), woven polyethylene terephthalate (PET) composites (PP), and interwoven hemp /PET hybrid composites in the hemp direction (HP) and PET direction (PH), as shown in Fig. 6. The dry interwoven hybrid composite has a tensile strength of 74 MPa, whereas the wet specimen (after 1400 h of water immersion) displays a tensile strength of 56 MPa. Tensile strength gradually decreases with increasing water aging time.

Dry hybrid composites show the elastic modulus of 3.8 GPa, and it then steadily decreases up to 24 h of water aging. After that, the elastic modulus significantly declines to 1.9 GPa at 1400 h of water aging. The reduction in fiber-matrix interfacial

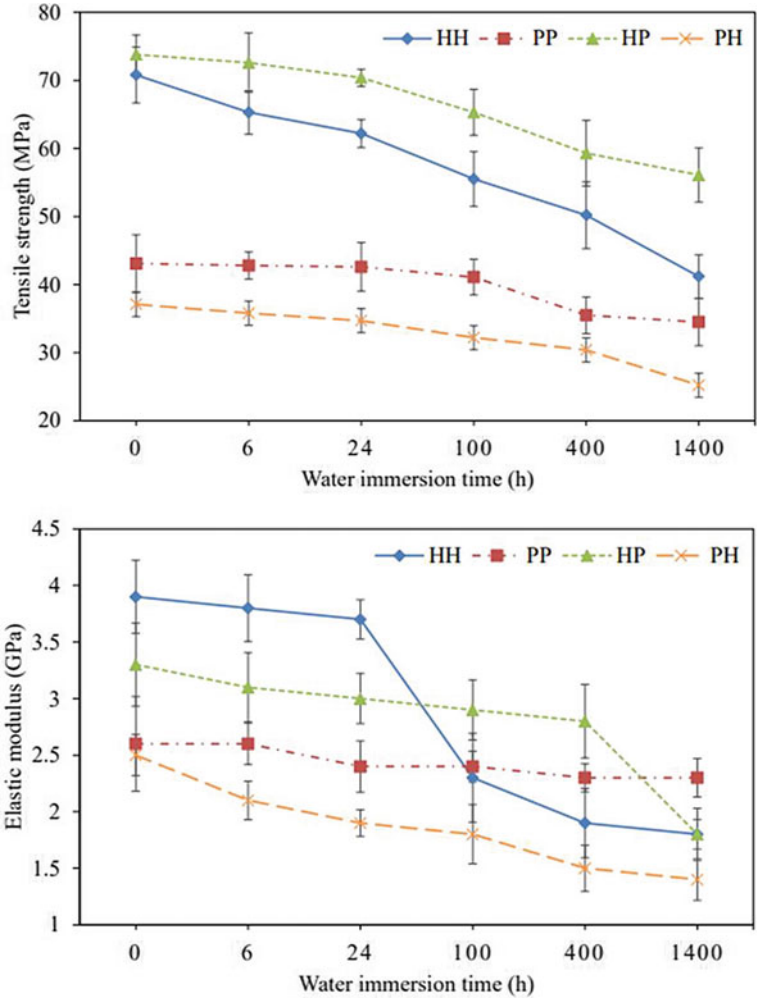


Fig. 6 Tensile properties of HH, PP, HP, and PH (Ahmad et al. 2018)

bonding reduces the tensile properties. The presence of cellulose content in the fiber allows the water absorption through the microcracks' interfaces, resulting in a decrease in the stiffness of the fiber. Also, the interface experiences shear stress, leading to the deboning between the fiber and matrix. However, hemp hybridization with PET improves tensile properties (Ahmad et al. 2018). Figure 7 depicts the tensile strength of roselle-sisal polyester (RSPE) hybrid composites as a function of moisture, fiber length, and fiber content.

Roselle/sisal polyester hybrid composites (with fiber weight fractions of 0.10 and 0.30) have tensile strengths of 32.4, and 48.8 MPa for 50 mm fiber length at the dry condition. For fiber length of 50 mm at wet condition, the tensile strength

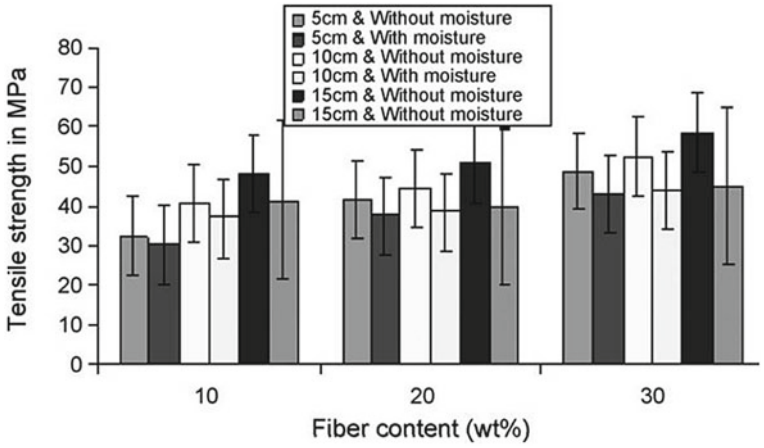


Fig. 7 Effects of moisture, fiber length, and fiber content on the tensile strength of RSPE hybrid composites (Athijayamani et al. 2009)

reduces to 30.1 and 43.1 MPa for 10 and 30 wt%, respectively (Athijayamani et al. 2009). Tensile strength increases with fiber content and fiber length at wet as well as dry conditions. Maslinda et al. (2017) reported the tensile properties of kenaf-hemp hybrid composites (KH) and kenaf-jute hybrid composites (KJ) at dry as well as wet conditions. After water absorption, the tensile strengths of KJ and KH are reduced by 72 and 69%, respectively, compared to the dry condition, whereas the reduced tensile moduli of KJ and KH are 81 and 79%, respectively. They also show higher tensile strain at failure in the wet condition than the dry condition. This is because water fills the voids and cracks in the material and acts as a plasticizer, making it more ductile, which contributes to increasing strain as the aging period progresses. Overall, moisture absorption has a significant impact on tensile properties.

5.2 Fracture Toughness

The double cantilever beam method is commonly used for evaluating inter-laminar fracture toughness (G_{IC}). It can be determined using Eqs. (7–9). These three equations are based on linear elastic fracture mechanics theory (Prasad et al. 2011). Equation (7) is based on the modified compliance calibration method as follows.

$$G_{IC} = \frac{3F^2C^{\frac{2}{3}}}{2nbh} \tag{7}$$

where G_{IC} is the critical energy release rate, F is the applied load, C is the displacement divided by applied load, n is the linear slope of the least square fit of log

(compliance) versus log (delamination length), b is the sample width, and h is the beam thickness.

Equation (8) is based on the modified beam theory, which is given by

$$G_{IC} = \frac{3F\delta}{2b(a + |\Delta|)} \tag{8}$$

where δ is the load point displacement (mm), a is the delamination length *and* Δ is the crack length factor.

Equation (9) is based on the compliance calibration method as follows.

$$G_{IC} = \frac{nF\delta}{2ba} \tag{9}$$

The fracture toughness of flax vinyl ester (FVE) composites and flax-basalt fiber vinyl ester unstitched (FBVEu) and stitched (FBVEs) hybrid composites were examined (Almansour et al. 2017). Figure 8 shows the load versus displacement curve, which is divided into three stages. Stage I shows the elasticity up to 140 and 125 N for the FBVEu and FBVEs hybrid composites, respectively, in a dry condition. These materials show low elasticity after water aging. Stage II represents the plastic nature of a material. Crack initiation occurs in this stage, and FBVEu and FBVEs hybrid composites require less force to initiate cracks in wet conditions than dry conditions. Stage III demonstrates the crack propagation to an ultimate failure. As water absorption weakens the fiber-matrix interfacial bonding, less force is required for crack initiation, propagation, and ultimate fracture in wet conditions.

The ductility of the hybrid composites is the same in dry and wet conditions. The strain energy release rate for crack initiation and propagation in FVE composite, and

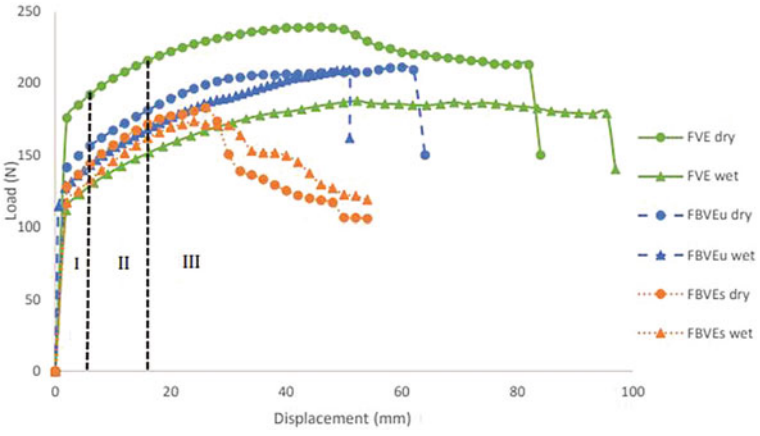


Fig. 8 Applied load versus displacement curves for FVE composite, and FBVEu and FBVEs hybrid composites at both dry and wet conditions (Almansour et al. 2017)

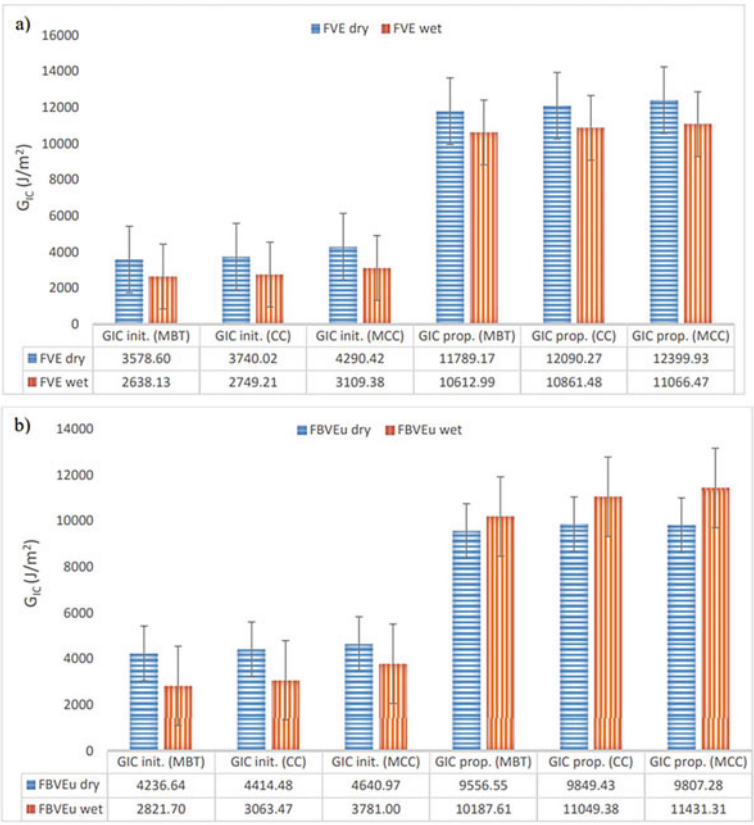


Fig. 9 Strain energy release rates for FVE composite, and FBVEu and FBVEs hybrid composites at dry and wet conditions (Almansour et al. 2017)

FBVEu and FBVEs hybrid composites under dry and wet conditions are illustrated in Fig. 9. For the unstitched specimens, $G_{IC\ ini}$ reduces by 23%, and $G_{IC\ pro}$ increases by 15.3% due to water absorption relative to the dry specimen. In contrast, $G_{IC\ ini}$ and $G_{IC\ pro}$ for the stitched specimens increase by 4.2 and 19.63%, respectively, over the dry sample.

5.3 Impact Strength

The influence of moisture on flax-basalt hybrid composites was discussed by Živković et al. (2017). Hybrid composites show impact energies of 15.49 and 24.26 J when impact heights of 2.5 and 3 m, respectively, at the dry condition, while impact energies of 15.85 and 22.66 J are observed at the wet condition. Since basalt fiber

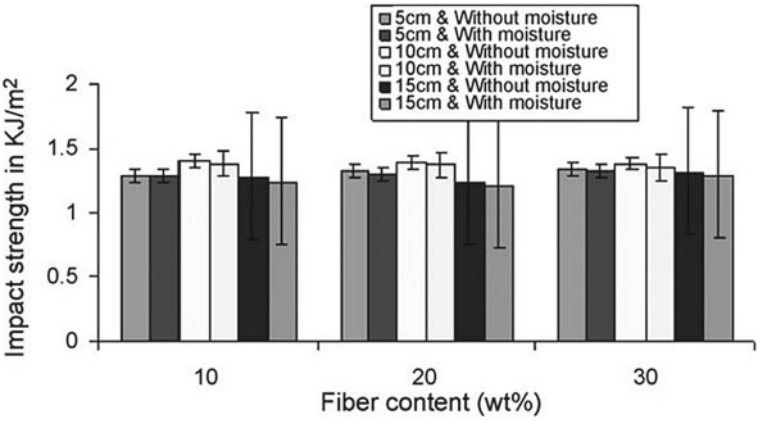


Fig. 10 Moisture, fiber content, and fiber length effects on the impact strength of RSPE hybrid composites (Athijayamani et al. 2009)

resists water absorption, hybrid composites have better structural integrity (strong fiber-matrix bonding) even after water aging. The impact strength of RSPE hybrid composites is also adversely affected by moisture absorption. Figure 10 depicts the effects of moisture, fiber content, and fiber length on the impact strength of RSPE hybrid composites at wet as well as dry conditions.

5.4 Flexural Properties

The flexural properties of the hybrid composites are also influenced by moisture absorption. Ahmad et al. (Ahmad et al. 2018) observed the moisture absorption effect on the flexural properties of HH, PP, HP, and PH (see Fig. 11). The HP hybrid composites have a flexural strength of 102 MPa and a flexural modulus of 4.9 GPa under dry condition.

After water immersion of the specimen for 1400 h, the reductions in flexural strength and modulus are 23 and 45%, respectively. The cellulose in the hemp fiber absorbs water because it contains many OH^- groups, and H^+ attached to OH^- promotes hydrogen bonds between molecules in the fiber and matrix (Yahaya et al. 2016). So, the mechanical interlocking of fiber-matrix interfaces becomes weaker. As a result, less stress is needed to break the bond between the fiber and matrix, and reduction in flexural properties occurs in the wet condition. Figure 12 shows the changes in the flexural strength of RSPE hybrid composites with moisture absorption.

The flexural strengths of RSPE hybrid composites are 51.3 and 64.1 MPa for fiber contents of 10% and 30% by weight, respectively, and fiber length of 50 mm. After water absorption, the flexural strengths of hybrid composites with fiber weight

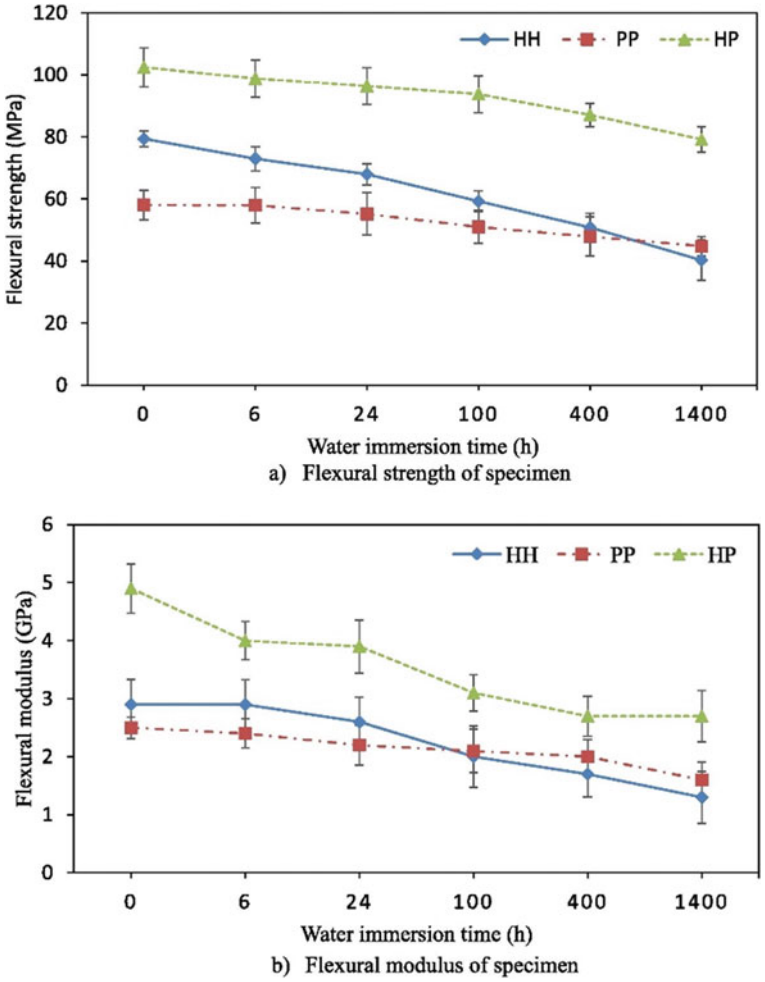


Fig. 11 Flexural strength and modulus of PP, HH, and HP composites (Ahmad et al. 2018)

fractions 0.10 and 0.30and fiber length of 50 mm drop to 48.4 and 57.5 MPa. Moisture absorption depends on the type of fibers and matrices, relative humidity, and manufacturing process.

