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Vegetable Fiber Composites and their Technological Applications

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

Anish Khan
Center of Excellence for Advanced
Materials Research
King Abdulaziz University
Jeddah, Saudi Arabia

ISSN 2662-1819 ISSN 2662-1827 (electronic)
Composites Science and Technology
ISBN 978-981-16-1853-6 ISBN 978-981-16-1854-3 (eBook)
https://doi.org/10.1007/978-981-16-1854-3

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Preface

In this book, we focus on eco-friendly, biodegradable, and sustainable vegetable fiber composite preparation, properties, and industrial applications. It is time to explore green materials, so we decided to discuss the latest technological aspects of vegetable fiber composite made from the biopolymer that are biodegradable. The vegetable fiber composite materials for the production of biocomposite because it is biocompatible, cheap and easy available, low density with high strength, and good mechanical properties. Present book discusses various properties and applications of composite materials made from renewable biomaterial and biofibers. They are more eco-friendly as compared by the composite made from synthetic fibers.

This book will help researchers, scientists, and industries to understand the need of vegetable fiber composites for the development of safe and sustainable products for various applications. The characterization of vegetable fiber composites plays a crucial role to find out its potentiality in different real-world applications. It elaborates the physical, mechanical, morphological, structural, thermal, and electrical properties of native or modified fibers-based polymer composites.

Present book covers a review on hybrid vegetable/glass fiber epoxy composites, mechanical and acoustic properties of wool/glass hybrid composites, potential applications of Peristophe roxburghiana in textiles, lightweight vegetable-based hybrid laminated composites, electrochemical sensing applications of vegetable fiber-based porous carbon materials, vegetable fiber pretensioning influence on the composites, improvement of fiber matrix adhesion of vegetable natural fibers by chemical treatment, study of thermal degradation of a phenolic resin, vegetable fibers, and derived composites, waste management and application of coconut biomass and fiber, chemical modifications on physical properties of banana fiber-reinforced polyester composites, review on hemp fiber-reinforced polymer composites, vegetables fibers and its composite for packaging products, modification of vegetable fiber for natural fiber composites, Ag nanoparticles/jute fibers bionanocomposites as an efficient fungi-free material for the automobile industry, tribological behavior of glass fiber-reinforced polyamide gears, identification of vegetable fiber origin, various natural fibers and green nano-reinforcements such as microcrystalline cellulose, cellulose nanocrystals, and bacterial cellulose, development of vegetable fiber-mortar composites of improved durability, roles of vegetable fibers in green chemistry, tribological behavior of glass/sisal fiber-reinforced polyester composite, and the understanding of fluorination process to hydrophobic natural fibers.

We are highly thankful to all authors who contributed chapters and provide their valuable ideas and knowledge in this edited book. We attempt to gather all the scattered information of authors from diverse fields around the world (Malaysia, Jordan, USA, Turkey, India, Saudi Arabia, Bangladesh, Oman, and Sweden) in the areas of vegetable fibers-based composites and its applications and finally complete this venture in a fruitful way. We greatly appreciate contributor's commitment for their support to compile our ideas in reality.

We are highly thankful to the Springer Nature-Singapore team for their generous cooperation at every stage of the book production.

Serdang, Malaysia — Mohammad Jawaid
Jeddah, Saudi Arabia — Anish Khan

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About the Editors

Mohammad Jawaid is currently working as Senior Fellow (Professor) at Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia (UPM), Serdang, Selangor, Malaysia, and also has been Visiting Professor at the Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia, since June 2013. He has more than 20 years of experience in teaching, research, and industries. His area of research interests includes hybrid composites, lignocellulosic-reinforced/filled polymer composites, advance materials: graphene/nanoclay/fire retardant, modification and treatment of lignocellulosic fibers and solid wood, biopolymers and biopolymers for packaging applications, nanocomposites and nanocellulose fibers, and polymer blends. So far, he has published 50 books, 70 Book chapters, more than 350 peer-reviewed international journal papers, and several published review papers under top 25 hot articles in science direct during 2013–2019. He also obtained two patents and six copyrights. H-index and citation in Scopus are 57 and 15427, and in Google scholar, H-index and citation are 71 and 21918. He is Founding Series Editor of Composite Science and Technology Book Series from Springer Nature and also Series Editor of Springer Proceedings in Materials, Springer Nature, and also International Advisory Board Member of Springer Series on Polymer and Composite Materials. He worked as Guest Editor of special issues of *SN Applied Science*, *Frontiers in Sustainable Food Systems*, *Current Organic Synthesis and Current Analytical Chemistry*, *International Journal of Polymer Science*, and *IOP Conference Proceeding*. He is also Editorial Board Member of *Journal of Polymers and The Environment*, *Journal of Plastics Technology*, *Applied Science and Engineering Progress Journal*, *Journal of Asian Science, Technology and Innovation*, and the *Recent Innovations in Chemical Engineering*. Besides that, he is also Reviewer of several high-impact international peer-reviewed journals of Elsevier, Springer, Wiley, Saga, ACS, RSC, Frontiers, etc. Presently, he is supervising 12 Ph.D. students (five Ph.D. as Chairman, and seven Ph.D. as Member) and six master's students (one master as Chairman, and five master as Member) in the fields of hybrid composites, green composites, nanocomposites, natural fiber-reinforced composites, nanocellulose, etc., 26 Ph.D. and 13 master's students graduated under his supervision in 2014–2020. He has several research grants at university, national, and international levels on polymer composites of around 3 million Malaysian ringgits (USD 700,000). He also delivered plenary and invited talks in international conferences related to composites in India, Turkey, Malaysia, Thailand, the UK, France, Saudi Arabia, Egypt, and China. Besides that, he is also Member of technical committees of several national and international conferences on composites and material science. Recently, he received Excellent Academic Award in Category of International Grant-Universiti Putra Malaysia-2018 and also Excellent Academic Staff Award in industry High-Impact Network (ICAN 2019) Award, beside that Gold Medal Community and Industry Network (JINM Showcase) at Universiti Putra Malaysia. He also received Publons Peer-Review Awards 2017 and 2018 (Materials Science), Certified Sentinel of Science Award Recipient 2016 (Materials Science) and 2019 (Materials Science and Cross-field). He is also Winner of Newton-Ungku Omar Coordination Fund: UK–Malaysia Research and Innovation Bridges Competition 2015. Recently, he got Fellow and Chartered Scientist from Institute of Materials, Minerals, and Mining (IOM), UK. He is also Life Member of Asian Polymer Association and Malaysian Society for Engineering and Technology. He has professional membership of American Chemical Society (ACS) and Society for polymers Engineers (SPE), USA.

Dr. Anish Khan is currently working as Assistant Professor in Chemistry Department, Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah, Saudi Arabia. He completed Ph.D. from Aligarh Muslim University, India, in 2010 and Postdoctoral from School of Chemical Sciences, University Sains Malaysia (USM), on the topic of electroanalytical chemistry in 2010. He is working in the field of synthetic of polymers composite, organic–inorganic electrically conducting nanocomposites, cation exchanger, natural fiber composite, metal organic framework's composite, and their properties and applications as sensor. He has published more than 200 research articles, 70 chapters, 35 books in referred international publishers and more than 20 international conferences/workshop. He is Member of American Nano Society, and his field of specialization is polymer nanocomposite/cation exchanger/chemical sensor/microbiosensor/nanotechnology, application of nanomaterials in electroanalytical chemistry, material chemistry, ion exchange chromatography and electro-analytical chemistry, dealing with the synthesis, characterization (using different analytical techniques), and derivatization of inorganic ion exchanger by the incorporation of electrically conducting polymers. Preparation and characterization of hybrid nanocomposite materials and their applications, polymeric inorganic cation exchange materials, electrically conducting polymeric, materials, composite material use as sensors, green chemistry by remediation of pollution, heavy metal ion-selective membrane electrode, and biosensor on neurotransmitter.

Hybrid Vegetable/Glass Fiber Epoxy Composites: A Systematic Review

Roberta M. Neves, Francisco M. Monticeli, José Humberto S. Almeida, and Heitor Luiz Ornaghi

1 Introduction

Nowadays, the increasing pressure about the preservation of natural resources and political awareness on exploring green alternatives to decreasing global fossil fuel emission [1]. Vegetable fibers arise from natural resources and they fulfill the renewability and marketing apse requirements. In the last four decades, thermoset composites with vegetable fibers have been extensively studied are mainly applied in the automotive interior components [2]. There is an increasing demand for applying natural composites in other areas, such as in civil structures due to their low density, good processability, low abrasion, and high resistance to corrosion [3]. However, the application is restricted to low-medium components and they cannot yet substitute com synthetic fiber composites, such as glass fiber structures. Seeking at minimizing these drawbacks and aiming to broaden the range of applications, there are increasing studies in hybrid synthetic/vegetable fiber-reinforced composites. When the fibers are adequately combined, the resulting properties can be comparable to pure synthetic fiber composite and hence replace synthetic fibers, depending upon the application [4-10].

R. M. Neves
Federal University of Rio Grande do Sul, PPGE3MAv. Bento Gonçalves 9500, Porto Alegre, RS, Brazil

F. M. Monticeli
Department of Materials and Technology, Sao Paulo State University, Guaratinguetá, SP 12516-410, Brazil

J. H. S. Almeida
Department of Mechanical Engineering, Aalto University, 02150 Espoo, Finland

H. L. Ornaghi (✉)
Federal University for Latin America Integration (UNILA), Edifício Comercial Lorivo - Av. Silvio Américo Sasdelli, 1842 - Vila A, Foz do Iguaçu, PR 85866-000, Brazil

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_1

Hybrid composites are tailorable materials, which are driven by the role of fibers arrangement in the composite system. The behavior of hybrid composites considers the contribution of each reinforcing phase (the type of reinforcement, geometry, etc.), in which the composite can be manufactured aiming at taking the best characteristics of each fiber. There are innumerous studies regarding glass/vegetable hybrid composites that can be found in the literature in different databases [4, 10–12]. Often, the chosen research topic is not immediately found in the performed searches, and when a review on this particular chosen topic is carried out, several times, it is identified that previous studies on the same topic have already been done, invalidating the approach. In this context, a systematic review is a powerful tool that helps the readers to rapidly find the lacks and most studied topics of a specific subject.

2 Systematic Review

Different than a conventional literature review, a systematic review aims to *identify, evaluate, and summarize the findings of all relevant individual studies* over a defined issue, *making the available evidence more accessible to decision-makers* [13]. Primarily, the protocol is employed based on a severe and rigorous scientific search allowing anticipate potential problems and indicating gaps in knowledge, which can be used as a starting point for developing new researches. An important characteristic is that some granting agencies require a systematic review to justify the planned research [14]. Another important characteristic is preventing arbitrary decisions (by respecting inclusion criteria and extraction of data), then, it follows a protocol.

Systematic reviews are very widespread in the area of medicine and health care. Some systematic reviews were published regarding low health literacy and health outcomes [15], insomnia, complementary medicine [16], and renal cancer [17]. In the polymeric fields, very few studies were released following the PRISMA protocol [18, 19]. However, until now, in the composites field, there is no systematic review that follows PRISMA methodology focusing on their mechanical, thermal, and dynamic mechanical properties, especially when it comes to vegetable fibers/cellulose chemically modified/epoxy composites.

Hence, the main aim of this book chapter is to compile data between 2016 and 2020, about composite laminates with epoxy resin as matrix and hybrid glass/vegetable fibers as the reinforcing phase. We focus on thermal, mechanical, and dynamic mechanical properties, as well as the manufacturing process to verify a future trend or gaps in this area. Moreover, we list the obtained data regarding the reinforcement type and processing method.

3 Systematic Review Methodology

The methodological guidelines outline the Transparent Reporting of Systematic Reviews and Meta-Analyses (PRISMA)[1] in which a determined protocol is followed before carrying out this systematic review. This protocol aims to rationale, hypothesize, and plan the review, being a guide. In this book chapter, three different literature databases are considered, and only research papers focused on recent studies in glass/vegetable fiber hybrid composites using epoxy resin as a matrix are taken into consideration. More details are presented next.

Papers are selected using Scopus (www.scopus.com), Web of Science (www.webofknowledge.com), and SciFinder (https://sso.cas.org/) databases. The terms of search are: ([epoxy] AND [hybrid] AND [composites] AND [natural] AND [glass] AND [fiber]). We choose the word “natural” instead “vegetable” because no paper was found with this term, despite being a well-accepted term in the field. The results are limited to papers published from 2016 to 2020. The identified articles have their titles and abstracts assessed independently by two reviewers (Neves, R.M., and Ornaghi Jr, H.L.) to screen their allocation in the systematic review.

This book chapter focuses on recent studies in the hybrid glass/vegetable fiber composites field. The type of vegetal fiber, manufacturing process, and thermal, mechanical, and dynamic mechanical properties are listed excluding microscopies (e.g. scanning electron microscopy—SEM, and optical microscopy) and chemical analyzes (e.g., FTIR, XRD, NMR) as well other results such as flammability, aging, wettability, and water absorption.

4 Results of Data Collection

The study selection can be better visualized in the flowchart (Fig. 1), in which the records for every database are identified as well the exclusion criteria and selected papers by eligibility. The total search is of 285 studies, including all chosen databases. In this step, conference papers, review studies, studies not presented in English language, book chapter, editorial, letters, and notes are not considered. With only research papers remaining, some studies which do not account for the present systematic review methodology are excluded: studies with other matrices other than epoxy resin [12 studies], no hybrid composites (7 studies), hybrid composites other than epoxy glass/fiber/vegetable fibers (14 studies), hybrid composites with epoxy matrix but without vegetable fibers as reinforcement [15], vegetable hybrid composites with epoxy matrix but without glass fiber as reinforcement [67], and composites that add another material as a third component [38] are excluded. After this step, 132 studies remained. From these, 84 are excluded for duplicity on the databases. After all, 48 meet all selected criteria, then composing the current systematic review.

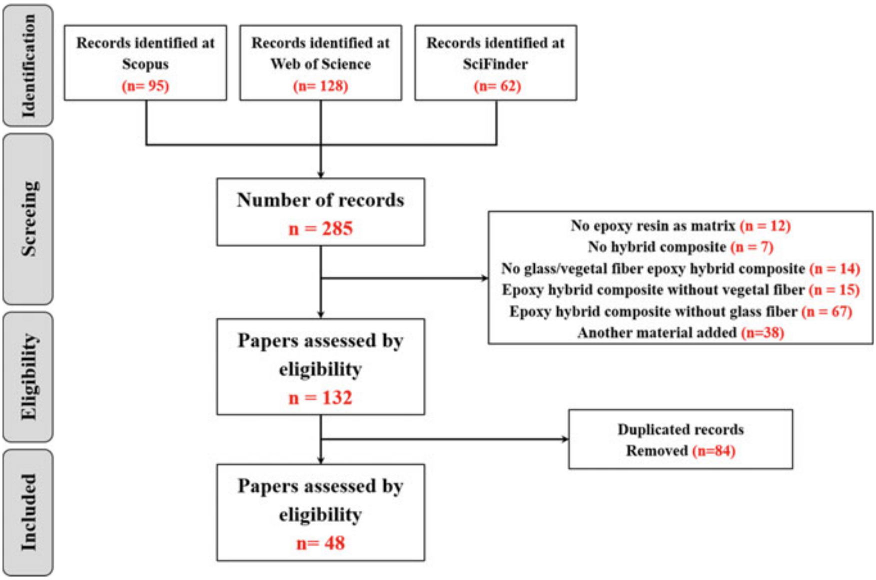

Fig. 1 Systematic review flowchart following PRISMA protocol

The type of glass fiber (chopped, unidirectional, and woven), natural fiber (chopped, continuous mat, woven, and powder), and composite are presented in Fig. 2. Highlighting the frequency of appearance in the selected research papers.