Zamri et al. (2011) reported the flexural properties of jute-glass unsaturated polyester hybrid composites in distilled water, seawater, and acidic solution (see Fig. 13). Jute fiber shows higher tendency for absorbing water, which increases the degradation rate of the fiber. The flexural strength and modulus of the targeted hybrid composites changes inversely with water immersion time. As the cellulose content of jute fiber is loosed from its structure after water absorption, it also shows ductility. Water fills voids and cracks and acts as a plasticizer, reducing the bending strength and stiffness of the material (Huang and Sun 2007).

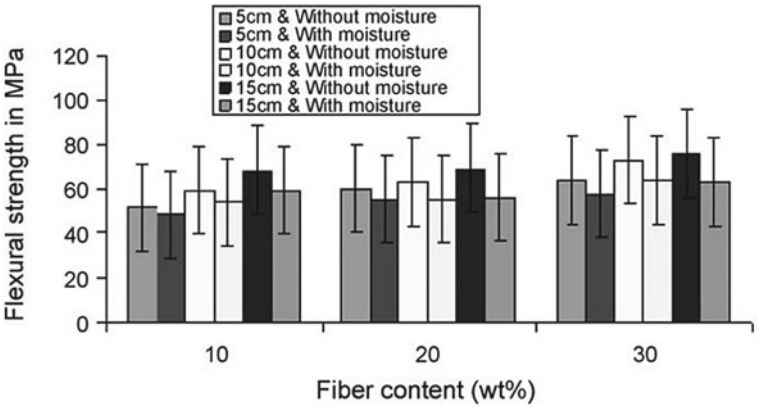


Fig. 12 Moisture absorption effect on the flexural strength of RSPE hybrid composites (Athijayamani et al. 2009)

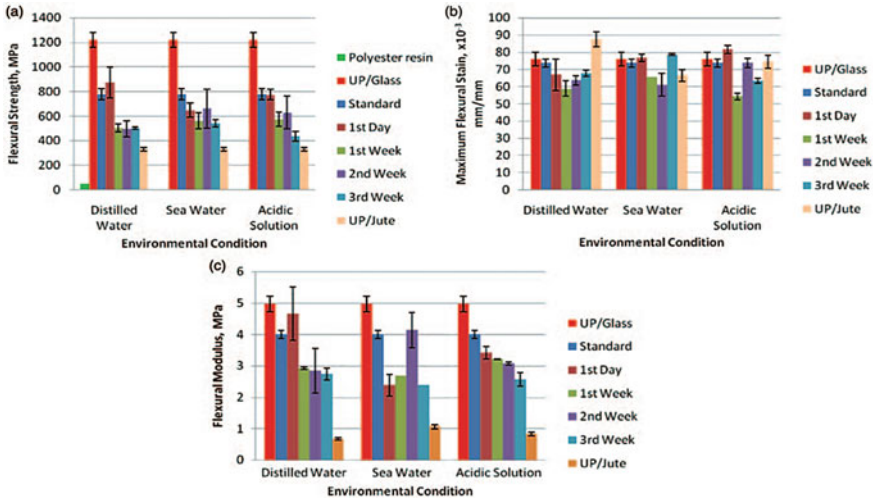


Fig. 13 Effect of three different conditions on the flexural strength, modulus, and strain of jute-glass polyester hybrid composites (Zamri et al. 2011)

6 Conclusions

This chapter discussed the moisture absorption by natural fiber-based hybrid composites and their effects on physical properties (glass transition temperature, weight, and dimensional stability) and mechanical properties (tensile strength and modulus, flexural strength and modulus, fracture toughness, and impact strength). Moisture absorption negatively affects all of the properties mentioned above. The moisture

sensitivity of the fiber needs to be reduced to achieve desirable performance in structural applications using natural fiber-based hybrid composites. One possible solution is to use synthetic fibers as outside layers of the composites. However, synthetic fibers are costly, and their use can lose the environmentally friendly image of natural fiber-based composites. So, further research is needed to find an alternative to prevent the absorption of moisture content by natural fiber-based hybrid composites.

References

Ahmad MAA, Abdul Majid MS, Ridzuan MJM, Mazlee MN, Gibson AG (2018) Dynamic mechanical analysis and effects of moisture on mechanical properties of interwoven hemp/polyethylene terephthalate (PET) hybrid composites. Constr Build Mater 179:265–276. https://doi.org/10.1016/j.conbuildmat.2018.05.227

Akil HM, Santulli C, Sarasini F, Tirillò J, Valente T (2014) Environmental effects on the mechanical behaviour of pultruded jute/glass fibre-reinforced polyester hybrid composites. Compos Sci Technol 94:62–70

Almansour FA, Dhakal HN, Zhang ZY (2017) Effect of water absorption on mode I interlaminar fracture toughness of flax/basalt reinforced vinyl ester hybrid composites. Compos Struct 168:813–825. https://doi.org/10.1016/j.compstruct.2017.02.081

Alomayri T, Assaedi H, Shaikh FUA, Low IM (2014) Effect of water absorption on the mechanical properties of cotton fabric-reinforced geopolymer composites. J Asian Ceram Soc 2(3):223–230

Ashik KP, Sharma RS, Jagannatha Guptha VL (2018) Investigation of moisture absorption and mechanical properties of natural/glass fiber reinforced polymer hybrid composites. Mater Today Proc 5(1):3000–3007

Asim M, Abdan K, Jawaid M, Nasir M, Dashtizadeh Z, Ishak MR, Hoque ME (2015) "A review on pineapple leaves fibre and its composites" edited by Y. Deng. Int J Polym Sci 2015:950567.https://doi.org/10.1155/2015/950567

Athijayamani A, Thiruchitrambalam M, Natarajan U, Pazhanivel B (2009) Effect of moisture absorption on the mechanical properties of randomly oriented natural fibers/polyester hybrid composite. Mater Sci Eng A 517(1):344–353. https://doi.org/10.1016/j.msea.2009.04.027

Atiqah A, Maleque MA, Jawaid M, Iqbal M (2014) Development of kenaf-glass reinforced unsaturated polyester hybrid composite for structural applications. Compos B Eng 56:68–73. https://doi.org/10.1016/j.compositesb.2013.08.019

Azwa ZN, Yousif BF, Manalo AC, Karunasena W (2013) A review on the degradability of polymeric composites based on natural fibres. Mater Des 47:424–442

Barjasteh E, Nutt SR (2012) Moisture absorption of unidirectional hybrid composites. Compos A Appl Sci Manuf 43(1):158–164. https://doi.org/10.1016/j.compositesa.2011.10.003

Barkoula NM, Peijs T (2011) 2—Interface engineering through matrix modification in natural fibre composites. In: Zafeiropoulos NE (ed) Interface engineering of natural fibre composites for maximum performance. Woodhead Publishing, pp 43–81

Bhagat VK, Biswas S, Dehury J (2014) Physical, mechanical, and water absorption behavior of coir/glass fiber reinforced epoxy based hybrid composites. Polym Compos 35(5):925–930

Braga RA, Magalhaes PAA Jr (2015) Analysis of the mechanical and thermal properties of jute and glass fiber as reinforcement epoxy hybrid composites. Mater Sci Eng C 56:269–273

Dan-mallam Y, Hong TW, Majid MSA (2015) "Mechanical characterization and water absorption behaviour of interwoven kenaf/PET fibre reinforced epoxy hybrid composite" edited by A. Sudo. Int J Polym Sci 2015:371958. https://doi.org/10.1155/2015/371958

Deshpande S, Rangaswamy T (2016) A comparative study on dry sliding wear characteristics of Al_2O_3 and bone powder filled hybrid composites. J Miner Mater Charact Eng 4(2):164–180

Dong J, Locquet A, Declercq NF, Citrin DS (2016) Polarization-resolved terahertz imaging of intra- and inter-laminar damages in hybrid fiber-reinforced composite laminate subject to low-velocity impact. Compos B Eng 92:167–174. https://doi.org/10.1016/j.compositesb.2016.02.016

Edhirej A, Sapuan SM, Jawaid M, Zahari NI (2017) Cassava/sugar palm fiber reinforced cassava starch hybrid composites: physical, thermal and structural properties. Int J Biol Macromol 101:75–83. https://doi.org/10.1016/j.ijbiomac.2017.03.045

Fong TC, Saba N, Liew CK, De Silva R, Enamul Hoque M, Goh KL (2015) Yarn flax fibres for polymer-coated sutures and hand layup polymer composite laminates. In: Salit MS, Jawaid M, Yusoff NB, Hoque ME (eds) Manufacturing of natural fibre reinforced polymer composites. Springer International Publishing, Cham, pp 155–175

Haniffah WH, Sapuan SM, Abdan K, Khalid M, Hasan M, Enamul Hoque M (2015) Kenaf fibre reinforced polypropylene composites: effect of cyclic immersion on tensile properties. Int J Polym Sci 2015:e872387. https://doi.org/10.1155/2015/872387

Huang G, Sun H (2007) Effect of water absorption on the mechanical properties of glass/polyester composites. Mater Des 28(5):1647–1650. https://doi.org/10.1016/j.matdes.2006.03.014

Jankowsky JL, Wong DG, DiBerardino MF, Cochran RC (1994) Evaluation of upper use temperature of toughened epoxy composites. In: Seyler R (ed) Assignment of the glass transition. ASTM International, West Conshohocken, PA, pp 277–292

Jawaid M, Abdul Khalil HPS, Noorunnisa Khanam P, Abu Bakar A (2011) Hybrid composites made from oil palm empty fruit bunches/jute fibres: water absorption, thickness swelling and density behaviours. J Polym Environ 19(1):106–109. https://doi.org/10.1007/s10924-010-0203-2

Jawaid M, Alothman OY, Paridah MT, Abdul Khalil HPS (2014) Effect of oil palm and jute fiber treatment on mechanical performance of epoxy hybrid composites. Int J Polym Anal Charact 19(1):62–69. https://doi.org/10.1080/1023666X.2014.858429

Maslinda AB, Abdul Majid MS, Ridzuan MJM, Afendi M, Gibson AG (2017) Effect of water absorption on the mechanical properties of hybrid interwoven cellulosic-cellulosic fibre reinforced epoxy composites. Compos Struct 167:227–237. https://doi.org/10.1016/j.compstruct.2017.02.023

Mochane MJ, Mokhena TC, Mokhothu TH, Mtibe A, Sadiku ER, Ray SS, Ibrahim ID, Daramola OO (2019) Recent progress on natural fiber hybrid composites for advanced applications: a review

Mokhothu TH, John MJ (2015) Review on hygroscopic aging of cellulose fibres and their biocomposites. Carbohyd Polym 131:337–354. https://doi.org/10.1016/j.carbpol.2015.06.027

Panthapulakkal S, Sain M (2007) Studies on the water absorption properties of short hemp—glass fiber hybrid polypropylene composites. J Compos Mater 41(15):1871–1883

Prasad MSS, Venkatesha CS, Jayaraju T (2011) Experimental methods of determining fracture toughness of fiber reinforced polymer composites under various loading conditions. J Miner Mater Charact Eng 10(13):13

Rahman MZ (2021) Mechanical and damping performances of flax fibre composites—a review. Compos Part C Open Access 4:100081. https://doi.org/10.1016/j.jcomc.2020.100081

Safri SN, Azrie MT, Sultan H, Jawaid M, Jayakrishna K (2018) Impact behaviour of hybrid composites for structural applications: a review. Compos B Eng 133:112–121. https://doi.org/10.1016/j.compositesb.2017.09.008

Sagadevan S, Pal K, Chowdhury ZZ, Enamul Hoque M (2017a) Structural, dielectric and optical investigation of chemically synthesized Ag-doped ZnO nanoparticles composites. J Sol Gel Sci Technol 83(2):394–404. https://doi.org/10.1007/s10971-017-4418-8

Sagadevan S, Pal K, Hoque E, Chowdhury ZZ (2017b) A chemical synthesized Al-doped PbS nanoparticles hybrid composite for optical and electrical response. J Mater Sci Mater Electron 28(15):10902–10908. https://doi.org/10.1007/s10854-017-6869-7

Sagadevan S, Chowdhury ZZ, Johan MRB, Khan AA, Aziz FA, Rafique RF, Hoque ME (2018) A facile hydrothermal approach for catalytic and optical behavior of tin oxide-graphene (SnO2/G) nanocomposite. PLoS One 13(10):e0202694. https://doi.org/10.1371/journal.pone.0202694

Salit MS, Jawaid M, Yusoff NB, Hoque ME (2015) Manufacturing of natural fibre reinforced polymer composites. Springer

Sule U, Isa MT, Ameh AO, Ajayi OA, Omorogbe O (2014) Studies on the properties of short okra/glass fibers reinforced epoxy hybrid composites. Int J Sci Technol 2(7):260

Thiruchitrambalam M, Alavudeen A, Athijayamani A, Venkateshwaran N, Elaya Perumal A (2009) Improving mechanical properties of banana/kenaf polyester hybrid composites using sodium laulryl sulfate treatment. Mater Phys Mech 8(2):165–173

Tshai KY, Chai AB, Kong I, Hoque ME, Tshai KH (2014) Hybrid fibre polylactide acid composite with empty fruit bunch: chopped glass strands. J Compos 2014:1–7. https://doi.org/10.1155/2014/987956

Venkateshwaran N, ElayaPerumal A, Alavudeen A, Thiruchitrambalam M (2011) Mechanical and water absorption behaviour of banana/sisal reinforced hybrid composites. Mater Des 32(7):4017–4021

Wang W, Sain M, Cooper PA (2006) Study of moisture absorption in natural fiber plastic composites. Compos Sci Technol 66(3–4):379–386

Yahaya R, Sapuan SM, Jawaid M, Leman Z, Zainudin ES (2016) Effect of fibre orientations on the mechanical properties of kenaf-aramid hybrid composites for spall-liner application. Def Technol 12(1):52–58. https://doi.org/10.1016/j.dt.2015.08.005

Zamri MH, Akil HM, Bakar AA, Ishak ZAM, Cheng LW (2011) Effect of water absorption on pultruded jute/glass fiber-reinforced unsaturated polyester hybrid composites. J Compos Mater 46(1):51–61. https://doi.org/10.1177/0021998311410488

Zhang D, Milanovic NR, Zhang Y, Su F, Miao M (2014) Effects of humidity conditions at fabrication on the interfacial shear strength of flax/unsaturated polyester composites. Compos B Eng 60:186–192

Zhou J, Lucas JP (1995) The effects of a water environment on anomalous absorption behavior in graphite/epoxy composites. Compos Sci Technol 53(1):57–64

Zhou J, Lucas JP (1999) Hygrothermal effects of epoxy resin. Part I: the nature of water in epoxy. Polymer 40(20):5505–5512. https://doi.org/10.1016/S0032-3861(98)00790-3

Živković I, Fragassa C, Pavlović A, Brugo T (2017) Influence of moisture absorption on the impact properties of flax, basalt and hybrid flax/basalt fiber reinforced green composites. Compos B Eng 111:148–164. https://doi.org/10.1016/j.compositesb.2016.12.018

Aging Effects on Mechanical Properties of Biocomposites with Recycled Polymers

Md. Sarif Sakaeyt Hosen, Md Enamul Hoque, Md. Zillur Rahman, and Suresh Sagadevan

Abstract This chapter discusses the aging effects (e.g., photochemical, hydrothermal, natural, thermal, freeze–thaw cycling, and xenon-arc light) on various mechanical characteristics of biocomposites with the recycled polymer. In general, biocomposites show a decrease in tensile strength after photochemical aging, but tensile modulus and strain to failure do not vary significantly with increasing aging time. In contrast, tensile modulus and ultimate tensile strength of biocomposites reduce significantly with hydrothermal aging, but the strain to failure increases. Also, flexural modulus, tensile modulus, tensile strength at break, and elongation at break increase after natural aging. Furthermore, there is an increased tensile modulus and strength of biocomposite under accelerated thermal aging. The process and result of aging depend on the type of biocomposites. As the use of biocomposites is widely increasing, this chapter can be useful for getting insight into the durability performance of the biocomposite materials.

Keywords Aging effect · Biocomposites · Hydrothermal aging · Mechanical properties · Natural aging · Recycled polymer · Thermal aging

Md. S. S. Hosen
Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

Md E. Hoque (✉)
Department of Biomedical Engineering, Military Institute of Science and Technology (MIST), Dhaka, Bangladesh

Md. Z. Rahman
Department of Mechanical Engineering, Bangabandhu Sheikh Mujibur Rahman Aviation and Aerospace University, Dhaka, Bangladesh

S. Sagadevan
Nanotechnology and Catalysis Research Centre, University of Malaya, Kuala Lumpur, Malaysia

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_17

1 Introduction

1.1 Biocomposites with Recycled Polymers

A biocomposite with recycled polymer is a composite material made by a matrix (polymer) and a reinforcement of natural fibers. Polymers are derived from renewable and nonrenewable resources. Polymers are two types: thermoplastic and thermosetting polymers. Thermoplastic polymers can be easily recycled, whereas thermosetting polymers are much more difficult to recycle. Thermoplastic polymers are polyethylene, cellulose acetate, polyvinylchloride, polystyrene, polypropylene, and polycarbonate. Natural fibers are derived from different plant and animal sources (AL-Oqla et al. 2015; Arifur Rahman et al. 2015). Some examples of natural fibers are cellulose-based cotton, jute, and flax. The animal fibers are protein-based, which include wool and silk. In this chapter, the focus is on the recycled polymer matrix (Salit et al. 2015). Natural fiber-reinforced polymer matrix composites can be cheaper, tougher, and environmentally friendly (Asim et al. 2015).

Like woods (Hoque et al 2016), when polymer matrix composites (PMC) are exposed for a long time to the environment their characteristics change irreversibly from the materials' original characteristics. The process in which characteristics change over time in polymer matrix composites can be termed as 'aging'. Composites' stiffness, strength, and fatigue life are time-dependent changes. These can all be related to changes in the mechanical characteristics of the polymer matrix. Aging processes can be categorized into three type's chemical, physical, and mechanical. All three aging processes depend on material type, the environment, and the mechanical loads (Enamul Hoque et al. 2014). However, the aging of biocomposites with recycled polymers makes uncertainties about the long-term performance of composites under conditions encountered in service (Martin 2008).

1.2 Significance of Aging

A matrix material experiences environmental condition which alters the characteristics of the matrix or mechanical loads that act over a lengthy time. Composite performance depends mainly on the viscoelastic nature of the matrix. As stiffness, strength, and fatigue life of composites vary over time, the mechanical characteristics of the polymer matrix also change. An aging study is generally conducted to know the mechanical, physical, and morphological changes of the composites exposed to the application environment. This study also helps to estimate the durability of the composites, thereby choosing the optimum material for a particular application (Stark 2006). The durability of a material can be known fully by long-term (real-time) testing. It also filters admissible postulant materials by aging then the long-term performance test can run. As a result, the expense may reduce involvement in confining the field of admissible postulant substances. In addition to materials

filtering, rapid testing provides information about the remaining service life of an existing structure and provide a suggestion for betterment (Brebu 2020). The decision for methods of material selection can be made by aging. This also gives a fundamental principle for manufacturers to adopt new and advanced specific methods.

2 Aging of Biocomposites with Recycled Polymer

2.1 Important Terms of Aging

Environmental deterioration factor is the general term for specific application conditions, which affects every material. Some examples of environmental deterioration factors are mechanical loads, moisture, heat, etc. Environmental deterioration of polymeric composites can occur by chemical, physical, and biological processes or a combination of them under different factors such as mechanical stress, temperature, moisture, light, air, high-energy radiation, and chemical agents. Variations in the material occur by these factors in two steps. Firstly, deterioration of appearance, physical and morphological characteristics or mechanical characteristics happen, and then the changes are converted in the form of H_2O, C_2O, and other simple inorganic compounds (mineralization).

Polymer materials are affected by environmental deterioration factors, including chemical, physical, and mechanical processes. When one or more physical characteristics of a material system change due to the environmental factors attack, then the critical deterioration process occurs. However, environmental deterioration factors should be inside the boundaries of the service environment to occur a critical deterioration process (Martin 2008).

The accelerated aging process of polymer matrix materials was performed simulating outdoor conditions (González-López et al. 2020; Seldén et al. 2004). The water spraying cycle and UV light incidence were carried out under temperature and emission. The degree of deterioration can be calculated considering the decreased molecular weight and mechanical characteristics or surface deterioration such as discoloration or erosion. The outcomes of this study can be useful to determine the stability of material for the different environmental conditions. Notably, accelerated aging and outdoor condition relations are not straightforward because the environmental condition can vary depending on the location of the applied material. The shift or acceleration factor put in the correlation between simulated and outdoor conditions.

2.2 Environmental Conditions and Variables

During the aging process of the polymer matrix, some environmental deterioration factors are always active, their work being conducted through a molecular process. that works on the network: these changes, severally, calculate remarkable variation at the stage of bulk mechanical characteristics. Therefore, a well-designed accelerating protocol should swift the work of deterioration factors without outgoing from the fundamental molecular processes. The aging processes on polymer matrix biocomposites may lead to unchangeable (damage accumulation) and changeable effects. Several parameters such as temperature and temperature changes of polymer matrix and polymer morphology, fiber structure, relative humidity, degree of damage, oxidative attack, mechanical loads and cyclic loads, internal moisture concentration, fiber volume fraction, air pressure, and related applied stress level, and aging time induce and drive the damage accumulation continuously. Different portions of the structure will not expand similar amounts if the temperature throughout the structure is different. As a result, it increases the thermal stresses, which are combined with various destined stresses. Consequently, the modification happening in real-time circumstances for long period solicitations, regenerating the deterioration processes copied by the swift testing. The deterioration process, kinetics, and their influence all need to understand to determine the deterioration, which is relatively difficult. However, assessing the initial deterioration can be an easy way to comprehend the deterioration. It is also significant to use physical characteristics (crack density, glass transition temperature, and weight) to evaluate the condition of a material exposed to long-term aging. This condition can be interrelated through a formative way to alter bulk characteristics connected for the material engagement. Overall, the accelerated aging and real-time aging have a significant impact on the mechanical characteristics of materials to evaluate the accelerating factor for every deterioration process.

3 Aging Processes for Mechanical Characteristics

3.1 Mechanical Deterioration Process

The mechanical deterioration process directly affects engineering characteristics such as strength because deterioration causes delamination, matrix cracking, fiber breaks, interface damage, and inelastic deformation (Ahmad et al. 2018). During high-temperature operation of polymer composites, lateral multiple cracks and micro-cracks (which are situated in a plane) in the polymeric matrix of multi-dimensional composites are the most critical damage process. Mechanical static and fatigue loadings are the main reason for lateral multiple cracks and micro-cracks. In contrast, mechanical and environmental factors, and hydrothermal exposure cause residual stresses. Lateral matrix cracks of composites laminates are produced due to hydrothermal cycling that begins within the surface and develops deeply in the

laminate with cycles. Lateral matrix cracking affects composite stiffness, strength, and thermal characteristics. Lateral matrix cracking can also increase the absorption of moisture in the laminate.

3.2 Physical Deterioration Process

Polymers below glass transition temperature are in a non-equilibrium condition and want to reach the equilibrium condition. In this process, volume, enthalpy, and entropy decrease with time. This process increases stiffness and brittleness, which helps to the rapid advancement of several damage situations. As a result, thermal behavior, associated reduction of free volume, and segmental dynamics are the factors on which the mechanical characteristics of glassy polymers and their composites depend. Viscoelastic relaxation times of polymers increase with increasing aging time because of the time aging and time–temperature factors (Babaghayou et al. 2016). This makes the exploration of polymer matrix composites difficult because physical aging is related to the time-dependent viscoelastic behavior of polymers at a higher or lower temperature than glass transition temperature under load.

3.3 Thermo-Oxidative Deterioration Process

Thermo-oxidative deterioration is an important deterioration process of polymeric matrices because of thermal instability and oxidative attack, thermo-oxidative reactions, chain scission, and crosslinking (Lila et al. 2019). In an inert atmosphere, thermal deterioration of PMCs is a thermolysis phenomenon, but in the air, it is subjugated by oxidation (Fong et al. 2015). Thermolysis is defined as the breaking of a covalent bond in the polymer network. Normally, the thermal stability of high-performance polymers is very good in an inert condition. In polymer matrix, chemical and mass variations occur from the surface, and these changes significantly happen when exposing to high temperature and long-term exposure (Callister and Rethwisch 2018). Even slight mass variations can be an indication of surface variations. Oxidation reactions depend on the circulation of O_2 inside and circulation of oxidized products outside mainly the mass transport process. The resin fracture toughness has a major effect on thermo-oxidative resistance. Large fracture toughness increases the thermo-oxidative resistance due to reduced weight loss during aging. The toughened structure also provides better resistance to crack formation, which could supply a trail way for O_2 circulation. The nature of oxidation reactions and their related chemical changes have a significant influence on the accelerated aging (Martin 2008). These figures on temperature determining changes in mechanical characteristics. The nature of the reaction can vary remarkably with the variation of the polymer matrix. The

presence of unreacted and defective groups is also the reason for the topical problems. For the desired application, if we can identify correct deterioration processes that will help significantly to conduct an appropriate test program.

3.4 Hygrothermal Deterioration Process

The polymeric matrix of composites can absorb and circulate the low molecular mass element such as H_2O. The equilibrium absorbed amount and mass transport kinetics vary according to the chemical structure and morphology of a polymer. The arrangement and quantity of the fibers and fiber-matrix interfacial behavior are related to these characteristics in the case of composites. A simple approach based on Fick's law can be used for determining the time evolution penetrant concentration profile of a low molecular mass element when the absorbed amount is vanishingly small. The combination of moisture and heat influences reinforced plastics in many ways. The high influence of moisture is reflected by changes in matrix-dominated mechanical characteristics that are closely associated with the glass transition temperature. Humidity and high-temperature plasticize the matrix and accelerate the polymers' sub-glass transition temperature relaxation process in the direction of thermodynamic equilibrium (Panthapulakkal et al. 2006). Moreover, the residual stresses within the composites are changed by the hydrothermal swelling that can lead to micro-crack formation. These micro-cracks provide fast circulation paths and then alter the moisture absorption characteristics of the laminate. Surface blistering and matrix cracking are the short-term hydrothermal effects on composites under micro void generation, hydrothermal cycling conditions, and no applied loads.

4 Effect of Aging on Mechanical Properties

4.1 Accelerated Photochemical Aging

This section discusses the mechanical characteristics of biocomposites before and after accelerated photochemical aging. Moreno et al. (2018) investigated the biocomposites consisted of recycled low-density polyethylene waste (LDPEW), pinewood waste (PWW), and maleic anhydride grafted polyethylene (coupling agent). The LDPEW/PWW composite has a tensile strength of 12 MPa before photochemical aging, as shown in Fig. 1. The tensile strength decreases with aging up to 48 h, but it restores after 672 h of aging in the case of LDPEW/PWW composite. A rise in tensile strength occurs up to 168 h of aging because of residual stress relaxation that is stored in the material during their thermomechanical molding, and then it remains the same up to 1344 h of aging before reducing slightly up to 4032 h of aging. In another study, Stark and Matuana reported that polyethylene experiences crosslinking at the

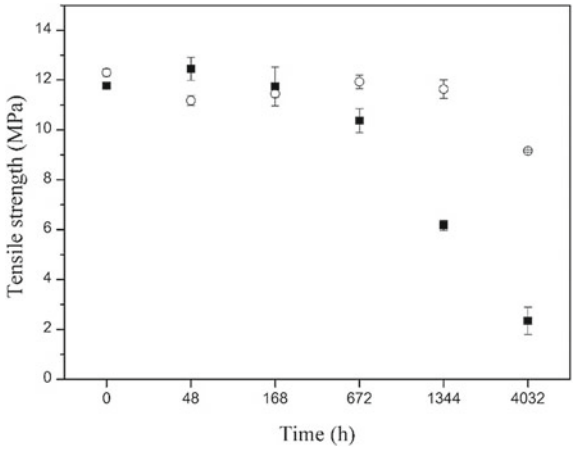


Fig. 1 Tensile strength of LDPEW (■) and LDPEW/PWW (○) composite as a function of time of aging (Moreno et al. 2018). Adopted with permission from copyright (2018), Elsevier

preliminary stage of accelerated aging, and the ability of polyethylene to crosslink is then hindered by wood flour (Stark and Matuana 2004). As a result, there is a potential for polyethylene chain scission to dominate in the primary aging stage.

The influence of accelerated weathering on the elongation at break for LDPEW and LDPEW/PWW is presented in Fig. 2. The LDPEW/PWW composite has an elongation of around 25% before aging. Elongation is slight because of the low deformation of the fiber. Elongation at break decreases substantially in LDPEW than LDPEW/PWW composite. Interestingly, after 4032 h of aging, elongation at break is the same for both neat LDPEW and LDPEW/PWW composite.

Figure 3 shows Young's modulus for LDPEW and LDPEW/PWW composite during accelerated aging. The increase in Young's modulus of LDPEW/PWW composite is 300% as compared to the LDPEW. However, there are no significant changes in Young's modulus of composites with aging time.

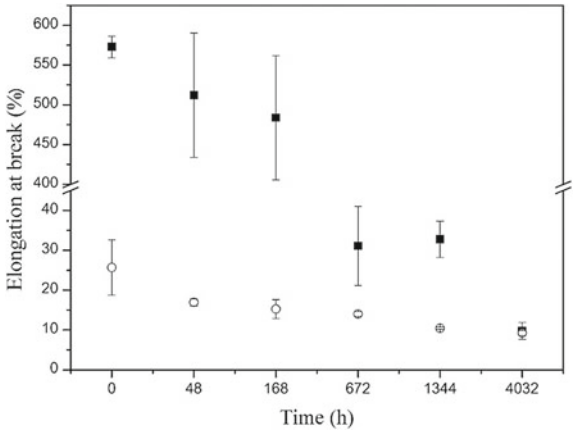


Fig. 2 Variation in elongation at breaks with weathering time for LDPEW (■) and LDPEW/PWW composite (○) (Moreno et al. 2018). Adopted with permission from copyright (2018), Elsevier

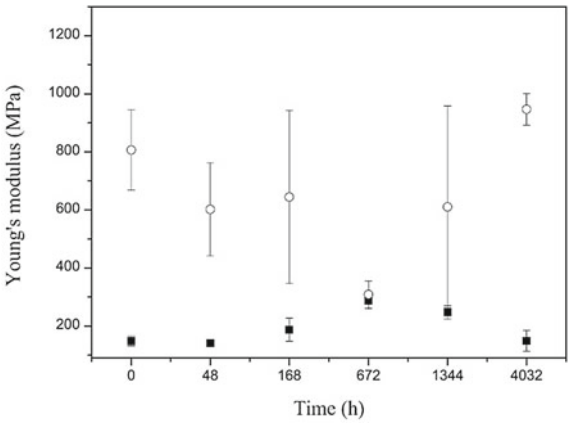


Fig. 3 Young's modulus of LDPEW (■) and LDPEW/PWW (○) as a function of weathering time (Moreno et al. 2018). Adopted with permission from copyright (2018), Elsevier

4.2 Hydrothermal Aging

The mechanical characteristics of the biocomposites during hydrothermal aging are discussed in this section. Kollia et al. examined the influence of the hydrothermal aging of flax/epoxy composites (Kollia et al. 2020). They used three different types of resins, such as greenpoxy56 (GP56) with hardener SD8822, greenpoxy56 (GZ56) with hardener SZ8525, RSF816RG (RSF816) with hardener RSF816, super sap INR (SP) with hardener super sap INS.