5 Results and Discussion

Table 1 presents all results of the 48 selected papers according to PRISMA flowchart (Fig. 1) summarized in the systematic review search. The type of fiber, processing manufacturing, and the description of thermal, mechanical, and dynamic mechanical properties are described in Table 1.

6 Conclusion and Future Perspectives

In this study, a systematic review on glass/vegetable hybrid composites between 2016 and 2020 was performed. The type of reinforcements and manufacturing processes were included. Thermal, mechanical, and dynamic mechanical properties were also targeted. The systematic review proved to be a useful tool for both young and the experienced researchers as a guideline in a specific(s) subject(s). It easily indicates the trends and lacks in a searched topic. This study showed an enormous lack of thermal

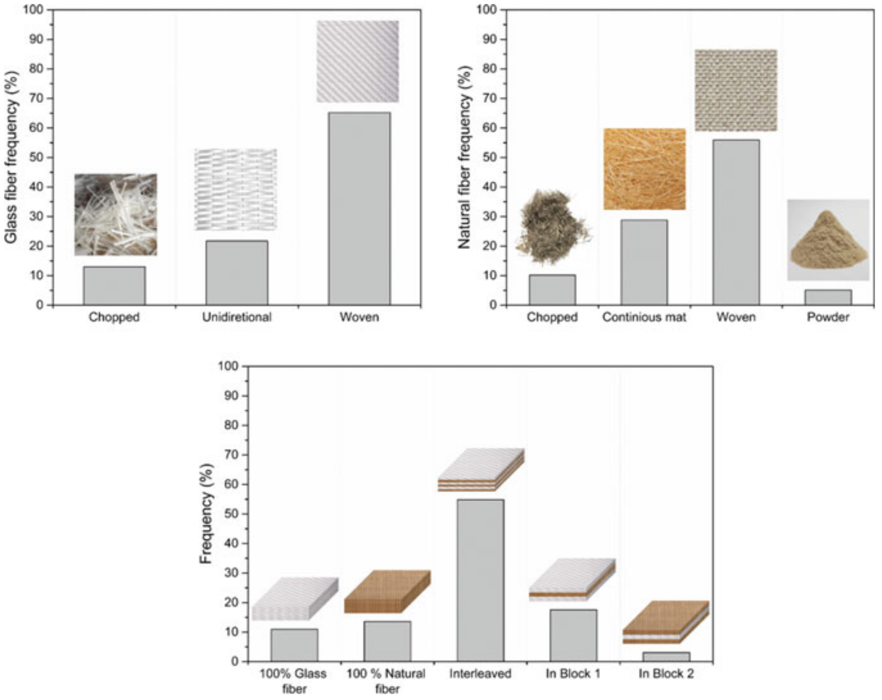

Fig. 2 Frequency of the glass fibers, natural fiber, and type of composites found on the systematic review

and dynamic mechanical properties that can be explored for further research. The main studied aspect is at the mechanical properties point of view, which include impact, flexural, compressive, and tensile tests, independently of the reinforcement. Hand lay-up is the most employed manufacturing process, which is certainly associated to the low cost of this process. Finally, the most employed type of both glass and vegetal fiber was woven fabric, being the interleaved composite the most used. Consequently, the fast and easy identification of studies and the possibility of new combinations of reinforcements/manufacturing processes and tested properties make the systematic review a powerful tool in any scientific field.

Vegetable fibers will be continuously employed, and the studies evaluated here pointed out that there is a growing trend for different reasons given ecological appeal and environmental benefits or combination with synthetic fibers for different applications. The weight reduction, easy formability, low cost and ease-processing are some of the many advantages promoted by the vegetal fibers even when combined with synthetic fibers. As a result, glass/vegetable hybrid composites will keep being applied in interior automotive components to add an eco-friendly character while still meeting design requirements [67]. In addition, the possibility to chemically/physically modify vegetable fibers aiming to improve their physical–chemical properties is attractive, although it is still ineffective from the mass production point

Table 1 Thermal, mechanical, and dynamic-mechanical properties of the hybrid composites

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[20]	Interleaved Hygrothermaly aged Pineapple leaf fiber (PALF)/glass (G): **Dry** (non-aged); **Wet** (aged) **i.** 4P **ii.** PGPG **iii.** PGGP **iv.** GPPG	PALF (P)	Hot compression molding	–	Tensile results: **Dry** X_t (MPa): **i.** 47.1; **ii.** 62.6; **iii:** 68.0; **iv:** 119.2 **Wet** X_t (MPa): **i.** 32.0; **ii.** 35.3; **iii:** 42.8; **iv:** 58.8 **Dry** E_t (GPa): **i.** 3.0; **ii.** 4.1; **iii:** 3.2; **iv:** 5.1 **Wet** E_t (GPa): **i.** 1.9; **ii.** 2.8; **iii:** 3.1; **iv:** 2.2 3-point bending results: **Dry** X_b (MPa): **i.** 78.1; **ii.** 124.6; **iii:** 130.4; **iv:** 170.7 **Wet** X_b (MPa): **i.** 58.3; **ii.** 96.1; **iii:** 83.6; **iv:** 94.9 **Dry** E_b (GPa): **i.** 2.9; **ii.** 4.4; **iii:** 2.1; **iv:** 3.3 **Wet** E_b (GPa): **i.** 1.2; **ii.** 1.4; **iii:** 1.2; **iv:** 1.6	–
[21]	Interleaved Banana/Glass (G): **i.** G8 **ii.** G4B1G3 **iii.** G3B2G3 **iv.** G3B3G2	Banana (B)	Hand lay-up	--	3-point bending results: X_b (MPa): **i.** 430; **ii.** 470; **iii:** 350; **iv:** 270	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[22]	Interleaved Calotropis Procera (CP)/glass (G)/epoxy (E) **i.** 0/0/100 CP/G/E **ii.** 20/0/80 CP/G/E **iii.** 15/5/80 CP/G/E **iv.** 10/10/80 CP/G/E **v.** 5/15/80 CP/G/E **vi.** 0/20/80 CP/G/E	Calotropis procera (CP)	Hand lay-up	–	**X_t:** **i.** 35 MPa **ii.** 37 MPa **iii.** 42 MPa **iv.** 46 MPa **v.** 47 MPa **vi**. 53 MPa **E_t:** **i.** 1351 MPa **ii.** 1896 MPa **iii.** 2364 MPa **iv.** 2626 MPa **v.** 2763 MPa **vi**. 2983 MPa	**i.** 2243 MPa **ii.** 2533 MPa **iii.** 2878 MPa **iv.** 2954 MPa **v.** 3102 MPa **vi**. 3151 MPa @40 °C

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[23]	Interleaved Flax (F)/Glass (G): **Aged** and **non-aged**: i. FFFFFFFF ii. FGGGGGGF iii. FFGGGGFF iv. FFFGGFFF v. GFFFFFFG vi. GGFFFFGG vii. GGGFFGGG viii. GGGGGGGG	Flax (F)	Hand lay-up	–	3-point bending results: **Non-aged**: **i.** 22 GPa; **ii.** 24 GPa; **iii.** 22 GPa; **iv.** 22 GPa; **v.** 33 GPa; **vi.** 41 GPa; **vii.** 52 GPa **Aged**: **i.** 10 GPa; **ii.** 18 GPa; **iii.** 13 GPa; **iv.** 12 GPa; **v.** 26 GPa; **vi.** 38 GPa; **vii.** 48 GPa	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[24]	Interleaved Sisal (S)/Glass (G) **i.** $[G]_{12}$ **ii.** $[S]_{12}$ **iii.** $[G/S]_6$	Sisal	Hand lay-up	–	3-point bending results: **i.** 788 MPa; **ii.** 107 MPa; **iii.** 365 MPa	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[25]	Interleaved Flax (F)/Glass (G): **Aged** in salt fog. Samples with circular holes with 4, 8, and 10 mm. **i.** GFA (non-aged); **ii.** GFB [30 days aging]; **iii.** GFC (60 days aging)	Flax (F)	Vacuum-assisted resin infusion	–	Maximum bearing stress: **D = 4 mm**: **i.** 200 MPa; **ii.** 164 MPa; **iii.** 157 MPa **D = 8 mm**: **i.** 180 MPa; **ii.** 175 MPa; **iii.** 152 MPa **D = 10 mm**: **i.** 159 MPa; **ii.** 125 MPa; **iii.** 107 MPa	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[26]	Interleaved Mustard cake powder (M)/Glass (G)/epoxy/E) **i.** 0/40/60 (M/G/E); **ii.** 10/40/50 (M/G/E); **iii.** 0/60/40 (M/G/E); **iv.** 10/50/50 (M/G/E); **v.** 0/80/20 (M/G/E); **vi.** 10/80/10 (M/G/E);	Mustard cake powder (M)	Hand lay-up	–	X_t (MPa): **i.** 28; **ii.** 35; **iii:** 90; **iv:** 97; **v.** 110; **vi.** 135 X_b (MPa): **i.** 164; **ii.** 251; **iii:** 172; **iv:** 313; **v.** 192; **vi.** 538 SBS (MPa): **i.** 1.7; **ii.** 2.0; **iii:** 2.5; **iv:** 2.6; **v.** 2.9; **vi.** 3.1	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[27]	Interleaved Pine apple (PA)/Glass (G): **i.** GPPP; **ii.** GGPP; **iii.** GGGP; **iv.** GGGG; **v.** PPPP	**Pine apple (PA)**	Hand lay-up	–	X_t (MPa): **i.** 130; **ii.** 144; **iii:** 168; **iv:** 194; **v.** 115 X_c (MPa): **i.** 98; **ii.** 115; **iii:** 138; **iv:** 175; **v.** 87 X_b (MPa): **i.** 115; **ii.** 132; **iii:** 141; **iv:** 131; **v.** 102 I (J/m): **i.** 260; **ii.** 345; **iii:** 379; **iv:** 411; **v.** 214	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[28]	Interleaved Jute (J)/Glass (G): **i.** J6; **ii.** G6; **iii.** GJ4G; **iv.** JG4J; **v.** CJ4C; **vi.** CGGGGC; **vii.** JGCCGJ; **viii.** CGJJGC; **ix.** CCGGJJ	Jute (J)	Hand lay-up	–	S (MPa): **i.** 23; **ii.** 61; **iii:** 31; **iv:** 56; **v.** 27; **vi.** 63; **vii.** 52 ; **viii.** 51; **ix.** 51 G (GPa): **i.** 0.8; **ii.** 2.8; **iii:** 1.2; **iv:** 2.7; **v.** 0.9; **vi.** 3.7; **vii.** 1.0 ; **viii.** 1.7; **ix.** 1.3	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[29]	Interleaved Jute(J)/Glass(G) and Flax (F)/Glass (G) **i.** J4; **ii.** GJJG; **iii.** FFFFFFFF; **iv.** GGFFFFGG	Jute (J) and Flax (F)	Hand lay-up	–	X_t (MPa): **i.** 47; **ii.** 70; **iii:** 76; **iv:** 127 E_t (GPa): **i.** 4.9; **ii.** 6.8; **iii:** 4.6; **iv:** 4.0	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[30]	Interleaved Cotton /G)/Glass (G): V_f = 20%: **i.** C; **ii.** G; **iii.** C/G; V_f = 30%: **iv.** C; **v.** G; **vi.** C/G	Cotton (C)	Hand lay-up	–	X_t (MPa): **i.** 45; **ii.** 82; **iii:** 84 **iv:** 57; **v.** 87; **vi.** 90 X_b (MPa): **i.** 52; **ii.** 60; **iii:** 67; **iv:** 64; **v.** 70; **vi.** 72 I (J/m^2): **i.** 80; **ii.** 141; **iii:** 145; **iv:** 98; **v.** 182; **vi.** 190	–
[31]	Unidirectional Flass (F)/Glass (G): **i.** $[0_{G2}/0_{F12}/0_{G2}]$; **ii.** $[0_{G2} \pm 45_{F12}/0_{G2}]$	Flax (F)	Hot compression	–	X_c (MPa): **i.** 262; **ii.** 232 E_c (GPa): **i.** 24; **ii.** 15 ν: **i.** 0.37; **ii.** 0.58 Fatigue: E_0^*: **i.** 15 (7% loss); **ii.** 10 (0% loss)	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[32]	Interleaved Kenaf (K)/Glass (G): **i.** 100% G; **ii**. 100% K; **iii**. 25% GF + 75% KF; **iv.** 30% GF + 70% KF; **v.** 50% GF + 50% KF; **vi**. 70% GF + 30% KF; **vii**. 75% GF + 25% KF	Kenaf (K)	Hand lay-up	–	F_t (kN): **i.** 46; **ii.** 11; **iii:** 14 **iv:** 19; **v.** 26; **vi.** 33; **vii.** 37	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[33]	Interleaved Jute (J)/Glass (G): **i**. Jute/epoxy; **ii**. 45:55 J:G; **iii**. 30:70 J/G; **iv**. Glass/Epoxy	Jute (J)	Hand lay-up	–	X_t (MPa): **i.** 143; **ii.** 283; **iii:** 329 **iv:** 428 E_t (GPa): **i.** 8; **ii.** 12; **iii:** 13; **iv:** 16	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[34]	Interleaved Jute (J)/Kenaf (K)/Glass (G): **i**. GGGGG; **ii**. JJJJJ; **iii**. KKKKK; **iv**. JKJKJ; **v.** KJKJK; **vi**. GJJJG; **vii**. GKKKG; **viii.** GJKJG; **ix**. GKJKG	Jute (J) and kenaf (K)	Vacuum bagging	–	I_{Izod} (J/m): **i**. 1469; **ii**. 122; **iii**. 152; **iv**. 134; **v.** 171; **vi**. 792; **vii**. 897; **viii.** 860; **ix**. 1078 SBS (MPa): **i**. 18; **ii**. 5; **iii**. 6; **iv**. 5; **v.** 6; **vi**. 8; **vii**. 11; **viii.** 9; **ix**. 13	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[35]	Interleaved Flax/(F)/Glass (G) **Aged** in salt fog for: **0 days**: **i.** $[G]_{16}$; **ii.** $[F]_{10}$; **iii.** $[G_3/F_3]_s$; **30 days**: **iv.** $[G]_{16}$; **v.** $[F]_{10}$; **vi.** $[G_3/F_3]_s$; **60 days**: **vii.** $[G]_{16}$; **viii.** $[F]_{10}$; **ix.** $[G_3/F_3]_s$	Flax (F)	Vacuum assisted resin infusion method	T_g (°C): **i.** 82; **ii.** 80; **iii.** 80, **iv.** 82; **v.** 82; **vi.** 80, **vii.** 83; **viii.** 80; **ix.** 80	X_b (MPa): **i.** 397; **ii.** 113; **iii.** 212, **iv.** 342; **v.** 82; **vi.** 159, **vii.** 317; **viii.** 36; **ix.** 144$_s$ E_b (MPa): **i.** 17; **ii.** 4; **iii.** 9, **iv.** 16; **v.** 2; **vi.** 7, **vii.** 16; **viii.** 2; **ix.** 6	E' (GPa): **i.** 12.0; **ii.** 4.2; **iii.** 6.3, **iv.** 11.4; **v.** 2.5; **vi.** 4.2, **vii.** 9.6; **viii.** 2.4; **ix.** 3.8