The stress–strain curves significantly change when specimens are exposed to distilled water. Stress–strain curves of the specimens at pristine state, and dry and wet conditions after saturation are illustrated in Fig. 4. Strain to failure affected by hydrothermal aging. A significant increase in strain to failure is observed due to water absorption, which even becomes higher with an increase in temperature. Strain to failure of the samples tends to decrease after drying.

Figures 5 and 6 show the tensile modulus and strength of GP56, GZ56, RSF816, and SP biocomposites, respectively, at both dry and wet conditions. During hydrothermal aging, the modulus of elasticity decreases for all samples, especially at 60 °C due to higher water uptake. Maximum reduction in stiffness happens for the GZ specimen and minimum for the SP specimen because of the variations in the production processes. Improvement in stiffness happens after drying.

The tensile strength of specimens reduces when exposing to water and high temperature. Water molecules are absorbed by the fiber due to its hydrophilic nature, which affects the fiber-matrix interfaces and minimizes interfacial bonding strength. Therefore, there is a reduction in tensile properties (stiffness and strength) after water aging.

Figures 7 and 8 show the flexural modulus and strength of biocomposites, respectively, during hydrothermal aging. The flexural modulus of GZ56 and SP816 specimens decreases by 55 and 26%, respectively, after hydrothermal weathering at 40 °C. Flexural modulus decreased further when water aging was conducted at 60 °C. The

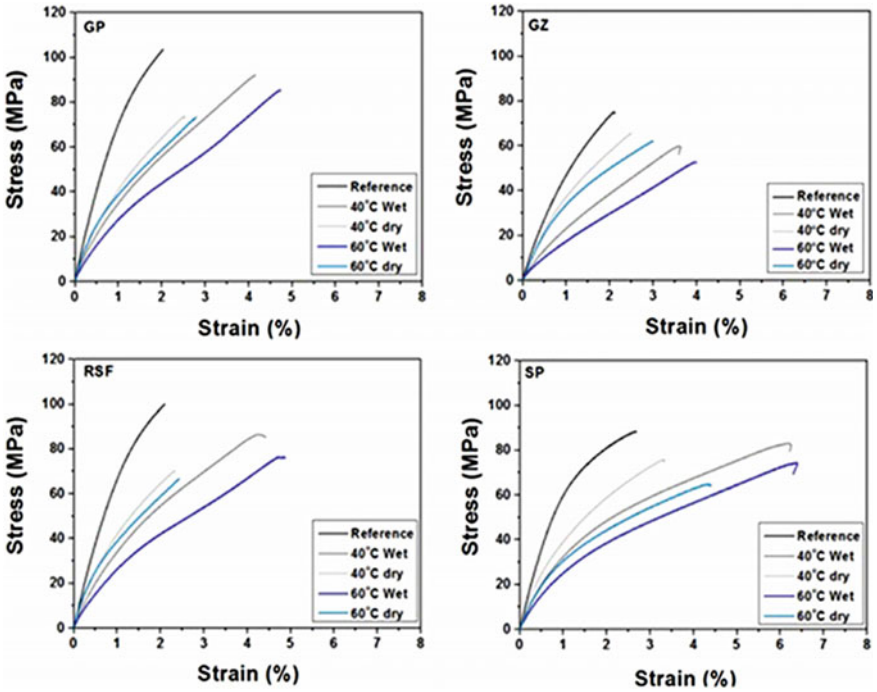


Fig. 4 Stress–strain curves of GP56, RSF816, GZ56, and SP biocomposites at the pristine state and wet and dry conditions for 40 and 60 °C (Kollia et al. 2020)

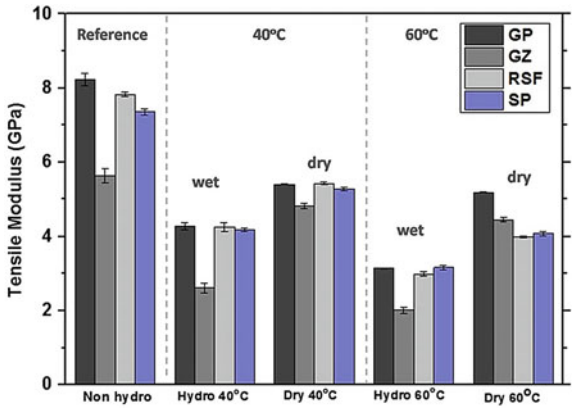


Fig. 5 Tensile modulus of GP56, RSF816, GZ56, and SP biocomposites before and after hydrothermal weathering at 40 and 60 °C (wet and dry conditions) (Kollia et al. 2020)

flexural modulus of the samples recovers slightly after drying. For all aged samples, the strain to failure is 5% higher than the dried samples. Strain to failure is increased in wet condition because water molecules act as a plasticizer.

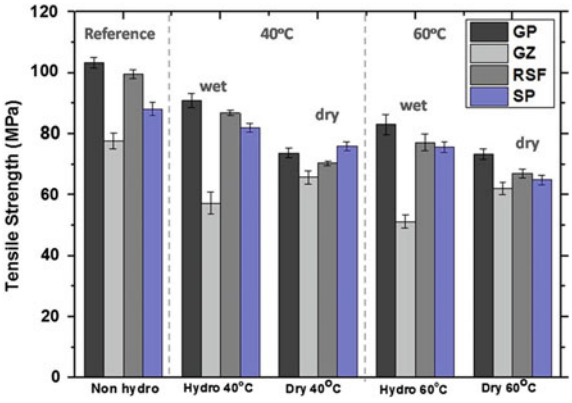


Fig. 6 Tensile strength of GP56, RSF816, GZ56, and SP biocomposites before and after hydrothermal weathering at 40 and 60 °C (wet and dry conditions) (Kollia et al. 2020)

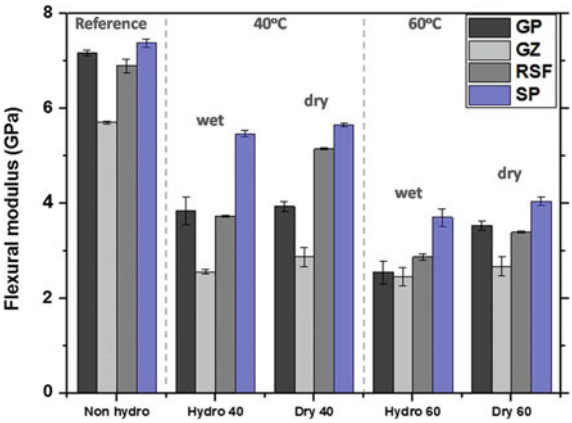


Fig. 7 Flexural modulus of GP56, RSF816, GZ56, and SP biocomposites before and after hydrothermal weathering at 40 and 60 °C (wet and dry conditions) (Kollia et al. 2020)

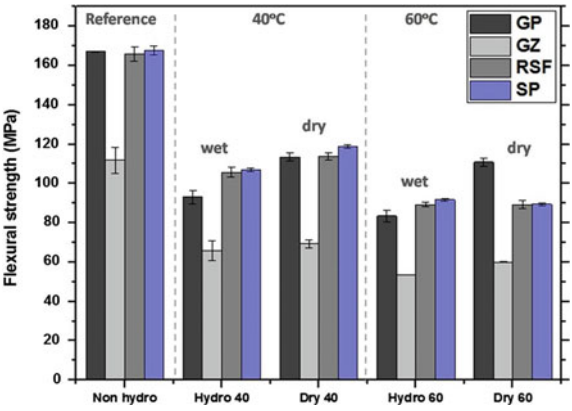


Fig. 8 Flexural strength of GP56, RSF816, GZ56, and SP56 biocomposites before and after hydrothermal weathering at 40 and 60 °C (wet and dry conditions) (Kollia et al. 2020)

The ultimate flexural strength is significantly affected by the aging process. For example, flexural strength decreases around 50% for all specimens at 60 °C after aging. This is again because of the decline in fiber-matrix adhesion after water absorption by the plant fiber. However, the flexural properties (stiffness and strength) of the samples restore slightly after drying.

4.3 Natural Aging

Natural aging affects the mechanical characteristics of recycled polypropylene, ethylene vinyl acetate, and wood flour composites (PP, EVA, and ITA), as discussed in this section. Natural aging was conducted for 4, 8, and 12 months for these materials by Silva et al. (2017). They found that different environmental conditions (rain, humidity, and solar radiation) affect the samples during natural aging. The effects can even be severe on the mechanical characteristics of the sample when the coupling effect of environmental conditions occurs (Homkhiew et al. 2014). Elastic modulus PP/EVA and PP/EVA/ITA specimens increase with the exposure time (see Fig. 9). The rise in tensile modulus happens from 483 to 1095 MPa under natural aging. This is because the chain scission phenomenon occurs during aging, which results in shorter macromolecular chains and promotes PP crystallization.

Figure 10 demonstrates the tensile strength of PP/EVA and PP/EVA/ITA at natural aging. The tensile strength at break decreases significantly for both composites because of the chain scission reaction induced by irradiation. Elongation at break of the composites also decreases with increasing natural aging.

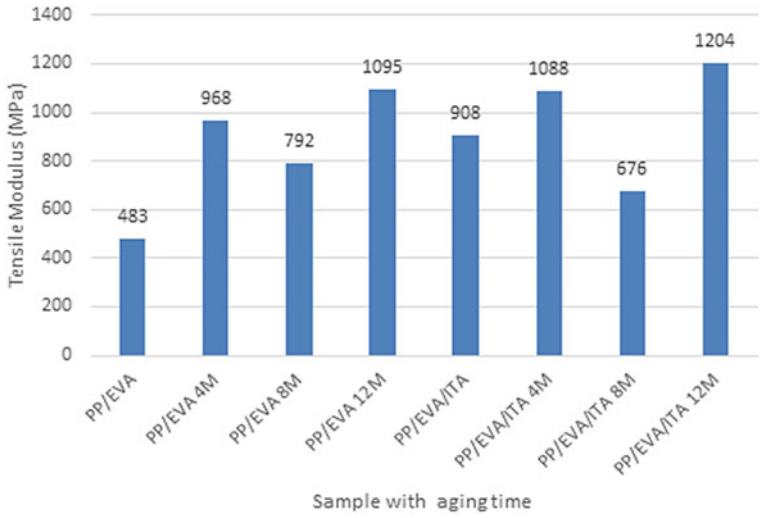


Fig. 9 Changes in tensile modulus after natural aging (Silva et al. 2017)

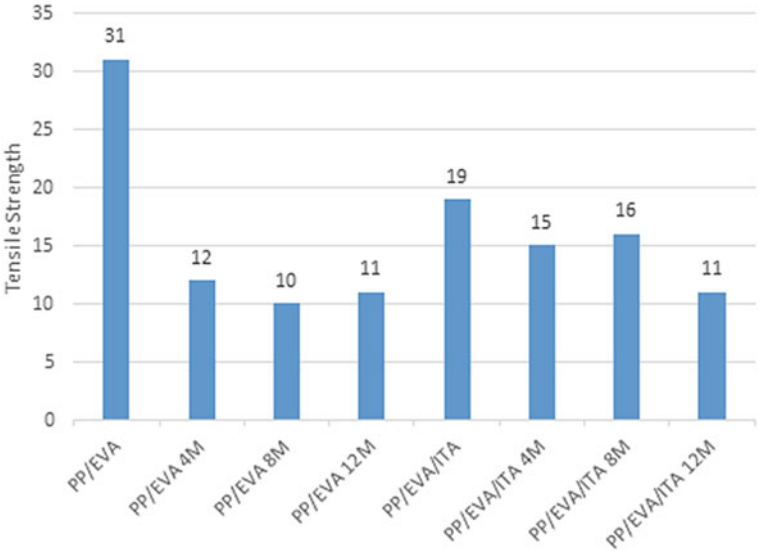


Fig. 10 Changes in tensile strength after natural aging (Silva et al. 2017)

Figures 11 and 12 show the flexural modulus and strength of PP/EVA and PP/EVA/ITA specimens, respectively, under natural aging. Flexural modulus and strength increase by 13.45 and 5.16%, respectively, after four weeks of exposure time in the case of PP/EVA/ITA specimens. All properties (tensile and flexural) reduces substantially after eight weeks of aging time. The decrease in flexural strength is

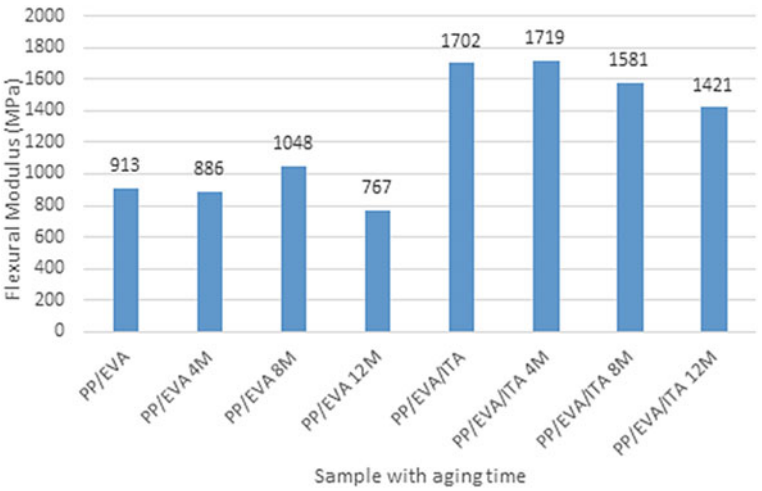


Fig. 11 Changes in flexural modulus after natural aging (Silva et al. 2017)

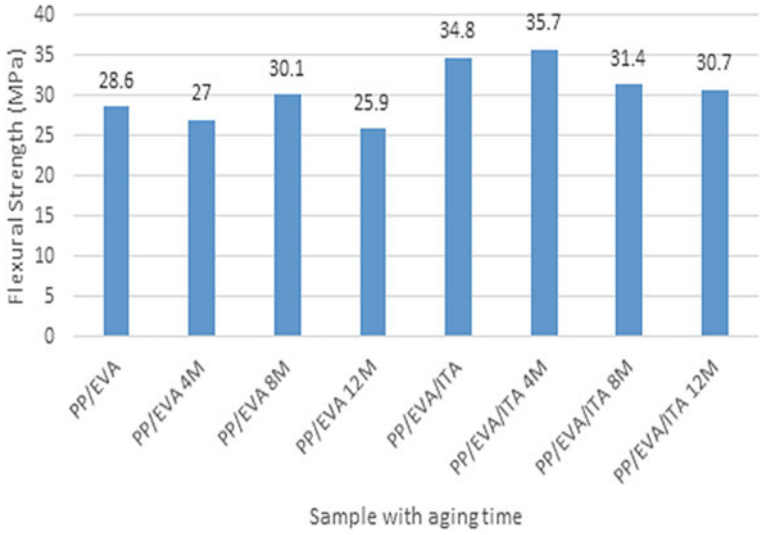


Fig. 12 Changes in flexural strength after natural aging (Silva et al. 2017)

because of the inability to transfer stress from wood flour to the plastic matrix and micro-cracks formation happened by wood flour swelling under the rain.

Elongation and contraction of materials happen due to the heating and cooling cycles. The thermal coefficients of natural fiber and polymer matrix are different, resulting in residual stresses generated within the structure after 8 weeks of exposure time. This also leads to structural deformation, thereby reducing the mechanical properties after eight weeks.