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[36]	Interleaved unidirectional Neem (N)/Kenaf (K)/Glass (G): **i**. GNKNG_90°; **ii**. GNKNG_0°	Neem (N) and Kenaf (K)	Hand lay-up	–	X_t (MPa): **i**. 33; **ii**. 31 X_c (MPa): **i**. 43; **ii**. 37	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[37]	Date palm seed (DS) filler/Glass (G)—Percentage of filler in glasss/epoxy composite: 5 w.t.%: **i**. SiC; **ii**. Al_2O_3; **iii**. DS 10 w.t.%: **iv**. SiC; **v**. Al_2O_3; **vi**. DS	Date palm seed (DS)	Semi hand lay-up	–	Wear rate: **i**. 4.5; **ii**. 2.1; **iii**. 2.5; **iv**. 8.2; **v**. 6.8; **vi**. 7.3	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[38]	Intraply filament wound kenaf (K)/glass (G) tubes at 30°, 45°, 70°: Hybrid K/G: **i**. $[\pm30]_6$; **ii**. $[\pm45]_6$; **iii**. $[\pm70]_6$ Non-hybrid (glass): **iv**. $[\pm30]_9$; **v**. $[\pm45]_9$; **vi**. $[\pm70]_9$	kenaf (K)	Filament winding	–	EA (J) in axial crushing test: **i**. 1780; **ii**. 2912; **iii**. 3695; Non-hybrid (glass): **iv**. 1588; **v**. 1734; **vi**. 1852	

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[39]	Interleaved aged flax (F)/sisal(S)/glass (G): Without treatment **i.** GFG-UT; **ii**. GSG-UT; **iii**. SGF-UT With alkali NaOH treatmen: **iv**. GFG-T; **v**. GSG-T; **vi**. SGF-T	Flax (F) and sisal (S)	Hand lay-up	T_d (°C): **i.** 316; **ii.** 313; **iii:** 312; **iv:** 313; **v.** 317; **vi**. 307	X_t (MPa): **i.** 53; **ii.** 62; **iii:** 30; **iv:** 96; **v.** 69; **vi**. 46; X_b (MPa): **i.** 155; **ii.** 189; **iii:** 96; **iv:** 224; **v.** 188; **vi**. 198 I (J/m): **i.** 13; **ii.** 17; **iii:** 13; **iv:** 22; **v.** 18; **vi**. 20	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[40]	Interleaved chemically treated Tea particulate (T)/pineapple fiber (P)/glass (G): stacking sequence: GPGTGPG with different weight fraction: **i.** 5:25:10 (T:P:G); **ii.** 10:20:10 (T:P:G); **iii.** 15:15:10 (T:P:G); **iv.** 20:10:10 (T:P:G); **v.** 25:5:10 (T:P:G)	Chemically treated Tea particulate (T)/pineapple fiber (P)	Hot compression molding	–	X_t (MPa): **i.** 36; **ii.** 43; **iii:** 39; **iv:** 38; **v.** 71 E_t (GPa): **i.** 5.5; **ii.** 6.2; **iii:** 5.6; **iv:** 5.4; **v.** 22.6 X_b (MPa): **i.** 430; **ii.** 451; **iii:** 481; **iv:** 295; **v.** 422 I_{Izod} (J): **i.** 122; **ii.** 128; **iii:** 122; **iv:** 102; **v.** 104 SBS (MPa)**:** **i.** 87; **ii.** 86; **iii:** 79; **iv:** 83; **v.** 87	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[41]	Interleaved jute (J)/glass (G) with biaxial fabrics at ±45° [45] or 0°/90° (0/90): **i**. GGGGG (G45); **ii**. GJJG (H45); **iii.** GJJG (H0/90); **iv.** GJJG (H45//0/90)	Jute (J)	Vacuum infusion		SBS (MPa): **i.** 26; **ii.** 23; **iii.** 26, **iv.** 21 X_c (MPa): **i.** 121; **ii.** 90; **iii.** 150, **iv.** 90	E’ (GPa): **i.** 6959; **ii.** 6043; **iii.** 8347, **iv.** 7186

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[42]	Date palm seed filler (DS)/glass (G): **i**. 0 w.t.% DS; **ii**. 5 w.t.% DS; **iii**. 10 w.t.% DS	Date palm seed filler (DS)	Semi hand lay-up	–	X_t (MPa): **i**. 130; **ii**. 170; **iii**. 183 I_{Izod} (MPa): **i**. 1.6; **ii**. 3.7; **iii**. 7.2	

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[43]	Interleaved chemically-treated cotton dust waste (CDW)/jute (J) and cotton dust waste (CDW)/glass (G). Untreated (U). **i**. 20UCDW15G; **ii**. 10CDW25G; **iii.** 15CDW20G; **iv.** 20CDW15G; **v.** 25CDW10G; **vi.** 20UCDW15UJ; **vii.** 10CDW25J; **viii.** 15CDW20J; **ix.** 20CDW15J; **x.** 25CDW10J	Cotton dust waste (CDW) and jute (J)	Hand lay-up		X_t (MPa): **i**. 42; **ii**. 53; **iii.** 55; **iv.** 59; **v.** 50; **vi.** 40; **vii.** 52; **viii.** 57; **ix.** 61; **x.** 54 E_t (MPa): **i**. 1200; **ii**. 2042; **iii.** 1945; **iv.** 1773; **v.** 1520; **vi.** 808; **vii.** 1368; **viii.** 1420; **ix.** 1472; **x.** 1550 X_b (MPa): **i**. 86; **ii**. 109; **iii.** 111 **iv.** 121; **v.** 113; **vi.** 84; **vii.** 104; **viii.** 108; **ix.** 122; **x.** 110 E_b (MPa): **i**. 1819; **ii**. 2930; **iii.** 2910; **iv.** 2890; **v.** 3346; **vi.** 1700; **vii.** 3267; **viii.** 2958; **ix.** 2658; **x.** 2776 I_{Charpy} (J): **i**. 6.5; **ii**. 14.5; **iii.** 13.3; **iv.** 12.2; **v.** 10.5; **vi.** 5.7; **vii.** 8.2; **viii.** 8.5; **ix.** 8.8; **x.** 9.5	

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[44]	Interleaved composites (Woven E-glass—G): G:R:A:R:A:R:G	Woven aloevera fiber (A) Woven roselle fiber (R)	Hand lay-up	–	Tensile test: Xt (MPa): 38.6 E_t (GPa): 0.8 ε (%): 5.4 Flexural test: Xt (MPa): 5.9 E_b (GPa): 0.13 ε (mm): 4.6 Izod impact test: I (J): 5.6	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[45]	Interleaved composites (Woven E-glass—G): i—H:G $[(0/90)^H/G/[45]^H]_s$ ii—F:G $[(0/90)^F/G/[45]^F]_s$ iii—F:H:G $[(90)^F/G/(45)^H]_s$	Flax (F) Ham fiber (H)	Hand lay-up	–	Flexural test: Xt (MPa): **i**—88.3; **ii**—18; **iii**—86.3 Hardness test: H (Rockwell): **i**—92.6; **ii**—90.6; **iii**—94.8	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[46]	Interleaved composites (NCF E-glass—G): **i**—G:K:G (70/30) **ii**—K:G:K (35/65) 40% of fiber content for all laminates	Plain weave Kenaf fabric (K)	VARTM	–	Tensile test: Xt (MPa): **i**—55.1; **ii**—48.0; E (GPa): **i**—7.5; **ii**—6.5 ε (%): **i**—1.2; **ii**—1.0 Fatigue test: **i**—Xt = 50.9 $N^{-0.47}$ **ii**—Xt = 58.4 $N^{-0.66}$	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[47]	Interleaved composites (Woven E-glass—G): **i**—Glass **ii**—G:J	Jute (J)	VARTM	TGA: First degradation (°C): **i**—322.8; **ii**—325 Second degradation (°C): **i**—400.2; **ii**—405.7 Residue (%): **i**—44.5; **ii**—42.1	–	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[48]	Interleaved composites (chopped fibreglass mats—G): **i**—Jute **ii**—G:J (25/75) **iii**—G:J (50/50) **iv**—G:J (75/25) **v**—Glass **vi**—G:B (75/25) **vii**—G:B (50/50) **viii**—G:B (25/75) 40% of fiber content for all laminates	Jute (J) Bagasse (B)	Hand lay-up	–	Tensile test: Xt (MPa): **i**—40; **ii**—60; **iii**—62; **iv**—70; **v**—80; **vi**—35; **vii**—30; **viii**—16 Hardeness test: H (Rockwell): **i**—40; **ii**—61; **iii**—66; **iv**—70; **v**—80; **vi**—30; **vii**—40; **viii**—25	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[49]	Interleaved composites (chopped fibreglass mats—G): i—Glass ii—G:CS (80/20) iii—G:CS (60/40) iv—G:CS (40/60) v—G:CS (20/80) vi—CS 25% of fiber content for all laminates	Cotton shell (CS)	Hand lay-up and compression moulding	–	Tensile test: Xt (MPa): **i**—50.6; **ii**—55.1; **iii**—71.8; **iv**—57.3; **v**—40.6; **vi**—20.4 Flexural test: Xt (MPa): **i**—100.2; **ii**—112.3; **iii**—123.8; **iv**—103.0; **v**—80.1; **vi**—66.7 Compressive test: Xt (MPa): **i**—85.8; **ii**—99.8; **iii**—115.2; **iv**—105.4; **v**—90.7; **vi**—84.9 Hardness test: H (Brinell): **i**—38; **ii**—40; **iii**—44; **iv**—41; **v**—36; **vi**—34 Izod impact test: I (J): **i**—5; **ii**—6; **iii**—8; **iv**—6; **v**—4; **vi**—3	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[50]	Interleaved composites (E-glass fabric—G): i—G:PP (80/20) ii—G:PP (60/40) iii—G:PP (20/80) iv—G:PP (20/80) v—PP 30% of fiber content for all laminates	Pennisetum purpureum fiber (PP)	VARTM	–	Tensile test: Xt (MPa): **i**—130; **ii**—100; **iii**—75; **iv**—46; **v**—32 E (GPa): **i**—6.0; **ii**—5.8; **iii**—5.8; **iv**—3.5; **v**—3.0 Flexural test: Xt (MPa): **i**—120; **ii**—108; **iii**—76; **iv**—70; **v**—52 E (GPa): **i**—12.0; **ii**—10.7; **iii**—8.2; **iv**—5.8; **v**—3.9	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[51]	composite tubes (glass fiber—G): Cilyndrical **i**—Jute 50 mm **ii**—Jute 100 mm **iii**—G:J 50 mm **iv**—G:J 100 mm Square **v**—Jute 50 mm **vi**—Jute 100 mm **vii**—G:J 50 mm **viii**—G:J 100 mm [G/J_2]	Jute (J)	Hand lay-up	–	Compression test: EA (kJ): **i**—0.9; **ii**—0.6; **iii**—1.1; **iv**—0.9; **v**—0.4; **vi**—0.1; **vii**—0.7; **viii**—0.6 SEA (kJ kg^{-1}): **i**—19.0; **ii**—7.0; **iii**—21.6; **iv**—9.0; **v**—3.5; **vi**—1.0; **vii**—8.6; **viii**—4.6	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[52]	Interleaved composites (twill glass fabric—G): **i**—Flax **ii**—G:F (85/15) $[G/F_4]_s$ **iii**—G:F (75/25) $[G_2/F_3]_s$ **iv**—G:F (55/45) $[G_3/F_2]_s$ **v**—G:F (30/70) $[G_4/F]_s$ **vi**—Glass	2 × 2 twill flax fabric (F)	Pre-preg compression moulding	–	Tensile acustic emission: Amplitude (dB): **i**—F 60, M 35, D 45; **ii**—F 68, M 33, D 40; **iii**—F 50, M 32, D 39; **iv**—F 72, M 32, D 41; **v**—F 51, M 31, D 37; **vi**—F 70, M 32, D 40 Damage hit contribution (%): **i**—F 49, M 9, D 42; **ii**—F 70, M 1, D 29; **iii**—F 91, M 1, D 8; **iv**—F 68, M 2, D 30; **v**—F 86, M 3, D 10; **vi**—F 78, M 10, D 12 * Fiber failure (F), matrix crack (M), fiber-matrix desbonding (D)	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[53]	Interleaved composites (unidirection fibreglass—G): Horizontal orientation **i**—G:A$_3$:G **ii**—G:N$_3$:G **iii**—G:A$_3$N$_3$:G Vertical orientation **iv**—G:A$_3$:G **v**—G:N$_3$:G **vi**—G:A$_3$N$_3$:G 45° orientation **vii**—G:A$_3$:G **viii**—G:N$_3$:G **ix**—G:A$_3$N$_3$:G	Neem (N) Abaca (A)	Hand lay-up	–	Tensile test: Xt (MPa): **i**—83; **ii**—86; **iii**—91; **iv**—94; **v**—92; **vi**—102; **vii**—90; **viii**—100; **ix**—120 Flexural test: Xt (MPa): **i**—8; **ii**—14; **iii**—16; **iv**—13; **v**—16; **vi**—22; **vii**—14; **viii**—23; **ix**—26 Double shear test: Xt (MPa): **i**—45; **ii**—55; **iii**—80; **iv**—39; **v**—50; **vi**—72; **vii**—59; **viii**—40; **ix**—80 Interdelamination test Xt (MPa): **i**—5; **ii**—11; **iii**—17; **iv**—3; **v**—8; **vi**—16; **vii**—7; **viii**—9; **ix**—18 Charpy impact test: I (J): **i**—10; **ii**—11; **iii**—13; **iv**—11; **v**—12; **vi**—14; **vii**—15; **viii**—18; **ix**—20	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[54]	Interleaved composites (unidirection fibreglass—G): **i**—J:G 20% **ii**—J:G 30% **iii**—F:G 20% **iv**—F:G 30% **v**—B:G 20% **vi**—B:G 30% 50/50 (v/v) for all laminates	Jute (J) Banana (B) Flax (F)	Hand lay-up	–	Tribological test: Wear rate 1 km (mm^3 Nm^{-1}): **i**—1.33; **ii**—1.1; **iii**—1.38; **iv**—1.17; **v**—1.12; **vi**—0.82 Wear rate 1.5 km (mm^3 Nm^{-1}): **i**—0.97; **ii**—0.73; **iii**—1.00; **iv**—0.81; **v**—0.87; **vi**—0.61 Wear rate 2 km (mm^3 Nm^{-1}): **i**—0.75; **ii**—0.56; **iii**—0.79; **iv**—0.62; **v**—0.68; **vi**—0.48	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E’: glassy region
[55]	Interleaved composites (unidirection fibreglass—G): **i**—Glass **ii**—G:B	Banana (B)	Hand lay-up	–	Tensile test: T (kN): **i**—57.9; **ii**—38.9 Xt (MPa): **i**—498.9; **ii**—296.7 E (GPa): **i**—10.8; **ii**—11.1	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[56]	Interleaved composites (twill glass fabric—G): **i**—Flax **ii**—G:F (85/15) $[G/F_4]_s$ **iii**—G:F (75/25) $[G_2/F_3]_s$ **iv**—G:F (55/45) $[G_3/F_2]_s$ **v**—G:F (30/70) $[G_4/F]_s$ **vi**—Glass	2 × 2 twill weave flax fabric (F)	Pre-preg compression moulding	–	Tensile test: Xt (MPa): **i**—108.2; **ii**—140.7; **iii**—168.1; **iv**—274.6; **v**—354.2; **vi**—489.5 E (GPa): **i**—13.4; **ii**—14.5; **iii**—15.9; **iv**—20.6; **v**—24.4; **vi**—33.2 ε (%): **i**—1.4; **ii**—1.5; **iii**—1.6; **iv**—1.8; **v**—1.9; **vi**—2.11	–

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Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[57]	Interleaved composites (plain weave glass fabric—G): I—Glass ii—G:SC (75/25) iii—G:SC (55/45)	Short coir fiber (SC)	Pre-preg vacuum bag + autoclave	–	Tensile test: Xt (MPa): **i**—350; **ii**—220; **iii**—125 Dynamic vibration test: E (GPa): **i**—6; **ii**—16; **iii**—12	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[58]	Cylindrical composite tubes (glass fiber—G): **i**—Glass (15 layers) **ii**—NS (15 layers) **iii**—G:NS (3G + 9NS layers)	Woven natural Silk (NS)	Hand lay-up	–	quasi-static compression: T (kN): i—100; ii—90; iii—180 EA (J): i—2457; ii—950; iii—3660 SEA (kJ.g^{-1}): i—85; ii—31; iii—130 Crush efficiency (%): i—43; ii—13; iii—51	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[59]	Interleaved composites (E-glass—G): **i**—Glass $[(0/90)_3]_s$ **ii**—Jute $[(0/90)_2]_s$ **iii**—Flax $[(0/90)_2]_s$ **iv**—G:J (60/40) $[(0/90/0)^G/(0)^J]_s$ **v**—J:G (40/60) $[(0)^J/(0/90/0)^G]_s$ **vi**—G:F (60/40) $[(0/90)^G/(0)^F]_s$ **vii**—F:G (60/40) $[(0)^F/(0/90)^G]_s$	Plain weave Jute (J) Plain weave Flax (F)	VARTM	-	Tensile test: T (kN): **i**—8.1; **ii**—1.2; **iii**—1.6; **iv**—4.5; **v**—4.4; **vi**—6.6; **vii**—6.7 Xt (MPa): **i**—450; **ii**—70; **iii**—95; **iv**—239; **v**—233; **vi**—372; **vii**—358 E (GPa): **i**—5920; **ii**—1392; **iii**—1489; **iv**—3012; **v**—2891; **vi**—3417; **vii**—3432 ε (%): **i**—13.7; **ii**—8.1; **iii**—11.3; **iv**—11.6; **v**—10.6; **vi**—13.2; **vii**—12.5 Flexural test: T (N): **i**—617; **ii**—106; **iii**—101; **iv**—533; **v**—329; **vi**—429; **vii**—212 Xt (MPa): **i**—500; **ii**—95; **iii**—84; **iv**—418; **v**—258; **vi**—348; **vii**—171 E (GPa): **i**—17.3; **ii**—2.9; **iii**—1.4; **iv**—17.7; **v**—6.5; **vi**—14.2; **vii**—5.5 ε (%): **i**—3.1; **ii**—3.8; **iii**—2.4; **iv**—2.6; **v**—5.1; **vi**—2.5; **vii**—4.1	DMA: E' (MPa): **i**—7571; **ii**—3371; **iii**—3370; **iv**—6332; **v**—6554; **vi**—4245; **vii**—4510 E'' (MPa): **i**—1020; **ii**—430; **iii**—438; **iv**—890; **v**—985; **vi**—543; **vii**—592 Tan delta: **i**—0.345; **ii**—0.391; **iii**—0.401; **iv**—0.352; **v**—0.354; **vi**—0.325; **vii**—0.354 Tg (ºC): **i**—79.5; **ii**—80.3; **iii**—82.2; **iv**—79.4; **v**—79.9; **vi**—80.1; **vii**—77.8

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[60]	Interleaved composites (E-glass—G): **i**—Glass **ii**—Jute **iii**—Kenaf **iv**—J:K (60/40) **v**—J:K (40/60) **vi**—G:J (60/40) **vii**—G:K (60/40) **viii**—G:J:K (60/25/15) **ix**—G:J:K (60/15/25)	Plain weave Jute (J) Plain weave Kenaf (K)	Hand layup vacuum bag-autoclave	–	Tensile test: Xt (MPa): **i**—331.8; **ii**—34.7; **iii**—45.2; **iv**—42.9; **v**—47.4; **vi**—85.4; **vii**—101.4; **viii**—88.5; **ix**—129.2 E (GPa): **i**—12.7; **ii**—1.9; **iii**—2.4; **iv**—2.3; **v**—2.4; **vi**—5.0; **vii**—5.4; **viii**—5.1; **ix**—5.9 Flexural test: Xt (MPa): **i**—309.3; **ii**—170.9; **iii**—190.1; **iv**—177.0; **v**—182.0; **vi**—198.4; **vii**—232.8; **viii**—218.2; **ix**—235.5 E (GPa): **i**—18.6; **ii**—10.6; **iii**—11.8; **iv**—10.9; **v**—11.4; **vi**—12.3; **vii**—13.9; **viii**—13.6; **ix**—14.3 Micro-hardness: H (Vickers): **i**—24.6; **ii**—10.5; **iii**—13.5; **iv**—11.6; **v**—15.9; **vi**—20.1; **vii**—22.3; **viii**—22.0; **ix**—23.2	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[61]	Interleaved composites (chooped fibreglass mats): i—Glass fiber ii—Kenaf iii—Glass:K	Woven Kenaf fabric (K)	VARTM	–	Drop impact test: T for 3J (kN): **i**—1.4; **ii**—0.7; **iii**—1.2 T for 6J (kN): **i**—2.2; **ii**—0.7; **iii**—1.4 T for 9J (kN): **i**—2.7; **ii**—0.8; **iii**—1.5 u for 3J (cm): **i**—0.5; **ii**—0.7; **iii**—0.5 u for 6J (cm): **i**—0.6; **ii**—1.2; **iii**—0.7 u for 9J (cm): **i**—0.7; **ii**—1.5; **iii**—1.0 r for 3J (mm): **i**—10.8; **ii**—47.7; **iii**—25.6 r for 6J (mm): **i**—12.2; **ii**—82.6; **iii**—45.4 r for 9J (mm): **i**—16.1; **ii**—100.6; **iii**—52.9	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[62]	Interleaved composites (glass—G): **i**—G:S:G **ii**—G:C:G **iii**—G:B:G	Sisal fiber (S) Coir fiber (C) Banana fiber (B)	VARTM	–	Tensile test: T (kN): **i**—2.81; **ii**—2.89; **iii**—2.77 Flexural test: Xt (MPa): **i**—44.4; **ii**—87.7; **iii**—76.6 E (GPa): **i**—3101.3; **ii**—130.5; **iii**—474.8	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[63]	Interleaved composites (E-glass—G): **i**—G:C **ii**—G:C:G **iii**—G:G:C	Coir fibers mats (C)	Hand layup	–	Tensile test: Xt (MPa): **i**—41.5; **ii**—53.8; **iii**—30.61	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[64]	E-glass:J	Jute fibers mats (J)	Hand layup	–	Tensile test: Xt (MPa): 48.6 E (GPa): 4.2 Compression test: Xt (MPa): 35.0 E (GPa): 1.0 Flexural test: Xt (MPa): 4.4 E (GPa): 3.1 Izod impact test: I (J): 3.3	–
[65]	Interleaved composites (E-glass—G): **i**—G:J (50/50) **ii**—G:J (45/55) **iii**—G:J (40/60) **iv**—G:J (30/70)	Jute chopped fibers (J)	Hand layup method	–	Double shear test: L (kN): **i**—1.4; **ii**—1.2; **iii**—1.1; **iv**—1.0 u (mm): **i**—1.1; **ii**—1.2; **iii**—1.4; **iv**—1.7 Mode I delamination: L (kN): **i**—8.5; **ii**—8.4; **iii**—8.1; **iv**—8.0 u (mm): **i**—4.2; **ii**—3.8; **iii**—3.2; **iv**—2.9 Hardness test: H (Rockwell C): **i**—88.2; **ii**—86.4; **iii**—81.3; **iv**—76.2	–

(continued)

Table 1 (continued)

References	Hybrid composite type	Natural fibser type	Process	Properties		
				Thermal	Mechanical	Dynamic-mechanical E': glassy region
[66]	Interleaved composites (E-glass—G): **i**—B:P:G (25/25/50) **ii**—E-glass **iii**—B **iv**—B:G (30/70) **v**—B:G (40/60) **vi**—B:G (50/50) **vii**—P **viii**—P:G (30/70) **ix**—P:G (40/60) **x**—P:G (50/50) **xi**—B:P (50/50)	Banana pseudo stem fiber (B) Pineapple leaf fiber (P)	Hot Compression Method	–	Tensile Loading Test: Xt (MPa): **i**—66.9; **ii**—132.3; **iii**—38.7; **iv**—52.5; **v**—54.0; **vi**—65.9; **vii**—35.4; **viii**—52.0; **ix**—54.0; **x**—57.5; **xi**—36.1 E (GPa): **i**—6.2; **ii**—11.5; **iii**—4.6; **iv**—5.4; **v**—6.4; **vi**—6.3; **vii**—4.7; **viii**—4.8; **ix**—6.4; **x**—6.4; **xi**—3.7	–

Abbreviations:

X_t = tensile strength; X_b: bending strength; X_c: compressive strength; I_{Izod}: Izod impact strength; EA: Energy absorption; F_t: maximum tensile force; E_t: tensile modulus; E_c: compressive modulus; E_b: bending modulus; SBS: short beam strength; S: in-plane shear strength; G: shear modulus; ν: Poisson's ratio of view. Other promising applications included load-bearing structural members for application in civil applications, including concrete elements, roofing components, bridges, decks, among many others. Other applications include textile and yarn industries, furniture, housing (door, panels, roofing sheets), sporting goods (tennis racket, snowboarding), window frame, fencing, bicycle frame, mobile cases, insulations, bags, flush door shutters, mirror casing, filling material for upholstery, among others [68].

Acknowledgements The authors would like to thank the following granting foundations. HL Ornaghi Jr (Cnpq Process number 151438/2020-0); RM Neves (CAPES); FM Monticeli (FAPESP); and JHS Almeida Jr (CAPES).

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Mechanical Characterization and Acoustic Insulation of Wool-Polyester-Glass Hybrid Composite Material

Harpalsinh M. Vaghela, Nikunj V. Rachchh, and Dhaiwat N. Trivedi

1 Introduction

In the present situation, composite materials are turning into a substantial alternative over conventional materials because of their high quality to low weight proportion and other better properties. Composite materials have better physical, mechanical, electrical, acoustical, and warm properties than of its parental materials [1]. Fang et al. [2] proved that thermoplastic elastomeric (TPE) composite materials filled with micro $CaCO_3$ and hollow glass microsphere (HGM) provides better and enhanced sound insulation efficiency compared to the pure polymer material. Cellulose acetate, which is the product of used Cigarette filters, was evaluated for its acoustical behavior and was compared with non-used cellulose acetate and other commercial products by Ruben maderuelo-Sanz. It was observed that the sound absorption performance of these cigarette filters was better for low-frequency range may be due to the higher value of porosity, better density, and lower value of flow resistivity [3]. Clement Piegay et al. [4] studied the acoustical property of vegetal wools (hemp wool and flax wool) for the building insulation purposes. They applied the Tarnow approach for validation of results. Influence of polymer fibers on the acoustic property of the material is also estimated by acoustic model. Santhanam et al. [5] developed the sound absorption nonwoven material by the recycling of cotton and polyester fibers with the help of spun laid techniques. They observed that the value of sound absorption coefficient is improved by increasing the thickness of the nonwoven sample

H. M. Vaghela
Marwadi Education Foundation Group of Institutions, Rajkot, Gujarat, India

N. V. Rachchh (✉) · D. N. Trivedi
Marwadi University, Rajkot, Gujarat, India
e-mail: nikunj.rachchh@marwadieducation.edu.in

D. N. Trivedi
e-mail: dhaiwat.trivedi@marwadieducation.edu.in

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_2

but decreased with fabric density. Acoustical behavior of corn husk was evaluated by Tang et al. [6]. They observed that sound absorption is not the function of a number of layers in the sample. However, it has been observed that increasing the back cavity causes an increase in sound absorption at a lower frequency range. Lim et al. [7] studied the acoustical behavior of natural kenaf fiber under normal and random sound incidence. It has been observed that the sound absorption coefficient is increased significantly by an increment of thickness and density value. The air gap also provides an important role to improve sound absorption at a lower frequency. Schiavi et al. [8] developed a model which is used to define the improvement of sound insulation impact for floating floors in building industry. Several floor materials were investigated in various situations for the flooring of building industry. Various physical parameters, along with process parameters and their effect on the sound insulation property of glass fiber felt were investigated by Yang et al. [9]. Gulbrun et al. [10] investigated various factors which affect the sound insulation property of low weight exterior green roofs. Iannace et al. [11] has studied various natural plant fibers for its acoustic performance in between the frequency range of 200–2000 Hz. It has been noticed that as the value of the thickness of sample increased, the sound absorption behavior of material also increased significantly towards the lowest frequencies and the distance between two highest values of sound absorption coefficient also decreases. By increasing the numbers of layers of bark cloth fiber layers, the value of sound assimilation coefficient has been achieved higher at higher frequency [12]. Bujoreanu et al. [13] performed the acoustical analysis of various waste materials and combination of them with various backing plates. It has been observed that the samples consisting textile materials and with plasterboard backing plate have a higher sound absorption coefficient in the higher frequency range. Also, the effect of density of backing plates is more than the thickness of plates on sound absorption. The acoustical characterization of broom fibers has been carried out by Berardi et al. [14]. It has been noticed that the samples with a higher value of thickness have higher sound absorption coefficient. The material developed from the sugarcane waste has been evaluated for its acoustical behavior by Othmani et al. [15] and it has been noticed that sound absorption capacity of the material decreased by a reduction in the resin content. Pohler et al. [16] have developed new material made of 100% softwood fibers for sound absorption purpose. It has been observed that sound absorption coefficient of 100% softwood fiber material is nearly identical to the commercial sound absorbers possesses. The mixture of Recycled Polyester and waste wool by 50/50 proportion gives the best acoustical property [17]. Cuiyun et al. studied the noise assimilation attributes of permeable zeolite by large scale pores, the clay material manufactured by high temperature sintering [18] Absorber material which is developed with the help of thermal compression molding is analyzed and it is found that the absorption coefficient is decreased by increasing pressure and increased by increasing thickness of specimen [19]. The lower sound absorption coefficient is gained from all of the nonwovens for low frequency, and higher sound absorption is found at a higher value of frequency [20]. Biomass materials or recycled materials can be used as sustainable absorbers and lots of other replaceable which are developed from biomass [21]. Zhang et al. studied the acoustical properties of bamboo/cotton/PLA composites and found that the acoustical properties of the composite panel depend upon the fineness of natural fiber, density, and thickness of the composites [22]. Due to higher thickness, the sound waves are entrapped into the fiber layers so they cannot pass throughout the material, and sound waves of higher frequency are absorbed more by the layers of fiber material [23]. Acoustical, flammability properties, and biodegradable behavior of natural fiber jute are increased by increasing the fiber content [24]. The effect of the carbon footprint from the utilizing and disposal of material can be reduced by a hundred times by proper sound insulation of building [25]. In another study, the numbers of problems have to be faced for an alternative of sheep fleece material, which satisfies the demand of the construction industry for better acoustic products [26]. Wool is the natural product obtained from the sheep, and it has the best insulating property and lower flammability [27]. Generally, wool fibers are available mostly in continental areas like Europe and Asia. The fiber with shorten length is not useful for clothing purpose and declared as waste material. Lots of non-usable wool is available at a very cheap value, like 0.3 $/kg [28]. From the environmental aspect, the materials prepared from the wool fiber consumes low energy, better recyclability, and possesses good biodegradable nature. Since the material developed from the waste wool is not capable enough of standing alone, so the glass fiber was added into the composite material to increase the mechanical strength [29].