4.4 Thermal Aging

The mechanical characteristics of bagasse fiber/polylactic acid (PLA) composite under accelerated thermal aging are discussed in this section, based on the study made by Lila and co-workers (Lila et al. 2019). A temperature cycle of −20 to 65 °C was applied to the biocomposites for twelve hours a day at each temperature for 12 weeks. The tensile strength and tensile modulus increase up to 8 weeks exposure time due to multiple annealing of biocomposites, as shown in Figs. 13 and 14, respectively. Multiple annealing also increases the stability of PLA. There is a reduction in tensile properties after 8 weeks of exposure time due to decreased interfacial adhesion between the fiber and matrix. The weak interfacial bonding is owing to the residual thermal stresses derived from different thermal expansion coefficients of fiber and matrix material under continuous heating and cooling cycles.

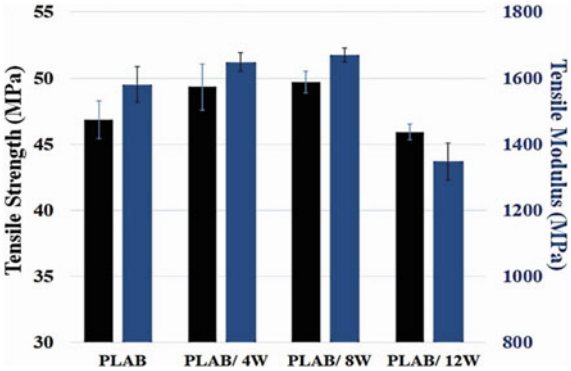


Fig. 13 Variation in tensile modulus of bagasse fibers reinforced PLA biocomposites under accelerated thermal weathering (Lila et al. 2019)

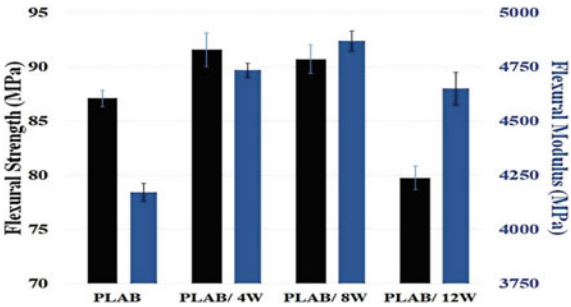


Fig. 14 Variation in flexural strength of Bagasse fibers reinforced PLA biocomposites during accelerated thermal aging (Lila et al. 2019)

4.5 Water Immersion-Freeze–Thaw Cycling Accelerated Aging and Xenon-Arc Light Accelerated Aging

The stability of composites largely depends on moisture. Lignocellulose fibers absorb moisture, and fiber swelling happens. As a result, cracks are formed in composites by destroying interfacial interaction. The stability of composites decreases with increasing the wood content (Turku et al. 2018). Changes in flexural and tensile properties due to freeze–thaw cycling are demonstrated in Fig. 15. The stability of composites can be increased using less hydrophilic filler material. The decrease in composite stability can happen because of removing lignin, washing of wood fibers, and reducing the amount of hemicellulose (Pilarski and Matuana 2005).

The mechanical properties (tensile and flexural) of wood-plastic composites decrease by 2–30% under accelerated freeze–thaw cycling and xenon-arc light conditions. Mechanical properties loss after full freeze–thaw cycling is similar to the properties loss after only water immersion. Mechanical properties reduce due to the decreased interfacial interaction by absorbed moisture in the composite (Matuana and Kamdem 2002). The swelling of wood particles also happens due to the existence of water. As a result, stress is generated into the matrix, and crack formation

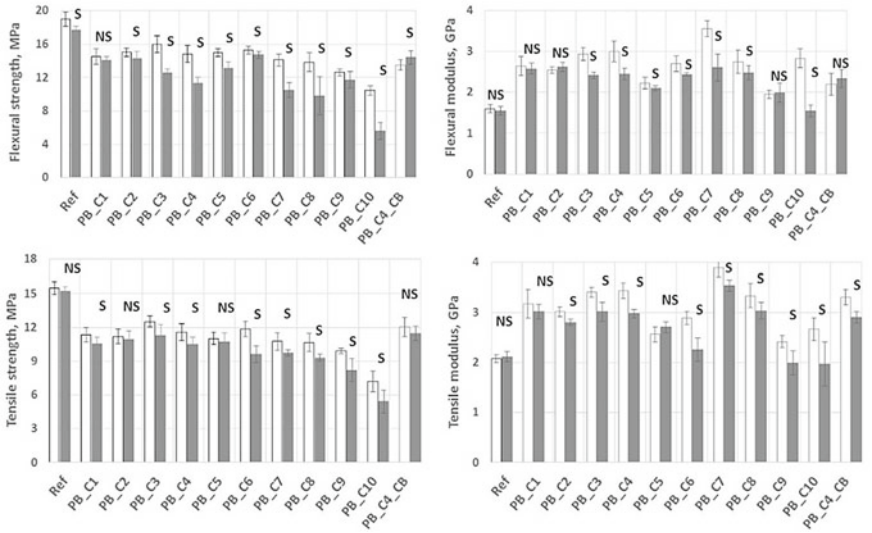


Fig. 15 Changes in flexural and tensile characteristics due to freeze–thaw cycling and xenon arc accelerated aging (Turku et al. 2018)

occurs. However, the mechanical properties of the composites can be restored by drying.

5 Conclusions

This chapter discussed the effect of aging on the mechanical properties of biocomposites with recycled polymers. Mechanical characteristics of biocomposites during aging depends on the aging process (Natural aging, Thermal aging… etc.). The mechanical properties (tensile and flexural) of wood-plastic composites decrease by 2–30% under accelerated freeze–thaw cycling and xenon-arc light conditions, bagasse fiber/polylactic acid (PLA) composites under accelerated thermal aging reduced due to weak interfacial adhesion between the fiber and matrix, recycled PP/EVA and PP/EVA/ITA composites under natural aging showed a positive effect. Generally, biocomposites have better resistivity against environmental factors. Mechanical properties (tensile modulus and strength, and flexural modulus and strength) reduce after aging, and they can be recovered after drying.. From the aging result, it is possible to obtain information about the suitability and durability of the composite materials for a specific application. Before application of any product if we conduct a suitable aging process that will be beneficial. Bio-composites with recycled polymers are not limited number. Everyday people think about it and find something new application. However, there is still an enormous research opportunity

for evaluating the aging effects on mechanical characteristics of biocomposites with recycled polymers.

References

Ahmad MAA, Abdul Majid MS, Ridzuan MJM, Mazlee MN, Gibson AG (2018) Dynamic mechanical analysis and effects of moisture on mechanical properties of interwoven hemp/polyethylene terephthalate (PET) hybrid composites. Constr Build Mater 179:265–276. https://doi.org/10.1016/j.conbuildmat.2018.05.227

AL-Oqla et al., 2015.AL-Oqla FM, Sapuan SM, Answer T, Jawaid M, Hoque ME (2015) Natural fiber reinforced conductive polymer composites as functional materials: a review. Synth Metals 206:42–54. https://doi.org/10.1016/j.synthmet.2015.04.014

Arifur Rahman M, Parvin F, Hasan M, Enamul Hoque M (2015) Introduction to manufacturing of natural fibre-reinforced polymer composites. In: Salit MS, Jawaid M, Yusoff NB, Hoque ME (eds) Manufacturing of natural fibre reinforced polymer composites. Springer International Publishing, Cham, pp 17–43

Asim M, Abdan K, Jawaid M, Nasir M, Dashtizadeh Z, Ishak MR, Enamul Hoque M (2015) "A review on pineapple leaves fibre and its composites" edited by Y. Deng. Int J Polym Sci 2015:950567. https://doi.org/10.1155/2015/950567

Babaghayou MI, Mourad A-H, Lorenzo V, Ulagares M, de la Orden J, Urreaga M, Chabira SF, Sebaa M (2016) Photodegradation characterization and heterogeneity evaluation of the exposed and unexposed faces of stabilized and unstabilized LDPE films. Mater Des 111:279–290. https://doi.org/10.1016/j.matdes.2016.08.065

Brebu M (2020) Environmental degradation of plastic composites with natural fillers—a review. Polymers 12(1). https://doi.org/10.3390/polym12010166

Callister WD, Rethwisch DG (2018) Materials science and engineering: an introduction, vol 9. Wiley, New York

Enamul Hoque M, Aminudin MAM, Jawaid M, Islam MS, Saba N, Paridah MT (2014) Physical, mechanical, and biodegradable properties of meranti wood polymer composites. Mater Des 64:743–749. https://doi.org/10.1016/j.matdes.2014.08.024

Fong TC, Saba N, Liew CK, De Silva R, Enamul Hoque M, Goh KL (2015) Yarn flax fibres for polymer-coated sutures and hand layup polymer composite laminates. In: Salit MS, Jawaid M, Yusoff NB, Hoque ME (eds) Manufacturing of natural fibre reinforced polymer composites. Springer International Publishing, Cham, pp 155–175

González-López ME, Martín AS, del Campo J, Robledo-Ortíz R, Arellano M, Pérez-Fonseca AA (2020) Accelerated weathering of poly(lactic acid) and its biocomposites: a review. Polym Degrad Stab 179:109290. https://doi.org/10.1016/j.polymdegradstab.2020.109290

Homkhiew C, Ratanawilai T, Thongruang W (2014) Effects of natural weathering on the properties of recycled polypropylene composites reinforced with rubberwood flour. Ind Crops Prod 56:52–59. https://doi.org/10.1016/j.indcrop.2014.02.034

Hoque ME, Khan MA, Islam MS, Asim M, Jawaid M, Othman OA (2016) Effects of natural degradation on the mechanical and morphological properties of tropical woods. Cellul Chem Technol 50(7–8):723–730. http://www.cellulosechemtechnol.ro/firstonline.php

Kollia E, Saridaki X, Karagiannis D, Kostopoulos V (2020) Effect of water aging on the mechanical properties of flax fiber/bio-based resin composites. J Appl Polym Sci 137(13):48787. https://doi.org/10.1002/app.48787

Lila MK, Shukla K, Komal UK, Singh I (2019) Accelerated thermal ageing behaviour of bagasse fibers reinforced poly (lactic acid) based biocomposites. Compos B Eng 156:121–127. https://doi.org/10.1016/j.compositesb.2018.08.068

Martin R (2008) Ageing of composites. Elsevier

Matuana LM, Kamdem DP (2002) Accelerated ultraviolet weathering of PVC/wood-flour composites. Polym Eng Sci 42(8):1657–1666. https://doi.org/10.1002/pen.11060

Moreno DDP, Hirayama D, Saron C (2018) Accelerated aging of pine wood waste/recycled LDPE composite. Polym Degrad Stab 149:39–44. https://doi.org/10.1016/j.polymdegradstab.2018.01.014

Panthapulakkal S, Law S, Sain M (2006) Effect of water absorption, freezing and thawing, and photo-aging on flexural properties of extruded HDPE/rice husk composites. J Appl Polym Sci 100(5):3619–3625. https://doi.org/10.1002/app.23152

Pilarski JM, Matuana LM (2005) Durability of wood flour-plastic composites exposed to accelerated freeze-thaw cycling. Part I. Rigid PVC matrix. J Vinyl Addit Technol 11(1):1–8. https://doi.org/10.1002/vnl.20029

Salit MS, Jawaid M, Yusoff NB, Enamul Hoque M (2015) Manufacturing of natural fibre reinforced polymer composites. Springer

Seldén R, Nyström B, Långström R (2004) UV aging of poly(propylene)/wood-fiber composites. Polym Compos 25(5):543–553. https://doi.org/10.1002/pc.20048

da Silva CB, Martins AB, Catto AL, Santana RMC (2017) Effect of natural ageing on the properties of recycled polypropylene/ethylene vinyl acetate/wood flour composites. Matéria (Rio de Janeiro) 22

Stark NM (2006) Effect of weathering cycle and manufacturing method on performance of wood flour and high-density polyethylene composites. J Appl Polym Sci 100(4):3131–3140. https://doi.org/10.1002/app.23035

Stark NM, Matuana LM (2004) Surface chemistry changes of weathered HDPE/wood-flour composites studied by XPS and FTIR spectroscopy. Polym Degrad Stab 86(1):1–9. https://doi.org/10.1016/j.polymdegradstab.2003.11.002

Turku I, Kärki T, Puurtinen A (2018) Durability of wood plastic composites manufactured from recycled plastic. Heliyon 4(3):e00559. https://doi.org/10.1016/j.heliyon.2018.e00559

Influence of Seawater Ageing on the Physical and Mechanical Properties of the Natural Fiber-Reinforced Composites

J. Jefferson Andrew and H. N. Dhakal

Abstract Due to the sustainable, and commercial outcomes of the natural fibers, along with their desired features such as high specific mechanical properties, natural fiber-reinforced composites (NFRCs) are exhibiting a strong potential to be employed in different applications such as aerospace, automotive, packaging, etc. This chapter presents a comprehensive discussion on the main characteristics of seawater ageing and moisture ingress mechanism influencing natural fibers and their performance as reinforcement in polymer matrix composites. This chapter presents the influence of seawater ageing on the physical and mechanical properties of NFRCs. Furthermore, the chapter also discuss various measures to prevent moisture ingress. Many researchers have been focusing attention to overcome the issues due to moisture absorption, with particular interest paid to the physical and chemical treatment of reinforcements and improving the fibre–matrix interface strength. Recent studies and developments dealing with moisture repellent coatings are also discussed.

Keywords Natural-fiber reinforced composites (NFRCs) · Moisture absorption · Ageing · Mechanical and thermal properties · Chemical and physical treatments · Coatings

1 Introduction

The application of natural fibers as a reinforcing phase in polymer matrix composites is continuously increasing, particularly in the aerospace and automotive sectors, due to a necessity to develop environmentally friendly and sustainable engineering materials. Potentially, the use of natural fibers in composite materials could increase their usage in the future owing to their plentiful benefits, such as low weight, availability,

J. J. Andrew
Department of Mechanical Engineering, Khalifa University, Abu Dhabi, UAE

H. N. Dhakal (✉)
Advanced Polymer and Composites (APC) Research Group, School of Mechanical and Design Engineering, University of Portsmouth, Portsmouth PO1 3DJ, UK
e-mail: Hom.Dhakal@Port.ac.uk

C. Muthukumar et al. (eds.), *Aging Effects on Natural Fiber-Reinforced Polymer Composites*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-8360-2_18

high specific mechanical properties, low production and maintenance cost, and corrosion resistance (Azwa et al. 2013). On the other hand, the main limitation of natural fibers is their hydrophilic behavior which leads to poor mechanical properties when integrated with a polymer matrix and thus limits their usage. Natural fiber-reinforced composites (NFRCs) experience a premature mechanical failure under a humid environment via water sorption leading to fiber/matrix debonding. This water sorption at elevated temperature or varying humidity further results in the occurrence of voids, swelling, and micro-cracks which critically influences the mechanical performance (Sen and Reddy 2013).

Previous investigations have demonstrated that the factors such as fiber and matrix type, fiber/matrix interaction, fiber/matrix volume fraction, and environmental conditions significantly affect the moisture absorption behavior. For example, in wood fiber reinforced polypropylene matrix composites it was reported that the moisture absorption rises with increasing the volume fraction of the fibers due to the higher cellulose content (Bledzki and Faruk 2004). The lignocellulose in natural fiber, which contains a high amount of polarized hydroxyl groups, is responsible for their hydrophilic nature (Zafeiropoulos 2011; Dhakal et al. 2007). This feature of natural fibers hinders their compatibility with hydrophobic polymers which leads to poor fiber/matrix interaction. Surface treatments of natural fibers have been used as a promising tool to enhance the compatibility with hydrophobic polymers (Dixit and Verma 2012). Nevertheless, the long-term exposure of NFRCs to elevated temperature and high relative humidity is challenging, further procedures such as nano-coatings, chemical treatment, and bio-based coatings want to be explored and optimized to improve their hydrophobicity. The influence of surface chemistry and topography of cellulose, which significantly influences the hydrophobicity, must be given more importance. Remarkably, investigation on superhydrophobicity of NFRCs has encouraged much industrial and research interest owing to their applications in friction reduction, self-cleaning, and antifouling (Song and Rojas 2013).