2 Noise Pollution: Problem

Noise pollution becomes major and most risky pollution which profoundly influence the air proportion and human wellbeing broadly. High level of noise at the workplace and the environment represents a basic risk to human comfort. So, it is essentially critical to decrease the damage done by noise pollution [30]. According to the World Health Organization, noise is considered to be the key factor for the environmental pollution of global industrialized urban settlements [31]. Due to the high noise production at industries and manufacturing sector, the demand for more effective and appropriate sound assimilation materials is increasing. Nowadays, many researchers and scientists are working on developing such new materials and technologies which improve the noise absorption properties. Acoustical materials are mainly used for building acoustic [32], studio acoustics, and car acoustics. Also, they can be utilized to prevent undesirable and hazardous noise effects reflections, and these materials provide reduced reverberant noise levels [33].

3 Suggested Solution

There are principally two means to control noise pollution:

- To control the sound source by such advance technology or instruments, this will produce less noise or no noise and work silently. This strategy is profoundly successful, however unrealistic at some applications because some advances are inaccessible.
- To utilize exceptionally powerful stable retention and sound protection materials, that reduces or kills the sound wave engendering or transmission of noise [33].

4 Experimental

4.1 Material and Method

The detail of composite preparation and experimental procedure followed for mechanical characterization and acoustic analysis is described in this section.

- The wool fiber was obtained from the indiamart site (Shreeji Felt, Jaipur, Rajasthan, India). The fiber was in woven mat form with a uniform area of 1 m × 1 m and thickness of 1–1.2 mm with relative density 0.42–0.44 g/cm^3.
- The polyester resin (R) (GP 7150) was obtained from EPP Composites Pvt Ltd. Rajkot, India. The density of unsaturated polyester resin is 1.35 gm/cc with an elastic modulus of 3.23 GPa. Cobalt naphthalene was used as an accelerator and Methyl ethyl ketone peroxide (MEKP) was used as a hardener.

4.2 Material Preparation

The wooden mold of 300 mm × 300 mm × 8 mm and 300 mm × 300 mm × 10 mm was prepared for casting the composite plate. Six composite plates were prepared in which three plates were having the 8 mm thickness and remaining to have the 10 mm thickness and possessing single layer, double layer and triple layer of the woven mat using hand lay-up process. To minimize the air entrapment, the polyester resin, hardener, and accelerator were thoroughly mixed with gentle stirring into a vessel resulting in slurry formation. The spray release gel was applied on the inner surface of the mold for easier removal of the composite plate. After that, the first layer of slurry was poured into the wooden mold and the woven mat was settled on it. Again the slurry was poured upon the mat and roller is used for proper distribution of slurry and removing the air bubbles from the composite plate. This process was repeated until the desired thickness of the composite plate was achieved. The composite plate was cured at room temperature for 24 h under the compression molding conditions at constant pressure. Various samples were cut from these plates after 24 h for further experiment purpose. Figure 1 shows the composite plate prepared by hand lay-up process and Fig. 2 shows the composite plates. Figure 3 shows the sample for the acoustic test.

Fig. 1 Preparation of composite plate

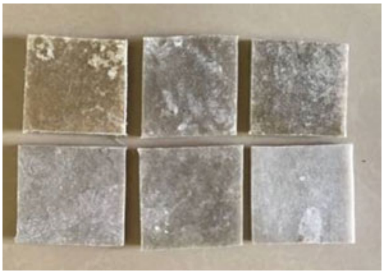


Fig. 2 Composite plates with different proportion

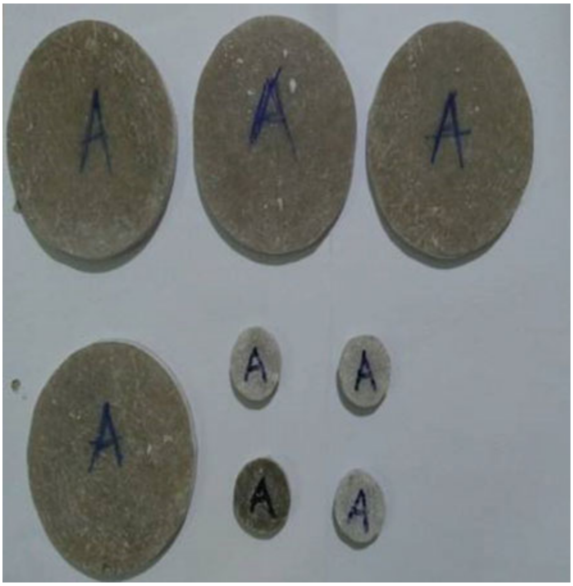


Fig. 3 Acoustic test samples

Table 1 Composition of different samples

Specimen	Thickness (mm)	Composition of sample	Number of layers
Sample-A	8	15% (W) 50% (R) 35% (G)	Single
Sample-B	8	20% (W) 45% (R) 35% (G)	Double
Sample-C	8	25% (W) 40% (R) 35% (G)	Triple
Sample-D	10	15% (W) 50% (R) 35% (G)	Single
Sample-E	10	20% (W) 45% (R) 35% (G)	Double
Sample-F	10	25% (W) 40% (R) 35% (G)	Triple

4.3 Sample Preparation

There were five samples taken out from each of the composite plates for experimental purpose according to the ASTM standard. The result is taken from the average reading of these five sample results. Following tests were carried out on composite samples for its complete mechanical and acoustic characterization. Table 1 shows the composition and physical property of the material.

- Tensile test (ASTM D-638)
- Flexural test (ASTM D790-10)
- Hardness test (ASTM D-2583)
- Density test (ASTM D-792)
- Water absorption test (ASTM D-570)
- Acoustic test (ASTM E 1050).

5 Experimental Acoustic Testing

The impedance tube method (ASTM E-1050) and reverberant room (ASTM C-423) method are generally utilized to evaluate the acoustic performance of material. The impedance tube method is a very cheaper and simple method. It requires only smaller size samples of 100 and 29 mm diameter to be evaluated. While 100 m^2 of space is for chamber and 72 m^2 of sample size is required in reverberant chamber method. Sometimes another method known as Alpha cabin is also used to determine the acoustical coefficient of material. It requires only 1.2 m^2 size of the sample. The acoustical ability of the material is depended on sound wave dissipation through the material. Various composite materials are arranged by rank numbers which are given according to their sound absorption coefficient for their various applications.

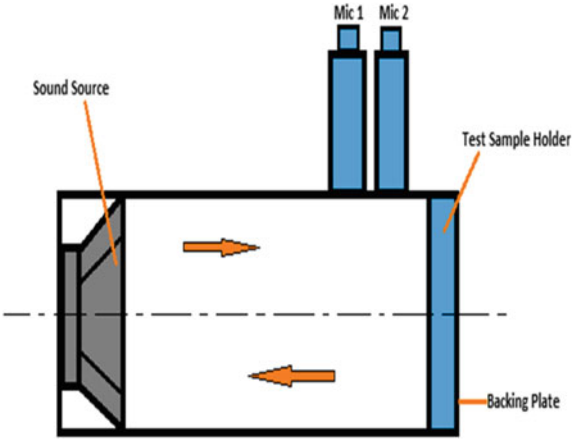


Fig. 4 Impedance tube method

The acoustical characteristics of composite material are evaluated by impedance tube method. This method is based on dual microphone, digital frequency analyzer, B and K data processing unit according to the ASTM E 1050 or ISO 10534-2. The experiment is based upon the dual microphone transfer function method. This method is for horizontally oriented tube system. Figure 4 shows the impedance tube setup for the acoustic test. Various acoustical parameters were evaluated over a frequency range of 500–6300 Hz using a smaller diameter tube of 29 mm. Frequency weighing unit provides various weighing like high pass, linear pass and low pass which is used for measuring acoustic parameters over the high-frequency range in a small tube, in a large tube and under the frequency of 100 Hz. At one end, the sample holder is available while at another end, the speaker is provided as a sound source. The speaker or noise generator generates the noise which is passed to the impedance tube, which was evaluated by dual microphones and calculates the transfer functions between them. From the transfer functions and distance between the microphones and prepared samples, the sound absorption coefficient was calculated. For proper adjustment of the test sample, the aluminium rod is used to push the sample at pre-defined depth. The four samples of each specimen tested, and the average of the result data is taken into consideration [33]. The acoustic test was carried out at PSGTECHS COE INDUTECH Textile University at Coimbatore-641062 (INDIA).

6 Result and Discussion

The mechanical properties of composite material such as tensile strength, flexural strength, and hardness, density, and water absorption are evaluated using relevant ASTM standards. Table 2 shows the results of mechanical characterization of composite material.

Table 2 Result of mechanical characterization of different samples

Sample	Tensile strength (MPa)	Flexural strength (MPa)	Hardness (BHU)	Density (kg/m^3)	Water absorption (%)
Sample-A	22.5	24.3	31	1.3456	0.193
Sample-B	20.9	23	28	1.3246	0.223
Sample-C	19.7	21.9	27	1.3157	0.226
Sample-D	28	31.7	34	1.2355	0.410
Sample-E	26.5	29.6	32	1.1991	0.479
Sample-F	23.4	27.9	30	1.0981	0.601

The maximum value of tensile stress is 22.5 MPa for plate containing 15% fiber, and the minimum value is 19.7 MPa for plate containing 25% wool fiber for the plate of thickness 8 mm, while maximum and minimum value of tensile strength for a plate of 10 mm thickness is 28 and 23.4 MPa. The strength of the composite material is affected by fiber and matrix material, particle loading and size of particles, interfacial adhesion between layers. The composite material which has better bonding of wool fiber and matrix material shows the great strength. While tensile strength is decreasing with addition of wool fiber mat due to poor adhesion between fiber, filler, and matrix. Due to poor bonding at high loads causes void formation, and it reduces the tensile strength [34]. When the composite material is applied under tensile stress, it produces transverse loads at the fiber overlap section of crimped fibers which attempt to straighten. Due to this, the convergence of fiber strength to fabric strength is get reduced and reduces long-term fatigue and creep failure performance. This kind of phenomena is based upon the density of the composite. Due to lower density value, it may cause the reduction in the tensile strength because the density of the composite is decreasing from sample A to sample F. The tensile strength of composite material is decreasing by an increment of wool fiber percentage into the material (Fig. 5).

Due to increment in the wool proportion, the load transfer capacity from fiber to fiber decreased, and a sufficient amount of load can't be transferred, so materials get failed. Flexural strength of composite plate rises with a decrease in the percentage of wool fibre from 25 to 15% due to the distance between two nearer fibers to transfer the load (Fig. 5). The flexural strength of the material is decreasing due to the incompatibility of the fiber and polyester matrix causes the poor interfacial bonding or may be due to the fiber-to-fiber interactions and void formations inside the material. Composite material faces both the fractures, tensile and compressive, during the flexural test. A compressive fracture occurs at the surface layer of the composite while the tensile fracture takes place at the bottom layer of composite.

It can be observed from Fig. 6 that hardness increases with decrease in wool fiber content from 25 to 15%. The hardness of composite material is a matrix dominant property. Thus higher fiber content implies reduced matrix content resulting in a reduction in hardness at higher fiber concentration.

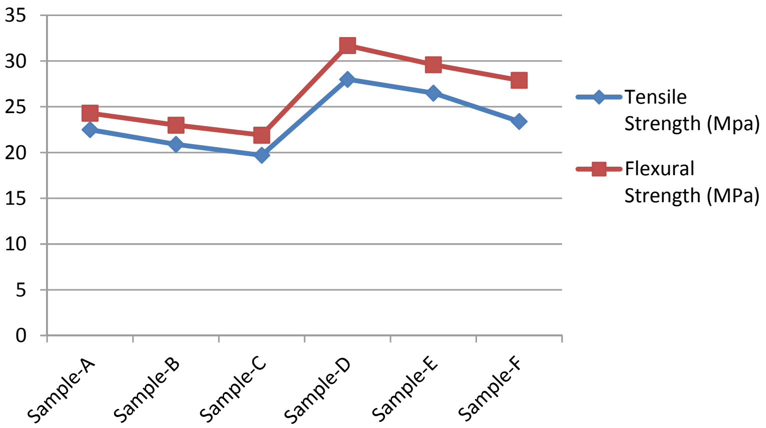


Fig. 5 Comparison of tensile strength and flexural strength

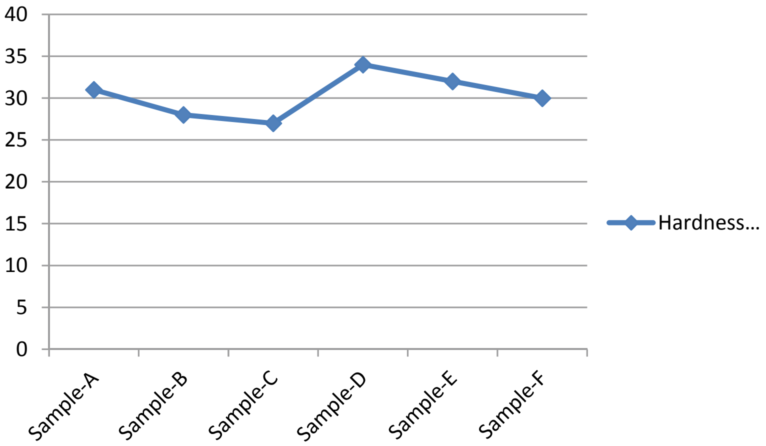


Fig. 6 Hardness of different samples

The density of the composite plate decreases with an increase in the content of wool fiber. The density of wool fiber (1.314 g/cm^3) is lower than the density of polyester resin (1.370 g/cm^3). So the higher fiber content reduces the polyester resin content inside the composite plate resulting into a reduction in the value of density. At lower fiber content composition of the polyester resin increases, so that will increase the density value at 15% wool fiber content. Wool fibers assimilate the humidity from atmosphere and, once submerged in liquid; they take up extensive measures of fluid. So water absorption increases by raising wool fiber content from 15 to 25% (Fig. 7).

Acoustical behavior of various composite samples is as shown in Table 3. The acoustic behavior of composite material depends on the orientation of reinforced material fiber and material thickness. Also, the sound absorption coefficient is directly

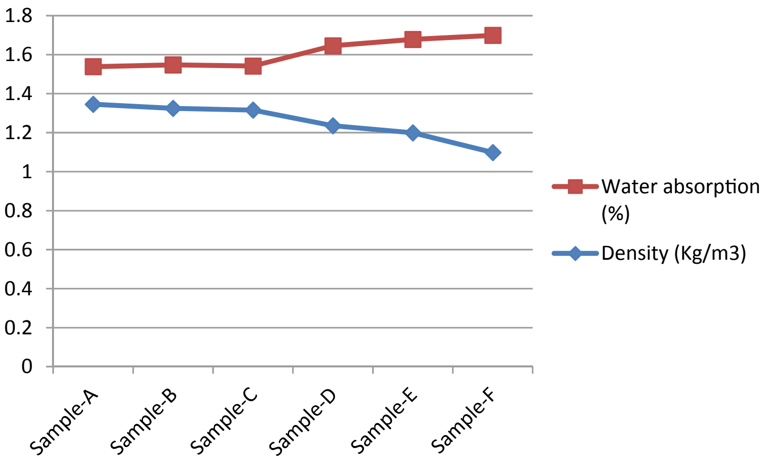


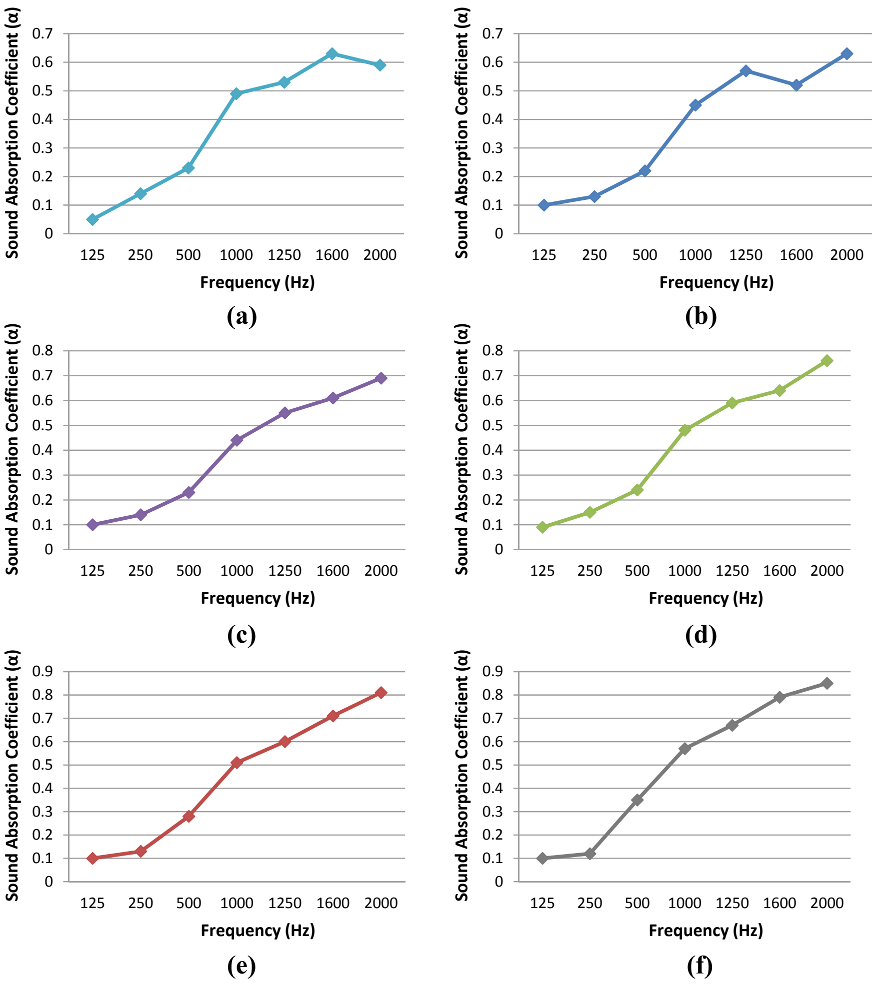
Fig. 7 Water absorption and density of different samples

Table 3 Acoustic behavior of various samples

Test specimens	t (mm)	Acoustic coefficient at different frequency range						
		$f = 125$	$f = 250$	$f = 500$	$f = 1000$	$f = 1250$	$f = 1600$	$f = 2000$
Sample-A	8	0.05	0.14	0.23	0.49	0.53	0.63	0.59
Sample-B	8	0.10	0.13	0.22	0.45	0.57	0.52	0.63
Sample-C	8	0.10	0.14	0.23	0.44	0.55	0.61	0.69
Sample-D	10	0.09	0.15	0.24	0.48	0.59	0.64	0.76
Sample-E	10	0.10	0.13	0.28	0.51	0.60	0.71	0.81
Sample-F	10	0.10	0.12	0.35	0.57	0.67	0.79	0.85

proportional to the percentage of wool fiber and material thickness. The sound absorption coefficient of 10 mm thick sample F is highest as 0.85 due to the presence of the higher amount of wool fiber at 10 mm thickness.

The detail of the acoustic response of various samples is shown in Fig. 8a–f. The sound absorption coefficient is measured in one third octave band frequency between 25 and 2000 Hz range. The increments in the sound absorption coefficient of all samples were started after reaching nearer to 200 Hz. The sound absorption coefficient of all sample had a higher value at frequencies greater than or equal to 500 Hz because the sound absorption coefficient is a function of frequency, so the value of sound absorption coefficient is more at higher frequency ranges. For frequencies up to 1250 Hz, the sound absorption coefficient of all sample has similar value. The value of the sound absorption coefficient is different for each sample in the 1250–2000 Hz frequency range. The measured results are shown that the sound absorption coefficient of sample F with triple wool layer and 10 mm thickness was 0.67 at 1250 Hz.



(a) (b) (c) (d) (e) (f)

Fig. 8 **a** Acoustic behaviour of sample-A. **b** Acoustic behaviour of sample-B. **c** Acoustic behaviour of sample-C. **d** Acoustic behaviour of sample-D. **e** Acoustic behaviour of sample-E. **f** Acoustic behaviour of sample-F

Further, the sound absorption coefficient of sample F was 0.85 at a high frequency of 2000 Hz. For all samples, from sample A to F, the density value of samples are decreasing it causes the higher value of flow resistivity and lower value of porosity, so both are inversely proportional to each other and results in a higher value of sound absorption coefficient. Results show that sample A has the lowest sound absorption coefficient value between the frequency range of 25–2000 Hz due to lower thickness and less amount of wool fiber contained in it. While sample F containing the highest amount of wool fiber with three layers of woolen mat and thickness of 10 mm has a higher amount of sound absorption coefficient in one third octave band frequency range. The sound absorption coefficient is gradually increased by increasing the frequency from low to higher value. As the higher amount of wool fiber was presented in the material causes a higher amount of sound was entrapped and absorbed by the material. While in sample B, the sound absorption coefficient is slightly decreased at 1600 Hz frequency value than the 1250 Hz it might be due to the air entrapment or air void generated in the material.

7 Conclusion

Experimental and Numerical analysis of wool hybrid composite leads to the following conclusions.

- At higher wool fibre content gives the lower value of physical and mechanical properties because of de-lamination of laminate and formation of voids inside the composite plate.
- At 15% wool fiber and with 8 mm thickness gives the better value of flexural and tensile strength due to appropriate stress distribution along with the fibers.
- At the higher percentage of wool fiber and higher thickness value gives the lower value of tensile strength due to delamination inside the composite, air voids formulation and matrix material are not sufficient to transfer load in fibre.
- The density of the composite plate increase with increases percentage of the wool fiber and thickness from 8 to 10 mm. 15% of wool fiber composite plate give lower value due to delamination inside the plate, and air void formation formed non-uniformed structure.
- The value of hardness for composite plate increase with a decrease of wool fiber content from 25 to 15%. This concludes that hardness is a matrix dominant property.
- The value of noise absorption coefficient of composite plate increases by an increase of the concentration of wool fiber from 15 to 25% and increment of plate thickness from 8 to 10 mm. So the material becomes more absorptive towards noise reduction.

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Potential of *Peristophe Roxburghiana* (Magenta Plant) for Application in Textiles: A Review

C. K. Oguzie, S. I. Ichetaonye, K. K. Ajekwene, M. E. Yibowei, S. B. Ulaeto, Imran Khan, Mohammad Mujahid Ali Khan, Anish Khan, and Abdullah M. Asiri

1 Introduction

Natural dyes have in recent times proven to be a suitable replacement for synthetic dye due to its better biodegradability, effluent treatment, low toxicity nature, etc., unlike synthetic dyes which could be toxic and unfriendly during usage being harmful to people/animal [24]. Natural dyes have found prominence due to environmental and health concerns offering not only a rich and varied source of dyestuff but a viable potential as a 'Green chemistry' option and a substitute or co-partner to some synthetic dyes. These natural dyes are comfortable to wearer's skin, non-carcinogenic, easily available, and they find their applications in the colouring of clothes, handicraft articles, food substrate, leather, and drugs [29]. However, these dyes can be gotten from either various parts of plants (leaves, barks, roots, flowers,

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C. K. Oguzie (✉)
Department of Polymer and Textile Engineering, Federal University of Technology Owerri, Owerri, Imo State, Nigeria

S. I. Ichetaonye · K. K. Ajekwene · M. E. Yibowei
Department of Polymer and Textile Technology, Yaba College of Technology, Lagos, Nigeria

S. B. Ulaeto (✉)
Department of Chemical Sciences, Rhema University Nigeria, Aba, Abia State, Nigeria

I. Khan · M. M. A. Khan
Applied Sciences and Humanities Section, Faculty of Engineering and Technology, University Polytechnic, Aligarh Muslim University, Aligarh 202002, India

A. Khan · A. M. Asiri
Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

A. M. Asiri
Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_3

stem), fungal species, and animals which can be used as a dye on textile materials [2, 6, 23].

According to the Plant of Africa database, *Peristophe roxburghiana* (*P. roxburghiana*) also known as *Peristophe bivalvis* [31] is called the magenta plant, or lá cẩm in Vietnamese. It belongs to a genus from the family of Acanthaceae, a herbaceous perennial plant that is seen widely in cool and humid climate zones across Southern Asia and Africa [11]. In Asia (Vietnam), the plant has been located in Muong Khuong, Lao Cai, Moc Chau, and in Africa (Nigeria) it has also been located in Uyo, Imo, and Bayelsa State. It has lanceolate-acute to ovoid-acute-shaped opposite leaves of 2–9 cm long, 1–4 cm wide, and a height to reach 30–50 cm. Its stem is 5 or 6 angles with much branching, sucate, and pubescent and also has a staminal filament of 1.3 cm long puberulent with seeds of 0.15 cm × 0.15 cm [48].

Figure 1 shows selected images of the plant that has stood the test of time and is commonly used by natural dyers. *P. roxburghiana* can be found in tropical, well-drained fertile soil, free from disease and pests. It is known as "hong si xian" by the Chinese, which means "red silk thread", because of the magenta/reddish dye in its leaves which can be obtained via boiling of leaves in water. Though the flowers are not attractive or flamboyant, they consist of two coloured pink lobed which grow from a small, terminal flower spike with magenta to reddish-violet appearance. Scientifically, it can be classified as; **Kingdom**: *Plantae,* **Clade**: *Tracheophytes,* **Clade**: *Angiosperms,* **Clade**: *Endicots,* **Clade**: *Asterids,* **Order**: *Lamiales,* **Family**: *Acanthaceae,* **Genus**: *Peristrophe,* **Sub-family**: *Acanthoideae* [30]. *P. roxburghiana* seeds are discoid, tuberculate, and black and also is better grown under perennial fruit trees to protect it from intense sunlight. The plant can also be harvested after 3–4 months of planting [7, 12, 25]. It has 64% free polyphenols and free radical scavenging activity (EC50 = 10). The peristrophe species is subdivided into four forms namely: red, purple, purple-magenta, and yellow where the various colours are based on the extraction method and morphological behaviour [41]. By the rural habitat, the plant is cultivated 2–3 times per year [5] and in Africa, not much is known of it for the same purpose.

Fig. 1 *P. roxburghiana* [37]

2 Extraction of *Peristrophe Roxburghiana* Leaves

A. *The healthy leaves of the plants are harvested as shown in Fig.* 2.
B. *The leaves are rinsed with clean tap water after harvesting to remove dirt (Fig.* 3*).*
C. *Put rinsed leaves in a pan filled with 625 mL of water (Fig.* 4*).*
D. *Boil at a high heat for 20 min and then reduce heating for the liquid to simmer constantly (Fig.* 5*).*
E. *Strain via a fine mesh to obtain the colour pigment for another usage (Fig.* 6*).*

Several methods have been applied and reported in the extraction of *P. roxburghiana.* Rama Krishna et al. [34] used an aqueous extraction method with distilled water as the solvent in their study to extract a compound that served a dual functional purpose of being a stabilizing and a reducing agent. Bushra, et al. [3] in their study to eliminate the stress caused by free radicals accumulation that often results in many viral diseases through finding the antioxidative potentials of

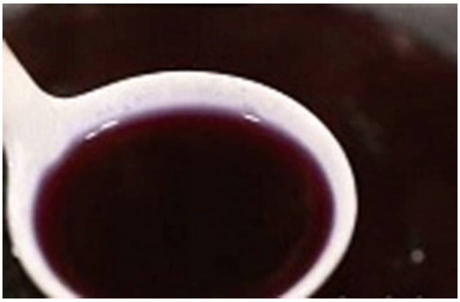
Fig. 2 Healthy leaves [10]

Fig. 3 Rinsed leaves [10]

Fig. 4 Leaves in pan [10]

Fig. 5 Boiled leaves [10]

Fig. 6 *P. roxburghiana* extract[10]



Dicliptera roxburghiana, used an aqueous extraction method with methanol as a solvent to extract Phenolic, flavonoids, and photochemical components from the plant. In a separate study, Jiang et al. [15] obtained a purple pigment by using an aqueous extraction method with ethanol as the solvent. Their results revealed that choosing 70% ethanol as an extraction solvent gave an outstanding effect for the pigment extraction from *P. roxburghiana* plant. They finally concluded that the extraction ratio increased with increasing ultrasonic power, extraction time, and solid to liquid ratio. Using the same extraction method, a red pigment was gotten from *P. roxburghiana* and the optimal extraction of ultrasonic power was 420 W at 70%

ethanol, extraction temperature, and time were 65 °C and 35 min respectively while the solid-liquid ratio was 1:35 [15].

Jiang *et al.* [16] used the microwave-assisted extraction technique using distilled water as a solvent to obtain a purple pigment from *P. roxburghiana.* Their results revealed that the optimal craft was microwave power at 480 W, with an extraction time of 85 s and mass ratio of material to the water of 1:15. Yi and Jiang [45] also used the microwave extraction technique and optimal innovation effects to obtain haematochrome from *P. roxburghiana.* The study concluded that the microwave technology posses' better advantages of less time-consumption and high efficiency for the natural pigments extraction. Thus, the ultrasonic technique of purple pigment extraction from *P. roxburghiana* has been established [18].

Jiang [17] reported that economically, the extraction of flavonoids from *P. roxburghiana* using concentrated ethanol was possible since the extraction temperature, ethanol concentration, ratio of the solid-liquid, and extraction time determines the optimal conditions of flavones extraction. In a study reported by Luu et al. [21], the authors reported a 19.73% extraction yield of yellow pigment from *P. roxburghiana* leaves using a hot water extraction technique which gave a good extraction yield. While in another research, Luu [20] used solvent extraction with 40% ethanol to obtained red, yellow, and purple pigments from the leaves of *P. roxburghiana.*

3 Characteristics of *Peristrophe Roxburghiana*

Perennial herbs 20–40 cm high, pilose throughout; leaves subentive, acuminate, base cuneate; flowers rose-purple, bracts foliaceous, ovate, 2 subtending a small fascicle, 2 cm long, 10–12 cm wide, base subcordate, villose, lanceolate, 0.6 cm long, 0.15 cm wide across the base. Calyx 5-parted to the base, sepals lanceolate, 0.4–0.6 cm long, pilose, tube slender, sepals lanceolate, 0.4–0.6 cm long, pilose tube slender, 1.8 cm long, limb 2–lipped, upper lip rounded, lower lip narrow. The apex shallowly 3–lobed, stamens 2, exserted, filaments subglabrous, authers 2–celled, connective narrow, thecae in a straight line, one high, the other low, style filiform. Flowers terminal, usually clustered cymes, 1-4 nate, compressed, 1-4 involucres. Ovary 2-locule, glabrous; ovules 2 in each locule; style ca 4 cm long, filiform; stigma shortly bifid. Capsule ellipsoidal, stalked, 1.5–2 cm long, pubescent; seeds 4, orbicular, slightly tuberculate, lacking trichomes [1, 7, 12, 13].

The *P. roxburghiana* leaf pigment is an orange-red hue at pH 11; at pH 12, the pigment is less stable and turns to a greenish-yellow hue. The pigment is also stable when exposed to heat and light [19]. Phytochemical evaluation of the major component of *P. roxburghiana* extracts, have identified and reported the *P. roxburghiana* essence of two alkaloids; peristrophamide and peristrophine (phenoxazine alkaloid) structures (Fig. 7), which are major pigments in the plant [26, 27, 39]. Another phenoxazine alkaloid isolated and identified in *P. roxburghiana* is perisbivalvine A. When compared to other red-colored natural pigments, such as anthocyanin and brazilin, phenoxazine *P. roxburghiana* provides better stability to pH and oxidation.