2 Natural Fiber-Reinforced Composites

2.1 Advantages of Natural Fiber Composites

The rising interest in employing natural fibers as reinforcement in polymer matrix based composite materials is mainly owing to their plenty availability, diverse source, relatively higher specific mechanical properties (strength and stiffness), lightweight, cost-effectiveness (for instance, flax plant fibers of density 1.5 g/cm^3 cost in the range between \$0.22 and 1.10/kg, while glass fibers of density 2.6 g/cm^3 cost in the range between \$1.30 and 2.00/kg) and similarity for biodegradable polymer systems when compared to glass fiber-based composites (Fakhrul and Islam 2013). Natural fibers as a renewable source, necessitate a low amount of energy for production. Their emission of hazardous gases (e.g. carbon dioxide) is negligible to the environment

when they are processed or combusted and have several beneficial impacts on the environment. The handling environment is user-friendly making the working conditions healthier and thus decreasing the hazard of allergic reactions (e.g. skin rashes). Unlike synthetic fibers, natural reinforcements also show safer handling and working conditions.

From a viewpoint of industrial manufacturing, the fabrication methodology for NFRCs consumes less amount of energy than that of synthetic reinforcement and produces a reduced amount of wear and tear on the equipment, and consequently leads to a substantial reduction of working costs. Moreover, they have high electrical resistance and thermal recycling is also possible. Due to their cellular geometry, NFRCs provides superior acoustic insulation. Above all, their worldwide availability is an added factor (John and Thomas 2008).

2.2 Drawbacks of Natural Fiber Composites

Natural fibers are considered promising alternatives for man-made synthetic fibers in fiber-reinforced composites. While natural fiber reinforcements have the advantages of being sustainable, lightweight, and cost-effective, they are not completely exempt from problems (Xie et al. 2010). One of the main issues is their high hydrophilic property which produces incompatibility and compounding difficulties with many polymer systems. This feature results in an uneven scattering of the reinforcements in the polymer matrix and thus weakens the performance of the resulting material. Natural fibers possess lower degradation temperatures (∼200 °C), which makes them inappropriate to process with polymer matrix at a temperature higher than 200 °C and this further hinders the choice of the polymer matrix.

Another limitation to the effective application of natural fibers in composites is their poor microbial resistance and susceptibility to rot. These features pose critical issues during fabrication, storage, and transportation. The heterogeneity, and change of dimensions and their properties induce another critical problem. Another serious drawback is the high moisture uptake of natural fibers leading to swelling and creating voids at the interface, which results in poor mechanical properties and decreases dimensional stability of composites.

Nevertheless, recent investigations have shown that the hydrophobic nature of natural fibers can be reduced by modifying the hydrophilic hydroxyl groups on the reinforcement surfaces via various treatments (e.g. alkali, acetylation, silane, etc.). These treatments are characteristically performed by using reagent functional groups which can react with the functional groups in the reinforcement surface and modify their configuration. This might lead to the diminishing of moisture absorption and make things easier for better compatibility with the polymer systems (Hashim et al. 2012).

3 Moisture Absorption Characteristics of Natural Fiber Composites

Moisture ingress could generate damage in the matrix, reinforcement, and their interface. A schematic depicting the degradation mechanisms of NFRCs exposed to high moisture or immersed in seawater is illustrated in Fig. 1. Synthetic fibers, namely glass or carbon, do not absorb moisture (Earl and Shenoi 2004). Nevertheless, natural fibers such as hemp or basalt, tend to absorb moisture resulting in a higher amount of fiber swelling and failure (Akil et al. 2009). The polymer matrix in a composite is the main constituent that absorbs moisture from the surrounding. Characteristically, moisture ingress into the matrix system occurs via capillary action and diffusion. The absorbed moisture could induce swelling and micro-crack propagation in the matrix, thus influencing the microstructure of e polymer matrix (Rocha et al. 2017).

Moreover, chemical and physical degradation such as hydrolysis and matrix plasticization can occur (Bergeret et al. 2001). The polymer chains could break due to hydrolysis and reduce the bonding force amid molecules (Earl and Shenoi 2004). The polymer matrix could soften due to matrix polymerization, thus decreasing the glass transition temperature (T_g) and the stiffness of the NFRCs (Wang et al. 2016). Matrix plasticization is moderately reversible, when the composite is dried, the mechanical

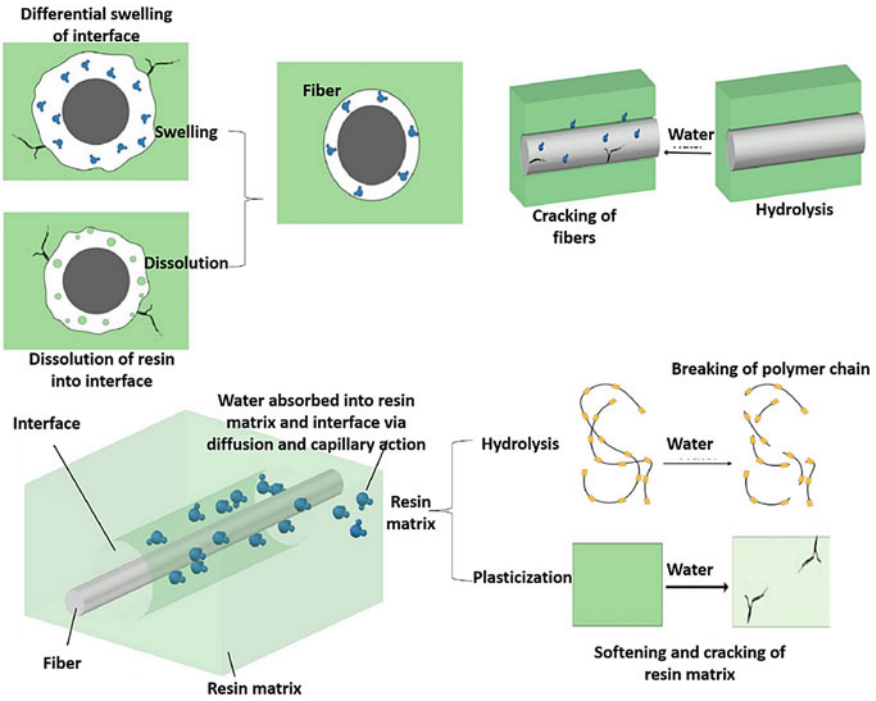


Fig. 1 Moisture absorption characteristics of natural fiber composites (Liu et al. 2020)

properties may be recovered (Hashim et al. 2012); while, hydrolysis is irreversible resulting in permanent damage. Furthermore, hydrolysis could be the main factor for the weakening of the mechanical properties of NFRCs. The fiber-matrix interface is also an important factor essential in the moisture ingression process. The fiber/matrix interface, due to a critical chemical heterogeneity in NFRCs, offers a convenient passage for moisture ingress (Sethi and Ray 2015). This effect is predominant for NFRCs with low-quality fiber/matrix interfaces. The moisture ingresses along the interface might induce differential swelling of the interface and growth of microcracks (Rocha et al. 2017). Moreover, the interface debonding can happen, and a part of the polymer matrix along the interface may dissolve into the moisture and leach away. Thus, a weakened interface directly reduces the interlaminar shear strength of the composite. Moreover, emphasized that the fiber/matrix interface is highly vulnerable to moisture and could initiate the degradation process of the NFRCs (Yu et al. 2015).

The moisture ingress into the polymer matrix and the interface might further expand the initial micro-cracks and passages and generate new pores and cracks, thus enabling additional moisture to be absorbed into the composite, allowing all the degradation mechanisms (John and Thomas 2008). Through moisture ingression-induced degradation, the fiber-dominated properties, viz., the tensile response, are only slightly influenced, while the fiber/matrix interface and matrix-dominated properties, viz., the shear and flexural response, are considerably weakened (Earl and Shenoi 2004; Grammatikos et al. 2016).

3.1 Seawater Ageing Main Characteristics

Seawater ageing induces various extents of degradation in NFRCs through chemical and/or physical reactions. Moisture ingress could considerably damage the composite at the fiber-matrix level. The moisture absorption behavior of a NFRCs can be characterized with two models:

(i) The pseudo-Fickian response, where the moisture weight gains didn't attain a saturation or equilibrium; and
(ii) Linear Fickian response, where the moisture weight gains progressively attained saturation or equilibrium.

The higher ingression of water molecules enables the microbial or fungal attack, resulting in a process called biodegradation. The penetration of water molecules in an NFRC can be enabled through various events. The moisture absorbed in the NFRC is grouped as bound and free moisture. The bound moisture is scattered water molecules that are bonded to the polar groups of the matrix system, whereas the free moisture can move through the pores and cracks. While excessive moisture is absorbed, the bound moisture raises whereas the free moisture reduces. The diffusion mechanism of moisture into an NFRC is shown in Fig. 2 (Banik et al. 2017).

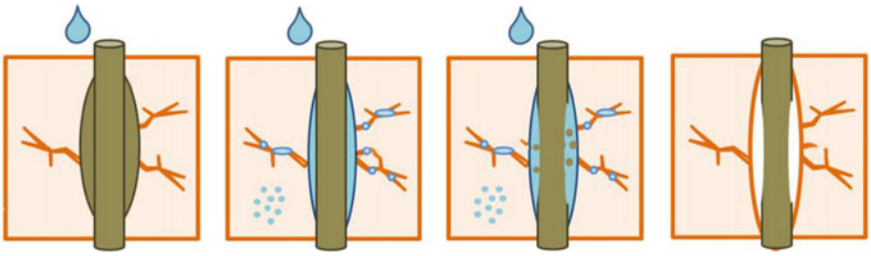


Fig. 2 The degradation of fiber/matrix interface due to seawater ageing (Azwa et al. 2013)

The moisture ingress induces all three dimensions of the NFRC to increase. However, the rise in the thickness of the composite is relatively larger than that of the rise in the length and width. The natural fibers are affected by the moisture ingression in the two directions: (i) variations in the density of the reinforcements via the weight of absorbed moisture; and (ii) swelling of the reinforcements. The hydroxyl and polar groups in the natural fibers significantly influence the water uptake behavior. The swelling and hydrolysis mechanisms occurring due to water uptake causes fiber/matrix debonding, interlaminar delamination, and matrix micro-cracking, which enhances the thermal and mechanical property degradation of NFRCs (Banik et al. 2017). Nevertheless, the swelling of reinforcement also has a positive outcome on the mechanical properties of NFRCs, as this induces the mechanical interlocking among the fiber and matrix. The moisture absorption is liable for raising the mobility of the molecular chains and side groups, which results in reversible matrix plasticization (Al-Maharma and Al-Huniti 2019). The plasticization event raises the fracture toughness and impact resistance, though it also decreases the mechanical properties such as strength, stiffness, fatigue resistance, and natural frequencies of the NFRCs. The variation in the responses amid tensile and impact properties can be explained via the swelling effect of the reinforcements and matrix plasticization (Dixit and Verma 2012). The moisture diffusion into some types of polymer matrices might considerably modify the intermolecular interaction, which substantially contributes to a higher thermal conductivity property, and thus decreases the thermal insulation characteristics of NFRCs (Banik et al. 2017).

3.2 Moisture Ingress Mechanisms

Natural fibers are typically hydrophilic owing to the presence of a high amount of hydroxyl groups (OH) in hemicellulose and cellulose. Nevertheless, not all the components contribute to moisture ingression. Even though cellulose has a high amount of hydroxyl groups to carbon ratio, a few hydroxyl groups are available as semi-crystalline. In cellulose, the extremely crystalline area is almost unreachable to moisture but the moisture is capable to enter and get in contact with the amorphous

part. In contrast, hemicellulose is largely amorphous, making them easily accessible to moisture. Lignin, on the other hand, is hydrophobic, contains low hydroxyl groups to carbon ratio. When moisture ingress occurs, the natural fiber swells up because the moisture dwell in the space stuck between the microfibrils. This area that the moisture stay is called the temporary micro-capillary network. The absorbed moisture can either generate a monolayer (moisture close contact with the hydroxyl groups) or form a multilayer (moisture intimate contact with hydroxyl groups) (Zafeiropoulos 2011). In NFRCs, moisture ingression relies mainly on the factors such as fiber/matrix volume fraction, environmental temperature, fiber orientation, and diffusivity. The diffusion process is the major mechanism by which the moisture penetrates the composite. The diffusion mechanism includes random molecular motion directly into the matrix system and to a much fewer amount into the reinforcements. The penetration and capillarity action via pores and micro-cracks are the most common water molecules transport mechanisms.

The capillarity action includes movement of the water molecules along with the fiber/matrix interface, afterward diffusion from the interface into the polymer matrix. This movement of water molecules via pores and micro-cracks comprises both storage and flow of the moisture as well as the formation of further micro damages. The polar nature of the reinforcements induces them to absorb moisture and swell. Consequently, the degradation process initiates with the swelling of the amorphous region in the reinforcement that generates residual stress at the fiber/matrix interface and induces matrix micro-cracking over and around the swelled reinforcements. The micro-cracks intensify moisture ingression and its influence on the interfaces. The absorbed moisture initiates to generate intermolecular hydrogen bonding with the reinforcements and as a result decreases the fiber/matrix interfacial adhesion, and soluble components will start leaking from the reinforcements. These events eventually result in the fiber/matrix debonding (Zhang et al. 2014).

4 Effects of Seawater Ageing on the Physical Properties of Natural Fiber Composites

4.1 Mechanical Properties

Water uptake is one of the main drawbacks encountered by NFRCs. The mechanical properties of a hydrolytically aged NFRC mainly depend on the fiber type, interfacial strength, surrounding temperature, fiber processing and treatments, and fiber arrangement. Swelling of the fiber reinforcements decreases the tensile, flexural, and compressive properties with an exception of impact response which is normally noticed to increase. Even though, in hydrophobic polymers (e.g. polypropylene (PP)), the tensile and flexural response of NFRCs deceases considerably over hydrolytic ageing for a few weeks with the rate of degradation raise at elevated temperatures (Hargitai et al. 2008). Maleated polypropylene employed as a coupling agent reduces

moisture absorption, decrease saturation moisture content, and offer higher mechanical properties after subjecting to hydrolytic ageing for reinforced PP based composites (Beg and Pickering 2008); nevertheless, an enormous drop in properties even with maleated polypropylene is noticed, with for instance degradation of mechanical strength for wood/PP composites after 7 months.

The water uptake behavior has been noticed to be varying based on the salt content of the seawater. The rate of moisture absorption for NFRCs exposed to seawater has been reported to be slower than that for the distilled water, ascribed owing to the NaCl ions migrating to the fiber surfaces. Higher diffusion of distilled water comparative to seawater in NFRCs is further supported by a study done with jute and glass unsaturated polyester (UP) composites (Zamri et al. 2012).

Although natural fibers normally considered to rise water uptake of the composite, the advantage of the inclusion of natural fibers in glass fiber/thermoset composites has been observed for prolonged exposure; while the rate of degradation with jute fibers was observed to quicker for duration around 70 h, beyond this period, jute was noted to decrease the degradation rate. This is ascribed due to the swollen jute being capable to put up the matrix swelling strain (Banik et al. 2017). In this same study, while the silane coupling agent was noticed to enhance flexural properties, the advantage was missing after approximately 12 days in boiling water.

The main factors that influence the mechanical response of NFRCs are:

4.1.1 Fiber Selection

Based on the origin, fiber is grouped as plant, animal, or mineral. All animal fibers contain protein as their major component, while plant fibers largely contain cellulose. Mineral fibers are obtained from the asbestos group of minerals. Mineral fibers were once utilized widely in composites, but they are now evaded owing to their carcinogenic nature. Compared to animal fibers, plant fibers exhibit higher strengths and stiffness properties. Silk fibers are an exception to this, but they are comparatively costly (Shah et al. 2014). This facilitates plant fibers the most appropriate for application in composites. The mechanical properties of natural fibers differ significantly based on the chemical structure and composition, which associate with the growing location, harvesting time, processing technique, and storage methods.