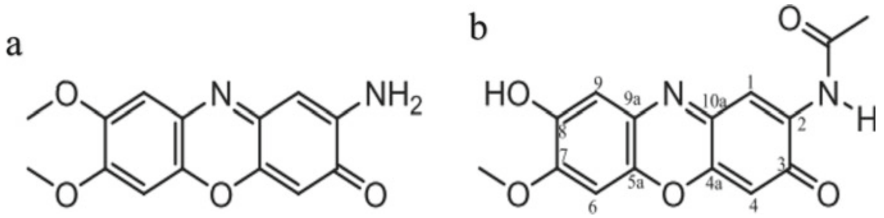


Fig. 7 Structures of **a** peristrophine **b** perisbivalvine Peristophine [8, 42]

Table 1 ^{13}C and H-NMR spectra data of peristrophine and perisbivalvine (125/500 MHz, δ ppm, DMSO-d_6 [39])

C	1.DMSO-d_6		2				
	δ ^{13}C	δ ^{1}H	δ ^{13}C DMSO-d_6	δ ^{1}H DMSO-d_6	δ ^{13}C CD_3OD	δ ^{1}H CD_3OD	HMBC ^{1}H/^{13}C
1	98.6	6.40 s	114.0	8.23 s	116.9	8.51 br s	C-3, C-2
2	146.7	–	146.3	–	148.5	–	–
3	179.4	–	171.2	–	173.0	–	–
4	102.5	6.33 s	99.6	6.06 s	102.1	6.51 s	c-2^a, c-10^a
4a	148.7	–	147.2	–	149.6	–	–
5a	137.4	–	126.7	–	130.6	–	–

Trinh et al. [42] also identified the main colour component of an aqueous extract of peristrophe leaves as peristrophine using H-NMR, C-NMR, and Electron-impact ionization mass spectrometry (EI-MS) techniques. Table 1 presents C-NMR and H-NMR spectra data of peristrophine and perisbivalvine.

More efforts are being made to use Micellar Electrokinetic Capillary Chromatography and Fluorescence Spectrophotometry spectral data to evaluate and explain the components present in the *P. roxburghiana* [9, 22, 43, 46].

4 Applications of *Peristrophe Roxburghiana* Extracts

4.1 General Applications

P. roxburghiana has established its application as a food colouring matter. Locally, *P. roxburghiana* is known as a therapy for hypertension, tuberculosis, phlegm, acute bronchitis, hepatitis B, diabetes, cough, dysentery, and diarrhoea etc. it also has anti-inflammatory properties [47]. It imparts a magenta tone to taro—filled cake called bánh da lón and glutinous rice dishes such as xôilá câm; a sweet dessert. It relieves skin complaints and the dye leaves extract such as purplish or orange-red could be used directly for cotton colouration or mixed with some other plants (*symplocos sp*, *melastoma sp* etc) parts [36].

Peristrophe roxburghiana offer immune booster properties and its extracts can be used for the treatment of cough from lung heat, swollen throat, mouth and tongue sores, blood hacking, unbearable swells from knocks or falls, infant fright wind, scrofula, stopping bleeding from wounds, blood ejection, snake bites, etc. due to the anti-inflammatory substance, it contains [4, 49]. Based on *P. roxburghiana* ability to contain colouring pigment, research efforts are published in this regard. Luu [20] used solvent extraction to obtain pigments from the leaves water which was used to enhance the beauty of glutinous rice and drinks. Jiaju et al. [14] reported that *P. roxburghiana* extracts showed the potential to slow or lower blood pressure in hyperlipidemic and renal hypertensive rodents as a result of higher and lower serum and angiotensin II found in the thoracic aorta respectively.

Nguyen et al. [28] created a model to improve the colouring material sources from *P. roxburghiana* plants in a village in Vietnam and also highlighted some primary research on chemical components and bioactivities of these plant extracts. Qin et al. [32] in their study reported that the Carbon tetrachloride (CCl_4)-induced rat model of acute liver injury was cured by *Peristrophe roxburghiana* as a result of the polysaccharides in the plant which gave protective effects to the rat livers.

Yang et al. [44] used the extract from *P. roxburghiana* to modify the hemorheological state and avert thrombosis forming in the vascular. Trinh et al. [42] reported that the plant had an anticancer capacity which significantly declined the osteoclast-like (OCI) cell number. The claim of the plant having anticancer abilities was buttressed by [38]. In their study, the ethanolic and aqueous extracts of the leaves and stems of Peristrophe in vitro by tryphan blue dye based on exclusion essay and brine shrimp lethality bioassay method showed anticancer activity. In the analytical evaluation of the major component of *P. roxburghiana* extracts, the study identified and reported the presence of peristrophine structure, which is a major pigment in the plant [26, 27]. Trinh et al. [42] also identified the main colour component of aqueous extract of peristrophe leaves as peristrophine using (2D NMR spectra) spectral analysis.

4.2 Textile Applications

Peristrophe roxburghiana categorized as fiber dye plant can potentially be used as plant-based dyes for textiles. Attempts by Rachma et al. [33] to dye cotton with *P. roxburghiana* dye extract along with mordant gave good fastness. Regardless of all this, limited research has been reported on the applications of *P. roxburghiana* for textile colouration.

P. roxburghiana leaves has been used as a popular pigment in Vietnam to replace synthetic dyes since synthetic dyes adversely affect the environment. Therefore, being a natural pigment from plants it have been chosen as an eco-friendly option to replace the harmful synthesis colorants. Presently, there is an increasing demand for textile with plant-based dye, for example batik and woven fabric with ethnic pattern and coloring, from both domestic and international consumers [45].

The possible application of *P. roxburghiana* as a dye for textiles apart from its medical and food application has been studied by Evitasari et al. [8]. The study investigated the influence of different mordant (alum, ferrous sulphate, calcium oxide) types, concentrations, and dyeing temperatures on colour strength parameter of cotton fabric dyed with *P. roxburghiana.* Increase in colour strength is due to complex formation during interaction of the dye compound with metals. The mordanting process in dyeing forms an ion bond between the fabric and the metal mordant. Thus, in the presence of mordants, perisbivalvine A and peristrophine (the natural dyestuff compounds in *P. roxburghiana*) bonds with the cotton fabric. While for unmordanted cotton fabric, only one bond between one site on the cotton fabric and the natural dye molecules exist. In dyeing of cotton fabric with *P. roxburghiana* leaf extract, colour strength in the presence of mordants is dependent on the type of mordant used. The order of mordants for increasing colour strength was found to be ferrous sulphate > alum > calcium oxide. Tia and Rahayuningsih [40] studied the effect of benzophenone and benzotriazole (UV absorbers) treatment on cotton fabrics dyed with *P. roxburghiana.* In the study, the UV absorbers were introduced before and after dyeing the fabrics. The reported results showed that ultraviolet rays protection *of P. roxburghiana* dyed fabrics (before and after UV treatment) was enhanced with increasing concentrations of benzophenone and benzotriazole. However, the textile application of *P. roxburghiana* and study of its adsorption mechanism is limited.

5 Conclusion

From the review of literature, documentation clarifying its phytochemical properties, its application in textile dyeing, and its adsorption behaviour is limited. Regardless, several scientific breakthroughs have been made on studying *P. roxburghiana* extract for medical purposes, therefore creating a need to explore its viability as a textile colourant and evaluate its colour fastness on textile materials as well as broadening the existing findings on its components characterization. Furthermore, efforts should be channeled in explaining its adsorption mechanism when used in colouring food or textile materials.

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Maximization of Buckling Resistance for Lightweight Vegetable Based Hybrid Laminated Composites Combined with Synthetic Fibers

Melih Savran, Levent Aydin, H. Arda Deveci, and Elif Gültürk

1 Introduction

Recently, studies on composite materials have increased considerably in order to obtain low-cost, long-lasting, environmentally friendly, durable and recyclable new products. In the last two decades, the use of natural fibers as an alternative reinforcing element in laminated polymer composites has attracted the attention of many researchers and scientists due to their advantages over traditional glass and carbon fibers [1]. Natural fibers-reinforced composites have a wide application area in the construction and automotive industry due to their unlimited availability, low cost, low density, comparable specific tensile properties, less health risk, non-irritation to the skin, advanced mechanical properties, good acoustic, thermal insulation, renewability, recyclability and bio-degradability [2–5] Natural fibers are classified according to their extraction from plants, animals and minerals. Lignocellulosic/cellulosic fibers (bio-fibers, vegetable fibers) sourced from plants. There is a large number of various bio-fibers can be used as reinforcement material in polymer matrices. These fibers include flax, hemp, jute, sisal, kenaf, ramie, pine apple, coir, kapok, cotton, oil palm, banana, henequen, curaua, bamboo and many others [3, 6–8] There are many studies evaluating the mechanical properties of laminated composites reinforced with different natural plant fibers or their combinations with synthetic fibers. Mechanical properties of laminated composites reinforced with natural fibers, such as kenaf [9, 10], sitka [11] jute, bamboo [12], flax [13, 14] etc. were investigated. Generally, natural fiber addition provides processing-related cost advantages, light

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M. Savran · L. Aydin (✉)
Department of Mechanical Engineering, Izmir Katip Çelebi University, Izmir, Turkey

H. A. Deveci
Department of Mechanical Engineering, Erzincan Binali Yıldırım University, Erzincan, Turkey

E. Gültürk
Department of Mechanical Engineering, Kocaeli University, Kocaeli, Turkey

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_4

composite structure with low density compared to those reinforced synthetic fibers. But, the mechanical properties of natural fiber reinforced composites are lower than synthetic fiber structure. For this reason, in subsequent studies, a hybrid (hybrid) structure was created using natural fibers, usually together with glass or carbon synthetic fibers. In this way, composites with less cost and better mechanical properties were obtained. Some of the researchers on mechanical properties; impact [15], tensile [16], fatigue [12], dynamic compression [17] behavior of flax/glass hybrid composites; the flexural [18], tensile [19] strength of kenaf/glass hybrid composites; the tensile and compressive strength of jute/glass, bamboo/glass epoxy composites [12]. In this way, composites with less cost and better mechanical properties were obtained. Apart from the tensile, compression, flexural and fatigue, vibration characterization of these materials, their behavior under service conditions such as buckling is also very important. Buckling load plays an important role especially in laminated composites used in high performance mechanical designs. A sudden sideways failure of structure under compressive stresses may occur in many composite structures. In composite structures exposed to axial compressive load, the structure stiffness and dynamic properties change due to the stress in the internal structure. Because of equilibrium position is not stable in buckling, the smallest difference arising in the system causes huge deformations and it becomes impossible for the system to return to its original position. The benchmark for buckling is the critical buckling load. Therefore, it is important to perform a buckling analysis of fiber reinforced laminated composites. Wankhade and Niyogi were examined the effect of plate thickness ratio on the buckling load in cross-layer laminated composite with using refined plate theory, taking in to account of simplified form of ruling differential equation. They found the buckling loads of thin and medium plates decrease by 36% as the aspect ratio of laminates increases [20]. Öndürücü et al. investigated the critical buckling loads of Jute and glass fiber composite specimens in different configurations with different stacking sequences kept in seawater experimentally. They found that the buckling strength of natural fiber reinforced composites kept in sea water is lower compared to natural fiber reinforced composite samples kept in room conditions [21]. Gençoğlu studied the buckling behavior of carbon fiber, graphite fiber and carbon-graphite fiber hybrid composite materials using the finite element method. Critical buckling stresses occurring in hybrid (carbon + graphite) reinforced samples were found to be higher than graphite reinforced ones and lower than carbon reinforced ones. In addition, results revealed that different layer orientations are significantly effective in critical buckling load [22]. In another study, the effect of edge ratios and anisotropy on the buckling analysis of rectangular thick and thin composite plates was examined theoretically under biaxial and uniaxial load. It was found that anisotropy and edge ratios are effective in buckling loads, and again, increasing the number of layers increases the buckling load factor [23]. Ahmad and Rajput used the finite element method to examine the effect of ply orientation and ply sequence on buckling behavior of interlayer hybrid composite plates, which consist of two synthetic (Carbon, Aramid) and one natural (flax) unidirectional layers. Results revealed that highest buckling load obtained under ply orientations of $[(0/90)_3]_S$ and ply sequence of Carbon-Aramid-Flax at symmetrical configuration.

The increase in angle orientation adversely affects the buckling load [24]. Madenci et al. analyzed experimentally, numerically and analytically the behavior of three different types of pultured glass fiber reinforced composites, made according to different directions(0, 90), against buckling and vibrational loads. Analytical and numerical solutions were made using first-order shear deformation theory and finite element software, respectively [25]. Experimental studies have shown that the buckling performance of laminated composites depends on various parameters such as the number of the layers, ply orientation, the volume ratio of the fibers and matrix, thickness ratio of layers and stacking sequence the plate thickness ratio to obtain the cheapest or lightest designs for a given application. The ability to change and optimize these parameters according to the designer's needs is a very important advantage for the designer in terms of both reducing experimental studies and saving time. However, finding optimum designs for the laminated composite structures is a little bit challenging problems. The arrangement of the layers plays an important role in minimizing weight and cost, determining resistance to environmental influences, and buckling. With the combination of laminas with different fiber orientations, sufficiently high strength values in different loading directions are obtained. Therefore, objective function and design variables are very important for optimization processes. The maximization of the critical buckling load leads to higher structural stability. Therefore, the motivation of some researchers has been to defer the buckling load by optimizing various parameters in these structures. Haftka and Le Riche, in the first part of their work, tried to optimize the laminate stacking order by maximizing the buckling load with the Genetic Algorithm (GA). In the other part of their work, they identified a problem-specific genetic operator, and demonstrated the effectiveness of this operator, which called permutation [26]. In another study, Critical buckling load of laminated composites was maximized at various biaxial compressive loading conditions and aspect ratios by performing genetic algorithm and Generalized Pattern Search Algorithm (GPSA). They optimized the stacking sequence of plate as the design variable and compared with other published research results [27, 28]. Genetic Algorithm (GA) has been used for the identification of optimum stacking sequence of composite laminates having different length of width (aspect ratios), number of plies and load conditions. A series of optimization designs have been carried out under the uniaxial, biaxial, shear and combination of these for maximum buckling load. As a result, the optimal and worst designed composite plates were compared and a significant difference was observed in post-buckling performance [29]. Both Genetic Algorithm (GA) and Simulated Annealing (SA) algorithms were performed to Sandwich and laminated plates under transverse uniform loadings by Sciuva et al. [30]. Maximum buckling load and minimum mass were assumed as objective functions. The authors demonstrated that although the results of the two evolutionary algorithms were almost the same, the SA approach took less time. Soremekun et al. maximized the critical buckling index by applying the combination of Standard Genetic Algorithm (SGA) and generalized elitist genetic algorithm (GEGA) for the best design of the plate, which they assumed to be symmetrical, balanced and simple supported [31]. Liu et al. used permutation Genetic Algorithms for stack sequence optimization of a composite laminate under maximum buckling load and proved that this algorithm is much more reliable than the Standard Genetic Algorithm (SGA) [32]. Ehsani and Rezaeepazhand employed GA approach for optimization study of composites grids plates. The objective function was to maximize buckling load and the design variables were chosen as grid pattern and fiber orientations [33]. Arda et al. were used a hybrid algorithm that combines the Genetic Algorithm (GA) with the confidence Zone Reflective Algorithm to find the optimum stacking array designs of laminated composite plates in different fiber angle areas for maximum buckling resistance. In order to obtain more reliable results, Puck fiber and inter-fiber failure (IFF) criteria were also applied as nonlinear constraints during optimization. Constrained optimization study has shown that realistic stacking sequence designs can be created even if laminated composites are subjected to very high buckling loads [34]. Rao and Arwind optimized layered composites using Scatter Search (SS) and standard Genetic Algorithm (SGA) and compared the results. They found that the Spread Search Algorithm (SS) gave better results. Different optimization methods have been used in problems where the critical buckling index is maximized as well as in design problems where weight is minimized [35]. Vosoughi et al. used a hybrid algorithm that is a mixture of Finite Elements, Genetic Algorithms (GA), Particle Swarm Optimization (PSO) Algorithms to optimize the buckling load of thick layer composite plates [36]. Maximizing the buckling load of laminated plates, Chang et al. [37] optimized the stacking sequence without any constraints on weight with using Permutation Discrete Particle Swarm Optimization (PDPSO) method. Results were compared with standard discrete particle swarm optimization (SDPSO), Gene Rank Crossover (GR) and Partially Mapped Crossover (PMC).They contended that the efficiency of PDPSO method for optimizing laminated structures was better in case constraints on the outer plies. Narita et al. optimized the plate placement configuration of laminated composite by performing Layer Based Optimization Algorithm (LOA). The buckling properties of the plates were examined for eighteen different combinations of boundary conditions. Objective function was taken as the maximization of buckling load under different compressive loads [38]. Erdal and Sönmez used the Direct Simulated Annealing (DSA) algorithm, which is an improved version of the Simulated Annealing Algorithm (SA), to maximize the critical buckling load of layered composites subject to in-plane loads and to find the fiber orientation angle [39]. Aymerich and Serra used Ant Colony Optimization (ACO) to maximize the critical buckling load by using strength and ply-contiguity as constraints, designed the stack order of plies, and compared them with studies using Genetic Algorithm and Taboo Search Algorithms. They showed that ACO is better in terms of robustness and performance [40]. Sebaey et al. performed also ant colony optimization algorithm (ACO) to optimize composite laminates and showed that diffused laminates are more beneficial than conventional laminates. During optimization, matrix cracking, fiber tensile failure minimization and stress constraint were taken into account for maximum critical buckling load [41]. A modified Ant Colony Algorithm (ACO) called multi-city-layer Ant Colony Algorithm (MCLACA) helped Wang et al. [42] to optimize stacking sequence of laminated plates for maximum buckling load. Obtained results were compared with those provided using conventional ACO and GA models in previous study and showed that the MCLACO algorithm is more effective and powerful in calculations. In another study, composite panels under axial compression load were experimentally examined and buckling behavior of plates using the Nonlinear Programming using the Quadratic Lagrangian (NLPQL) method in order to determine the optimum cross section [43]. Discrete Material Optimization (DMO) approach helped Lund [44]. for the development of buckling topology optimization of laminated multi-material composite shell structures.