Normally mechanical strength raises with increasing moisture content and reduces as temperature rises; Young's modulus or stiffness reduces with water uptake. Every so often it is uncertain in the research articles as to whether the investigations have been performed on single fibers or bundles. Generally, mechanical properties are calculated considering the total cross-section of fiber or bundle, nevertheless, single fibers have a hollow lumen at the middle which takes up a substantial amount of the area. For sisal, flax, and jute fiber the cross-sectional area covered by the lumen is 218.2, 6.8, and 34.0% respectively (Li et al. 2015) and calculation of mechanical properties without including this factor underestimates the result to some degree. Normally, the fibers are stiffer and stronger than the polymer matrix. The strength and stiffness of the FRP composites are normally seen to rise with a higher fiber volume

fraction. Nevertheless, this depends on having reasonable fiber/matrix interfacial strength, and strength may decrease much with incompatible hydrophobic polymer matrices with increasing fiber volume fraction unless some treatments or some other interfacial engineering technique is used; nevertheless, stiffness still normally raises with fiber volume fraction but very modestly than when the fiber/matrix interface is not optimized.

When desired fiber/matrix interfacial strength is achieved, mechanical strength normally peaks with a fiber volume fraction of 40–55 m% for thermoplastic polymer based NFRCs with decrement at higher volume fraction explained as being owing to poor wetting resulting in poor stress transfer over and around the interfaces and raising porosity. Stiffness increases up to fiber volume fraction of ~55–65 m% with the identical material system, perhaps owing to less reliance on fiber/matrix interfacial strength than composite strength (Madsen et al. 2009). Further insight has been given by researchers investigating the effect of fiber weight fraction on porosity, voids, and volume fraction of fiber. This has revealed that peak fiber volume fraction of fiber come about ~50–60 m% with further addition lead to higher porosity rather than increased fiber volume fraction, the influence of which has been integrated into the rule of mixtures and revealed to improve precision for stiffness and strength (Madsen et al. 2009).

Besides being a concern for short-term properties of NFRCs, higher content of fiber reinforcements are also of concern owing to the potential for higher moisture absorption resulting in degradation of longer-term composite properties. It has been reported that hemp/polypropylene composites with a fiber volume fraction of 0.7 absorbed ~53 m% moisture and had not attained saturation after 19 days, while only 7 m% moisture absorption was noticed in composites with a fiber volume fraction of 0.3, and saturation was attained in the same duration (Pickering et al. 2016).

4.1.2 Matrix Selection

The matrix system is a vital component of an NFRC. It offers an obstruction against critical service environments, safeguards the fiber surface from abrasion and it transfers mechanical stress to the fibers. Polymeric materials (e.g. thermoplastic or thermoset) are commonly used matrices for NFRCs because as they can be processed at low temperatures. Matrix materials are selected based on the degradation temperature of the fibers (~200 °C). However, under certain conditions, it is likely to process them at elevated temperatures for a short duration (Summerscales, et al. 2010). Owing to these constraints, thermoplastics (e.g. polyethylene, polypropylene, polyolefin, polystyrene, polyvinyl chloride, etc.) that soften below ~200 °C are often useable as a matrix. The most common thermosets employed for NFRCs are phenol–formaldehyde, unsaturated polyester (UP), epoxy resin, and VE resins. Thermoplastic polymers are capable of being repetitively softened and hardened via heating and cooling, respectively, and can be recycled, while better fiber properties can be realized by employing thermosets. Replacement of synthetic with biodegradable matrices has been extensively studied. Among them, polylactic

acids are the prime candidate from a mechanical property viewpoint and have been presented to provide higher mechanical properties with natural fibers than polypropylene (Faruk et al. 2014).

4.1.3 Fiber/Matrix Interface

The fiber/matrix interfacial bonding significantly influences the mechanical properties of NFRCs under sea water ageing. As mechanical stress is transferred amid fibers and matrix systems in the interface, optimal fiber/matrix interfacial bonding strength is necessary to realize the best possible reinforcement. However, it is the potential to have an excessively strong interface, allowing crack growth which can decrease strength and toughness. Nevertheless, for NFRCs there is commonly inadequate interaction amid the hydrophilic fibers and polymer matrices which are normally hydrophobic resulting in poor fiber/matrix interfacial bonding strength limiting mechanical response along with poor moisture resistance influencing their durability for long term application. For better interfacial bonding to ensue, fiber and matrix should be drawn into close contact; wettability can be considered as an important factor in bonding. Inadequate fiber wetting leads to interfacial imperfections which can function as stress concentration sites (Sinha and Panigrahi 2009). Wettability has been revealed to influence the tensile, bending, and impact strength of NFRCs. Fiber wettability can be enhanced by physical and chemical treatments. Fiber/matrix interfacial bonding is built by the mechanisms of mechanical interlocking, inter-diffusion, electrostatic and chemical bonding (Pickering et al. 2016). Polymer interfaces are built by polymer chains entanglement and rely on the chain length, number, and degree of entanglement/unit area. Several bonding types can arise at the same interface.

Optimal fiber/matrix interfacial bonding strength in NFRCs can be achieved via different chemical and physical approaches. Physical approaches comprise heat, plasma, corona, ultraviolet (UV) treatments fiber beating, and electron radiation. Chemical approaches provide superior enhancements to physical ones to date. Chemical treatments comprise acrylonitrile, titanate, peroxide, alkali, acetyl, benzyl, acryl, silane, permanganate, zirconate, and isocyanate treatments and the use of maleated anhydride grafted coupling agent (Faruk et al. 2014). Silane, alkali, acetyl treatments, and maleated anhydride grafted coupling agents are the most commonly used chemical approaches (Faruk et al. 2014). Numerous researches have reported enhancements in moisture resistance, thermal stability, tensile strength, stiffness, toughness, bending properties, etc. Alkali treatment takes out lignin, hemicellulose, wax, fat, pectin, etc. form the fiber surface and improves surface roughness offering enhanced fiber/matrix interfacial bonding. Alkali treatment also alters the cellulose structure; modest treatments increase crystallinity, while severer treatments convert crystalline cellulose to amorphous.

4.1.4 Fiber Dispersion

Fiber dispersion plays an important role in affecting the mechanical properties of NFRCs under sea water ageing, which mostly have hydrophobic matrices and hydrophilic fibers (Heidi et al. 2011). Normally, longer fibers tend to agglomerate. Ideal fiber dispersion enhances better interfacial bonding and decreases pores and voids (Heidi et al. 2011). Processing parameters (pressure and temperature) influences fiber dispersion. Further, additives such as stearic acid and fiber grafting enhance fiber-matrix interaction.

4.1.5 Porosity

Porosity largely influences the mechanical properties in general, and enormous research effort has gone into decreasing this effect. It occurs owing to the enclosure of air during fabrication, inadequate fiber wettability, and other hollow characteristics in the reinforcements (which could close while applying high pressure at elevated temperature) and owing to the low ability of reinforcements to compact (Madsen et al. 2009). Porosity in NFRCs increases with the rise in the fiber volume fraction.

4.2 Thermal Properties

Usually, moisture diffuses highly into the amorphous area of the NFRCs where diffusion takes place at a rate that relies on the crystallinity and the end-group contents. Water uptake may severely modify the mechanical and physicochemical properties in the matrix system or the interface: polymer chains may encounter a revisable plasticization event, which decreases glass transition temperature (T_g), be subjected to irrevocable hydrolysis (Jedidi et al. 2006) and the interface between the fiber and matrix may be damaged owing to the link with internal stresses, for instance. The degree of thermal properties degradation that occurs in an NFRC is directly associated with the amount of water uptake. The diffusion phenomenon is extremely reliant on temperature and relative humidity (Jedidi et al. 2006).

The thermo-physical properties are vital for numerous applications like heat dissipation and heat exchangers-based materials in electronic applications. From the previous literature, it is observed that the NFRCs have limitations in heat dissipation characteristics. To evaluate the water uptake percentage and other volatile elements present in the composites, the thermal properties have been evaluated. This is crucial since water content and volatile elements have a weakening effect on the properties of composites. To examine the heat transfer capability of the NFRCs, the thermal diffusivity, conductivity, and specific heat are the main properties to be evaluated. The moisture ingress into NFRCs could considerably modify the intermolecular interaction, which considerably increases the thermal conductivity, and consequently decreases the thermal insulation properties of natural composites.

5 Various Measures to Prevent Moisture Ingress

The natural fibers consist of non-cellulosic substances and waxes, which avert the reinforcements from generating ample adhesion with the polymer matrix. To fabricate NFRCs with enhanced mechanical, moisture resistance, and tribological properties, it is recommended to enhance the hydrophobicity of the natural fibers. This can be realized via exposing the fiber surfaces to physical or/and chemical treatments. This treatment removes the hydrophilic components from the fiber surface. The influence of different types of physical/chemical treatments on improving the moisture ingress nature can be examined via studying the improvement achieved on the moisture absorption behavior for various types of NFRCs, as illustrated in Fig. 3. It can be observed that certain types of surface treatments have adverse influences on the moisture absorption response of some NFRCs (e.g. sisal/starch and jute/UP), which are treated with alkalization and hot water, respectively. This lessening can be ascribed to the removal of hydrophobic constituents (e.g. lignin) from the composites, which consequently encourages the material to ingress more amount of water molecules. Based on the capabilities of different surface treatments method (how they modify the chemical structure and composition of NFRCs), they are grouped into chemical and physical treatments.

5.1 Chemical Treatments

The chemical treatment methods can remove the hydroxyl groups from the reinforcements and enhance the surface roughness, resulting in an obvious rise in the interlocking of the reinforcements with the polymer matrix (Nirmal et al. 2015). From Fig. 4, the treated reinforcements show a considerable rise in the roughness

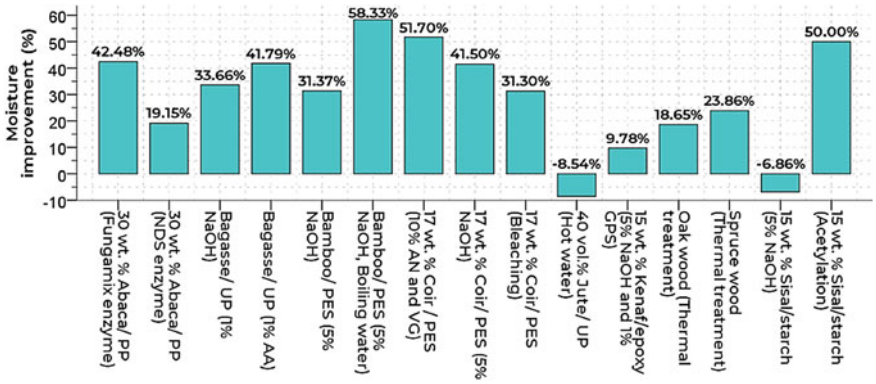


Fig. 3 The influence of different types of physical/chemical treatments on improving the moisture ingress nature (Al-Maharma and Al-Huniti 2019)

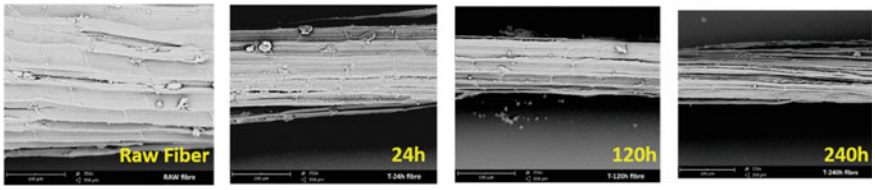


Fig. 4 Roughness of treated reinforcements with increasing treatment duration (Fiore et al. 2016)

with increasing treatment duration, and the impurities are removed to the maximum degree. When the hemicellulose and lignin are removed from the reinforcements, the interior restrictions positioned in the interfibrillar sites are released. Therefore, the cellulose fibrils restructure and form an extremely compacted structure, resulting in densely packed chains (Al-Maharma and Al-Huniti 2019). The following chemical treatments are generally employed to treat natural fibers.

5.1.1 Acetylation

Treating the natural fibers with acetic anhydride removes the lignin and hemicellulose components and improves the moisture resistance (Al-Maharma and Al-Huniti 2019). In this treatment, the hydroxyl group in the fiber reacts with the acetyl groups and makes the fiber surface more hydrophobic.

5.1.2 Benzoylation

In Benzoylation, the fibers are initially treated with alkali solution and then with benzoyl chloride. Hence, the hydroxyl group is altered with the benzoyl group (Al-Maharma and Al-Huniti 2019).

5.1.3 Peroxide

In peroxide treatment, the PE grafting sticks to the fiber surface. The fibers are pretreated with an alkali and then immersed with benzoyl peroxide (in acetone aqueous) for a time period of ~30 min (Al-Maharma and Al-Huniti 2019).

5.1.4 Isocyanate

The isocyanate treatment generates a strong covalent bond amid the polymer (mainly thermoplastic matrix) and the fiber. Also, the water molecules that present on the reinforcements react with isocyanate and produce urea, which can react more with

the hydroxyl groups of the celluloses. These secondary reactions result in a stronger linkage amid the fiber and matrix and result in a superior moisture resistance (Al-Maharma and Al-Huniti 2019).

5.1.5 Acidic Treatments

In acid treatment, various types of acids such as stearic, hydrochloric, and acrylic acids are employed to enhance the hydrophobic nature of the fibers. The carboxyl group in the acids react with the OH groups and improves the fiber/matrix mechanical interlocking via the fibrillation of the fiber bundle (Al-Maharma and Al-Huniti 2019). Nevertheless, treatment with hydrochloric acid causes considerable reduction of the out-of-plane mechanical properties of the NFRCs due to the removal of non-cellulosic elements of the fibers (Al-Maharma and Al-Huniti 2019).

5.1.6 Alkalization

Alkalization treatment with NaOH solution is the most practical and effective technique to improve the fiber/matrix interfacial adhesion and moisture resistance (Akhtar et al. 2016). Moreover, this alkalization can remove a particular part of the oil, wax, lignin, hemicellulose, etc. that is covering the fiber. After this treatment, the fiber surface turns more organized and rougher due to the elimination of microvoids, which improves the stress transfer capacity. Also, it lessens the fiber diameter and increases the aspect ratio. This increases the fiber surface area effectively for enhanced adhesion with the reinforced matrix. Alkalization treatment removes the amorphous compounds and raises both the hydrogen groups and crystallinity index of the fiber (Akhtar et al. 2016). The alkali concentration and treatment duration critically influence the fiber properties. If the fibers are not washed properly, the alkali treatment will degrade and lead to fiber swelling. Besides, there are some disadvantages allied with the alkalization treatment, such as high pH values, high surfactant content, and contaminants residue after treatment. Thus, the alkaline concentration must be maintained properly to evade the degradation (e.g. fibrillation) of the mechanical properties of natural fibers. Comparative to a single treatment, the combination of alkali and silane treatments shows an improving result on the moisture uptake properties (Sepe et al. 2018).

5.1.7 Coupling Agents and Grafting

The coupling agent encourages the fiber/matrix interfacial interaction, improving the compatibility at the interface. The moisture ingress behavior is reduced as the pores and gaps at the interface region are reduced to a larger extent via strengthening the adhesion at the interface. Silane coupling agents enhance the resistance to moisture absorption of various natural fibers in the range between 89 and 96% (Dixit and

Verma 2012). The coupling agent initially reacts with the functional groups of the polymers and then with the hydroxyl group found in cellulose. In specific, the silane molecule strengthens the interaction amid the cellulose and polymer by generating a chemical bond (siloxane bridge), whereas its organofunctional group link to the polymer (Thakur et al. 2014). This treatment decreases the number of hydroxyl groups. Compared to the alkali-treated NFRCs, the fiber/matrix interaction of silane-treated ones are much stronger.

Graft copolymerization is one of the most common chemical treatments employed to lessen moisture absorption without modifying its inherent properties (Al-Maharma and Al-Huniti 2019). The maleic anhydride (MA) reacts with the hydroxyl group to generate ester linkages and reduces moisture absorption. This treatment is often employed with a PP matrix, which has a remarkable enhancement on the moisture resistance characteristics (Xie et al. 2010).

5.1.8 Polymeric Coatings

To avert the quick diffusion of moisture into the NFRCs mainly in the fiber/matrix interfacial area, it is suggested to use an appropriate thickness of resin-rich surface and to maintain this layer intact and free of pores or cracks during their service life (Zhang et al. 2017). NFRC can be subjected to coating via films fabricated from either natural or synthetic materials, which demonstrated their ability on decreasing the water uptake. Comparative to the chemically treated NFRC, utilizing coatings develops a higher level of moisture resistance (Sepe et al. 2018). Polypropylene and polyethylene plastic adhesive tape, acrylated epoxidized soybean oil polymer and acrylic paint are commonly employed as coatings in NFRCs.

5.2 Physical Treatments

The physical treatments do not modify the chemical structure of the NFRC. The most common physical treatment methods are the production of hybrid yarns, thermal treatment, calendaring, and stretching. These treatments modify the structural and surface properties of the natural fiber and therefore influence the mechanical bonding with the polymer matrix (Al-Maharma and Al-Huniti 2019). Wood-based composites are subjected to thermal treatment to impede moisture from diffusing inside the composite. This process enhances the compactness of the structure owing to the macromolecular reconfiguration and water loss. This rearrangement gives the effective stabilization of the composite under hydrolytic ageing conditions.

Modifying the natural fibers through plasma treatment enhances the hydrophilic property. This process removes part of the lignin, converting it to an area with a greater degree of hydrophilicity (Dixit and Verma 2012). Through the oxygen plasma treatment process, various functional groups can be introduced on the fiber surface,

and these functional groups develop strong linking with the polymers via covalent bonds, resulting in high surface roughness and strong fiber/matrix adhesion.

The fungi treatment can be used to remove the non-cellulosic ingredients from the fibers by the influence of specific enzymes. The fungi produce hyphane, which generates pores and a rough interface on the fiber surface for better mechanical interlocking with the matrix (Xie et al. 2010). This process results in a significant rise in the surface hydrophilicity owing to the removal of lignin and hemicellulose, allowing the cellulosic element exposed to the moisture. It is vital to note that the physical treatment processes such as an enzyme, hot water, and electron beam radiation reduce the bending properties of the NFRC owing to the removal of the fibers extractives. Nonetheless, chemical treatment offers the treated NFRC with higher fungal resistance, more dimensional stability, and moisture resistance (Al-Maharma and Al-Huniti 2019).

5.3 Incorporation of Nanofillers

The moisture resistance of NFRCs can be enhanced by implementing nanotechnology via incorporating different nanofillers (e.g. polyethyleneimine-reduced graphene oxide, TiO_2, SiC) and nanotechnology-based coatings (methylcellulose composite films). They decrease the diffusivity, improve the interfacial adhesion, and prevents penetration of moisture and crack growth (Fig. 5). Some particulate nature fibers can further enhance the moisture resistance of NFRC composite to other types of short fibers or fabrics (Al-Maharma and Al-Huniti 2019). The fly ash nanoparticles are employed to fills the pores and gaps that exist in the structure of NFRCs. The addition of metal oxide fillers into NFRCs enhances their swelling and moisture resistance by developing bonds with the hydrophobic polymers. Incorporating magnetic particles in kenaf fibers reinforced composites provides paramagnetic and electromagnetic shielding as well as moisture resistance (dual-functional characteristics).

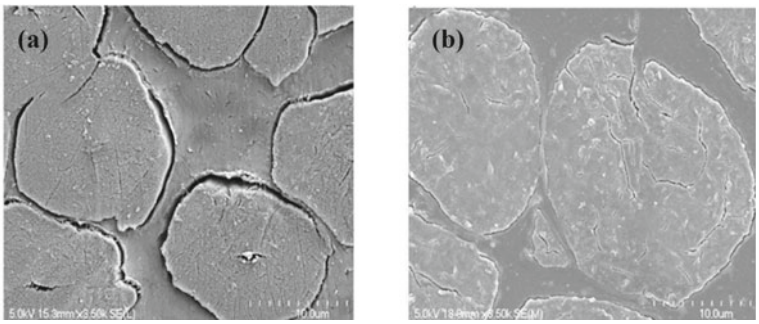


Fig. 5 SEM image of **a** raw, **b** modified flax fiber-based composites (Foruzanmehr et al. 2016)

Incorporating carbon nanotubes (CNTs) into the NFRCs reduces the water uptake tendency and reduces the time required to achieve the equilibrium thickness swelling (equilibrium time). This lessening is ascribed to the obstruction provided by CNTs, which hinder the water diffusion into the composite. CNTs can hinder the water diffusion into the NFRCs via two main mechanisms: (i) CNTs fill the pores and voids in the deeper regions of the composite; (ii) the hydrophobic CNT surface tries to immobilize the moisture (Liu et al. 2018).

5.4 Cellulosic Reinforcements

Cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) are natural fillers with high strength and surface area. The application of CNCs is being explored for various uses, as it is stronger than steel and stiffer than aluminum. It can be employed to fabricate composites with superior mechanical properties and good durability at various environmental conditions (Al-Maharma and Al-Huniti 2019; Popescu et al. 2017). CNCs extremely diminish the water sensitivity of NFRCs. This moisture stability initiates from the formation of hydrogen bonds between the OH groups via a 3D network. Bacterial cellulose (BC) nanofibers are added into the starch-based composites to improve their mechanical response and moisture resistance. Both the starch and bacterial cellulose nanofibers are hydrophilic, which may perhaps render the high water uptake of the composite. The higher moisture resistance of these composite materials comparative to a neat starch matrix is ascribed to the formation of strong hydrogen bonding between the fiber and matric interface (Popescu et al. 2017).

5.5 Clay Nanoparticles

Nanoclay and nano-silica carbide are added to the NFRCs to enhance their moisture absorption resistance and mechanical properties. The nanoclay provides an impermeable layer to obstruct moisture absorption and tends to force the water to flow along an indirect path, and as a result, a longer duration is required for the moisture diffusion (Dixit and Verma 2012). Nano clays are usually treated with a minor amount of silane coupling agents to produce NFRCs characterized with higher moisture resistance as well as better flexural and tensile properties. This improving effect can be ascribed to the development of covalent bonds with the polymer matrix and the effect of salinization on exfoliation, (Sharma et al. 2018). As the nanoclay is exposed to moisture, swelling occurs among the layers, which consequently alters the mechanical behavior of the resulting composite.

Organoclay (ammonia salts) is a different type of nano clay, with a high aspect ratio and surface area, that can considerably enhance the moisture resistance of natural composites. The efficiency of organoclays relies on various factors, such as

the morphology of fillers in the polymer matrix system and the polarity of organic moieties (Sharma et al. 2018). Based on the RH, a five-fold decrement in moisture absorption can be realized for NFRCs incorporated with organoclay comparative to those added with conventional clays.

6 Recommendations for Future Work

Recently, significant efforts have been made by numerous researchers to explore the mechanical performance of NFRCs exposed to long-term moisture ageing. The reported investigations have assisted to realize a good understanding of the moisture degradation behavior of NFRCs and, more notably, provided valuable guidance for future work. Based on the works reviewed in this chapter, the subsequent recommendations are suggested for future work.

(1) A longer ageing duration is required for all types of ageing conditions. Based on available data, it is observed that numerous moisture ageing tests are performed with an exposure duration of less than twelve months. In such a short period, inaccurate results might occur and compromise the dependability of the results to be employed for predicting the long-term performance of the composites.
(2) Compressive and out-of-plane properties should be focused on in future works. Numerous instigations have revealed that the degradation of the interface and polymer matrix mostly governs the overall degradation of NFRCs, as it is the matrix system that is adversely damaged while ageing. The out-of-plane and compressive properties of these composites are more influenced by the interface and matrix than the longitudinal ones; hence, the former are more vulnerable to ageing.
(3) The influence of the material constituents, the volume fraction of fibers, and geometric thickness must be considered when assessing the degradation response of NFRCs. These factors might influence the moisture uptake and the corresponding degradation of NFRCs.
(4) Each ageing effect must be exclusively defined for configuring the composite. In the practical design of NFRCs, the moisture ageing effects that are of interest must be determined by the designers. To support the designers, the degradation of NFRCs at each effect must be provided by the researchers.
(5) Standard tests and predictive methodologies must be developed in the future. Although many test results are available, those data are extremely dispersed, and identical conclusions are challenging to determine, which makes it hard to develop a reliable design method.

7 Conclusions

In summary, NFRCs have revealed their vulnerability to moisture absorption and in the long term, will induce them to lose their properties. Moreover, when subjected to elevated temperatures, the cracks induced by water uptake are known to raise, and thus, durable protections are necessary for the composites. This demands the fabrication of hydrophobic NFRCs that can be employed in adverse environmental conditions. The selection of appropriate modification measures is the important aspect to make certain that the reinforcements will have the specific features for superior moisture resistance. Chemical and physical modification techniques of natural fibers can decrease water uptake. Nevertheless, more research works are required to encourage a higher degree of hydrophobicity in the treated NFRCs when exposing them to long-term ageing. Furthermore, nano-coatings and bio-based coatings are also employed to realize super-hydrophobic composites. Investigation on super-hydrophobicity has encouraged much industrial and scientific attention owing to their applications in friction reduction, acid–base and solvent resistance, and antifouling. While there's not much literature reported on the application of moisture repellent coatings on composites exposed to moisture ageing, there is a potential for these coatings to be employed as appropriate material for lowering water uptake in NFRCs. Hence, further research wants to be exploited for coating NFRCs to develop high moisture resistance composites with superior thermal and mechanical properties.

References

Akhtar MN et al (2016) Influence of alkaline treatment and fiber loading on the physical and mechanical properties of kenaf/polypropylene composites for variety of applications. Prog Nat Sci Mater Int 26(6):657–664

Akil HM et al (2009) Water absorption study on pultruded jute fibre reinforced unsaturated polyester composites. Compos Sci Technol 69(11):1942–1948

Al-Maharma AY, Al-Huniti N (2019) Critical review of the parameters affecting the effectiveness of moisture absorption treatments used for natural composites. J Compos Sci 3(1):27

Azwa Z et al (2013) A review on the degradability of polymeric composites based on natural fibres. Mater Des 47:424–442

Banik N, Dey V, Sastry GRK (2017) An overview of lignin & hemicellulose effect upon biodegradable bamboo fiber composites due to moisture. Mater Today Proc 4(2, Part A):3222–3232

Beg M, Pickering K (2008) Mechanical performance of Kraft fibre reinforced polypropylene composites: influence of fibre length, fibre beating and hygrothermal ageing. Compos A Appl Sci Manuf 39(11):1748–1755

Bergeret A et al (2001) The hygrothermal behaviour of glass-fibre-reinforced thermoplastic composites: a prediction of the composite lifetime. Polym Testing 20(7):753–763

Bledzki AK, Faruk O (2004) Creep and impact properties of wood fibre–polypropylene composites: influence of temperature and moisture content. Compos Sci Technol 64(5):693–700

Dhakal H, Zhang Z, Richardson M (2007) Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. Compos Sci Technol 67(7–8):1674–1683

Dixit S, Verma P (2012) The effect of surface modification on the water absorption behavior of coir fibers. Adv Appl Sci Res 3(3):1463–1465

Earl JS, Shenoi RA (2004) Hygrothermal ageing effects on FRP laminate and structural foam materials. Compos A Appl Sci Manuf 35(11):1237–1247
Fakhrul T, Islam M (2013) Degradation behavior of natural fiber reinforced polymer matrix composites. Proc Eng 56:795–800
Faruk O et al (2014) Progress report on natural fiber reinforced composites. Macromol Mater Eng 299(1):9–26
Fiore V et al (2016) A new eco-friendly chemical treatment of natural fibres: effect of sodium bicarbonate on properties of sisal fibre and its epoxy composites. Compos B Eng 85:150–160
Foruzanmehr M et al (2016) Physical and mechanical properties of PLA composites reinforced by TiO_2 grafted flax fibers. Mater Des 106:295–304
Grammatikos SA et al (2016) On the response to hygrothermal ageing of pultruded FRPs used in the civil engineering sector. Mater Des 96:283–295
Hargitai H, Rácz I, Anandjiwala RD (2008) Development of hemp fiber reinforced polypropylene composites. J Thermoplast Compos Mater 21(2):165–174
Hashim MY et al (2012) Mercerization treatment parameter effect on natural fiber reinforced polymer matrix composite: a brief review. In: Proceedings of world academy of science, engineering and technology. World Academy of Science, Engineering and Technology
Heidi P et al (2011) The influence of biocomposite processing and composition on natural fiber length, dispersion and orientation. J Mater Sci Eng A 1(2A):190
Jedidi J, Jacquemin F, Vautrin A (2006) Accelerated hygrothermal cyclical tests for carbon/epoxy laminates. Compos A Appl Sci Manuf 37(4):636–645
John MJ, Thomas S (2008) Biofibres and biocomposites. Carbohyd Polym 71(3):343–364
Li Y et al (2015) Effects of resin inside fiber lumen on the mechanical properties of sisal fiber reinforced composites. Compos Sci Technol 108:32–40
Liu H et al (2018) Effect of polyethyleneimine modified graphene on the mechanical and water vapor barrier properties of methyl cellulose composite films. Carbohyd Polym 182:52–60
Liu T, Liu X, Feng P (2020) A comprehensive review on mechanical properties of pultruded FRP composites subjected to long-term environmental effects. Compos Part B Eng 191:107958
Madsen B, Thygesen A, Lilholt H (2009) Plant fibre composites–porosity and stiffness. Compos Sci Technol 69(7–8):1057–1069
Nirmal U, Hashim J, Megat Ahmad MMH (2015) A review on tribological performance of natural fibre polymeric composites. Tribol Int 83:77–104
Pickering KL, Efendy MGA, Le TM (2016) A review of recent developments in natural fibre composites and their mechanical performance. Compos A Appl Sci Manuf 83:98–112
Popescu M-C, Dogaru B-I, Popescu C-M (2017) The influence of cellulose nanocrystals content on the water sorption properties of bio-based composite films. Mater Des 132:170–177
Rocha IBCM et al (2017) Hygrothermal ageing behaviour of a glass/epoxy composite used in wind turbine blades. Compos Struct 174:110–122
Sen T, Reddy H (2013) Pretreatment of woven jute FRP composite and its use in strengthening of reinforced concrete beams in flexure. Adv Mater Sci Eng 2013
Sepe R et al (2018) Influence of chemical treatments on mechanical properties of hemp fiber reinforced composites. Compos B Eng 133:210–217
Sethi S, Ray BC (2015) Environmental effects on fibre reinforced polymeric composites: evolving reasons and remarks on interfacial strength and stability. Adv Coll Interface Sci 217:43–67
Shah DU, Porter D, Vollrath F (2014) Can silk become an effective reinforcing fibre? A property comparison with flax and glass reinforced composites. Compos Sci Technol 101:173–183
Sharma B, Chhibber R, Mehta R (2018) Seawater ageing of glass fiber reinforced epoxy nanocomposites based on silylated clays. Polym Degrad Stab 147:103–114
Sinha E, Panigrahi S (2009) Effect of plasma treatment on structure, wettability of jute fiber and flexural strength of its composite. J Compos Mater 43(17):1791–1802
Song J, Rojas OJ (2013) Approaching super-hydrophobicity from cellulosic materials: a review. Nord Pulp Pap Res J 28(2):216–238

Summerscales J et al (2010) A review of bast fibres and their composites. Part 1–Fibres as reinforcements. Compos Part A Appl Sci Manuf 41(10):1329–1335
Thakur VK, Thakur MK, Gupta RK (2014) Graft copolymers of natural fibers for green composites. Carbohyd Polym 104:87–93
Wang M et al (2016) Predicting false negative errors in digital breast tomosynthesis among radiology trainees using a computer vision-based approach. Expert Syst Appl 56:1–8
Xie Y et al (2010) Silane coupling agents used for natural fiber/polymer composites: a review. Compos A Appl Sci Manuf 41(7):806–819
Yu B, Jiang Z, Yang J (2015) Long-term moisture effects on the interfacial shear strength between surface treated carbon fiber and epoxy matrix. Compos A Appl Sci Manuf 78:311–317
Zafeiropoulos NE (2011) Interface engineering of natural fibre composites for maximum performance. Elsevier
Zamri MH et al (2012) Effect of water absorption on pultruded jute/glass fiber-reinforced unsaturated polyester hybrid composites. J Compos Mater 46(1):51–61
Zhang D et al (2014) Effects of humidity conditions at fabrication on the interfacial shear strength of flax/unsaturated polyester composites. Compos B Eng 60:186–192
Zhang J et al (2017) Natural and highly protective composite structures—wild silkworm cocoons. Compos Commun 4:1–4