A design issue used by researchers is the weight (thickness) minimization of layered composites..In some studies, various parameters were optimized to minimize the weight directly affecting the cost. The minimum weight and minimum material cost of layered composites exposed to in-plane loading is investigated by using Genetic Algorithm (GA). Maximum Stress, Tsai-Wu, and Puck failure criteria are considered as constraints in the optimization problem. Layer orientations, layer number and material are used as design variables [45]. Some researchers have revised and improved Genetic Algorithms (GA) to achieve more reliable results in optimum design of composite structures. A new Genetic Algorithm (GA) was proposed by Fan et al. [46] to optimize stacking sequence of composites with ply-drops for minimum mass and Critical buckling load was assumed as constraint. Results depicted that this algorithm is reliable to find optimal stacking sequence and reducing the weight of composite structure. Naik et al. are used Genetic Algorithms (GA) to minimize the weight of composite laminates by entering various ply orientation and loading as design variables. Constrains of the prescribed optimization are Failure Mechanism Based (FMB), maximum stress and Tsai-Wu failure criteria were used to optimize weight of laminas [47]. In another study, it was tried to minimize weight and cost by performing stacking sequence optimization using Puck failure criteria (PFC). First floor failure limitation has been accepted as a constraint [39]. Megahed et al. minimized the weight of a symmetrical hybrid carbon/flax/epoxy laminated composite with the lower frequency limit constraint. The Euler–Bernoulli Beam Theory was used to model four types of problems. Two types of problems are related to the validation of non-hybrid composites, while others involve optimum designs of carbon / flax, carbon / glass and neat glass / neat flax epoxy laminated structures. Optimum staking sequence of hybrid laminated beams was determined by using Particle Swarm Optimization (PSO) [48]. Reguera and Cortínez used a Simulated Annealing (SA) based optimization approach to maximize the buckling load capacity of composite beams and minimize the beam weight by taking design variables as the stacking order and geometry of beam cross-section [49] Akbulut and Sönmez were used fiber orientation angles and layer thickness as design variables in laminated composites subject to different plane loading, and thickness (weight) was minimized. In their study, Maximum Stress and Tsai-Wu failure criteria were used in damage control. The same team recently conducted a similar study by developing a new form of Simulated Annealing (SA) Method [50, 51]. A Pareto-based multi-objective Evolutionary algorithm was implemented by Irisarri et al. [52] to provide the optimum stacking sequence of composite structures under three hundred load cases. The maximization of buckling load and minimization of composite weight were noted as objective function. They emphasized that using new fiber orientations that differ from the classic orientations 0°, ± 45° and 90° is beneficial in terms of optimization.

Savran and Aydın [53] were used Different Stochastic optimization methods such as Differential Evolution (DE), Nelder Mead (NM) and Simulated Annealing (SA) method to maximize the fundamental frequency and minimize costs in symmetrical graphite-flax/epoxy hybrid laminate composites. Design variables were accepted as fiber orientations, number of surfaces and thickness, and core layer in their studies. They demonstrated the reliable applicability of stochastic optimization methods in natural fiber laminated structure and compared their results with the results obtained with ant colony optimization (ACO) method.

In this study, three different optimization problems, each with different scenarios, are defined and solved to buckling performance of vegetable, glass and vegetable/glass hybrid epoxy structures by performing Modified Differential Evolution (DE) Algorithm. In all cases, the use of fibers with an angle increase of 15° and the layers being symmetric and balanced were considered as constraints.

1. Optimum stacking sequences of 8- and 32-layered kenaf/epoxy, flax/epoxy, sitka spruce/epoxy and glass/epoxy composites were obtained with maximizing Critical Buckling factor (λ_{cb}) values for various aspect ratios.
2. Multi–objective optimization was performed to 8 layered glass-kenaf/epoxy, glass-flax/epoxy and glass/epoxy-sitka spruce hybrid laminated structures for different aspect ratios. Maximum buckling load and minimum weight were assumed as objective functions.
3. It is very similar to the second case, except that 32 layered glass-kenaf/epoxy, glass-flax/epoxy and glass/epoxy-sitka spruce hybrid laminated structures used for different aspect ratios.

The number of glass layers is determined by the algorithm to give the optimum result for each design case for the last two cases; total number of glass plies is evenly distributed on the outer parts of the composite structure.

2 Buckling of Laminated Composite Plates

In a flat rectangular fiber-reinforced composite laminate, buckling occurs when in-plane loads on the edges are compressive or at least relatively compressive to tensile and/or shear in order to deform its flatness. In this section, we consider the buckling of composite laminates subjected to in-plane compressive loading. Therefore, one is assumed that a composite laminate simply supported on four sides (Fig. 1) is loaded by λN_x, λN_y and λN_{xy} in-plane compressive loads, where λ is a scalar amplitude parameter for buckling load. Then, the governing differential equation for the buckling behavior of the laminate, considering the classical laminate theory, is

$$\begin{aligned} &D_{11}\frac{\partial^4 w}{\partial x^4} + 2(D_{12} + 2D_{66})\frac{\partial^4 w}{\partial x^2 \partial y^2} + D_{22}\frac{\partial^4 w}{\partial y^4} \\ &= \lambda\left(N_x\frac{\partial^2 w}{\partial x^2} + N_y\frac{\partial^2 w}{\partial y^2} + N_{xy}\frac{\partial^2 w}{\partial x \partial y}\right) \end{aligned} \tag{1}$$

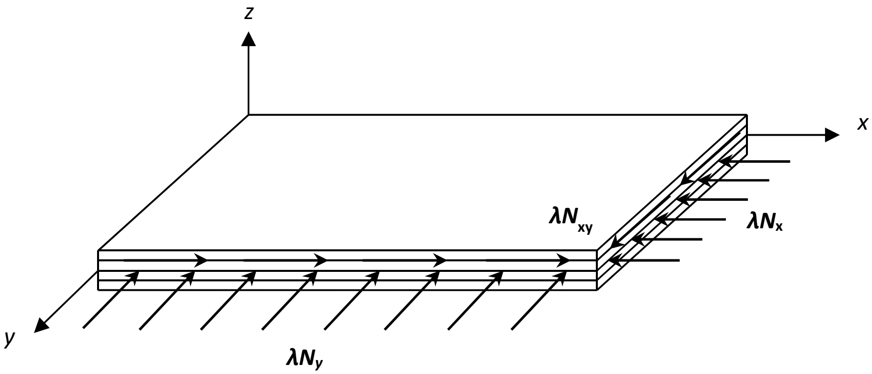


Fig. 1 A thin fiber-reinforced composite laminate subjected to in plane compressive loading

where $D_{11}, D_{12}, D_{22}, D_{66}$ are the terms of bending stiffness and w is the out-of-plane displacement term given by

$$w(x, y) = \sum_m \sum_n A_{mn} \sin \frac{m\pi x}{a} \sin \frac{n\pi y}{b} \tag{2}$$

Substituting the Eq. (2) into the Eq. (1), buckling load factor expression λ_b can be obtained as in the following form

$$\lambda_b = \frac{\pi^2\left[D_{11}\left(\frac{m}{a}\right)^4 + 2(D_{12} + 2D_{66})\left(\frac{m}{a}\right)^2\left(\frac{n}{b}\right)^2 + D_{22}\left(\frac{n}{b}\right)^4\right]}{N_x\left(\frac{m}{a}\right)^2 + N_y\left(\frac{n}{b}\right)^2 + N_{xy}\left(\frac{m}{a}\right)\left(\frac{n}{b}\right)} \tag{3}$$

It should be noted that the bending-twisting coupling terms D_{16} and D_{26} do not exist in Eqs. (1) and (3). Because these terms are negligible compared to the remaining D_{11}, D_{12}, D_{22}, and D_{66} terms and assumed to be zero for a specially orthotropic laminate [54].

The laminate buckles into m and n half-waves in the x and y directions, respectively, when the magnitude parameter reaches a critical value of λ_b [55]. m and n can be any combination of positive integers. Thus, there are infinite number of values for the buckling load factor λ_b [56]. However, a critical buckling load factor provides to restrict the maximum load which the laminate can withstand without buckling and the smallest value of λ_b under appropriate m and n values becomes the critical buckling load factor λ_{cb} as stated in the following,

$$\lambda_{cb} = \min \lambda_b(m, n) \tag{4}$$

Unless composite laminate has a very high aspect ratio (a/b) or extreme ratios of D_{ij}'s ($i, j = 1, 2, 6$), the critical values of m and n are small. The critical buckling load factor λ_{cb} varies with the plate aspect ratio, loading ratio and material, and should be greater than one to avoid any immediate buckling failure [57].

After obtaining the critical buckling load factor, critical buckling loads which the composite laminate can withstand prior to the onset of buckling can be determined by using the expressions of $N_{x,cr} = \lambda_{cb} N_x$, $N_{y,cr} = \lambda_{cb} N_y$, and $N_{xy,cr} = \lambda_{cb} N_{xy}$.

3 Optimization

In traditional manner, optimization can be defined as minimization and/or maximization process of objective function(s) under specified equality and/or inequality constraints in order to find the global optima satisfying all the constraints. Optimization algorithm to be used should be selected according to the type of problem being addressed to be able to obtain the best solution. Because optimization algorithms may not always yield the best result for all different types of phenomenological problems. In this regard, optimization algorithms can be classified as deterministic and stochastic search methods. Deterministic search methods perform derivative calculations to reach out the optimal solution. The use of deterministic methods is appropriate to solve the optimization problems involving differentiable objective functions. The main disadvantages of the deterministic optimization methods are complex solution procedures and long solution times. On the other hand, stochastic search methods are the algorithms that generate and use random variables to find the global optimum or optima. They do not require derivative information to solve the problems, and hence, produce better solutions in short calculation times [58]. Genetic algorithm (GA), differential evolution (DE) algorithm, particle swarm optimization (PSO) algorithm, and ant colony optimization (ACO) algorithm are some commonly used examples of these methods.

In this study, modified differential evolution (MDE) algorithm, one of the most powerful algorithms in stochastic search methods, is utilized to solve all the composite laminate optimization problems to be defined. MDE algorithm options and values used in the optimization are presented in Table 1.

3.1 Modified Differential Evolution (MDE) Algorithm

MDE algorithm is one of the aforementioned stochastic search methods for optimization and preferable to use in the optimum design problems of laminated composites. It is simple, powerful, and population-based similar to GA operationally. Differential evolution was introduced by Storn and Price [59] in 1996 for optimization problems over continuous domains. MDE algorithm involves four main steps: (i) initialization, (ii) mutation, (iii) crossover, and (iv) selection. The effective parameters of the algorithm on the optimum results are scaling factor, crossover, and population size. The solutions in the algorithm are evaluated and searched within a population

Table 1 MDE algorithm options

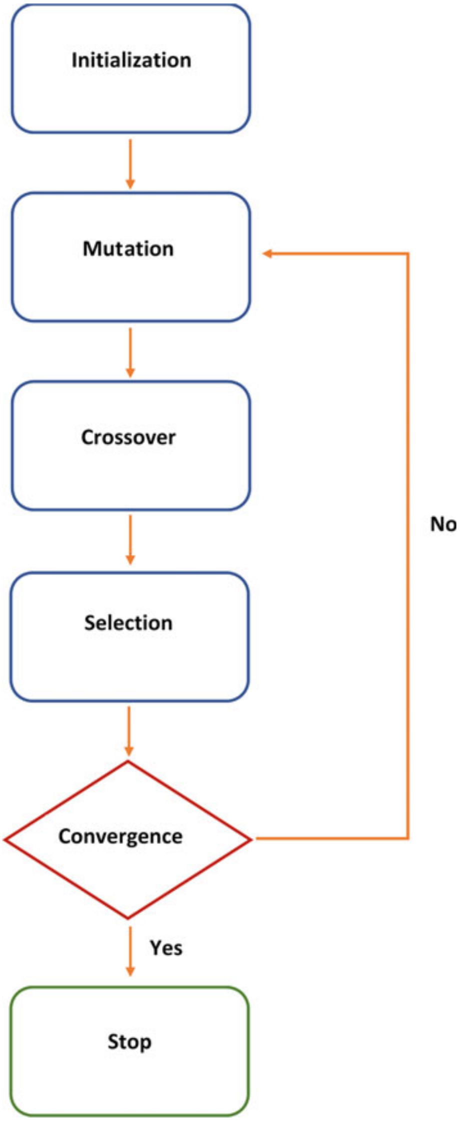
Options name	Value
Cross over fractions	0.5
Random seed	0
Scaling factor	0.6
Tolerance	0.001
Contract ratio	–
Expand ratio	–
Reflect ratio	–
Shrink ratio	–
Level iterations	–
Perturbation scale	–

unlike a single solution. Hence, its computational cost is high. The performance of MDE algorithm in the solution depends on the manipulation of target and difference vectors to obtain a trial vector. The other decisive parameters in the algorithm for the best results are problem complexity, maximum number of generations as stopping criterion, and boundary constraints [58]. MDE algorithm is robust and efficient in finding global optima. However, also in this algorithm, it is not guaranteed to find global optima for every type of optimization problem as being in other stochastic search methods. A flowchart briefly showing the process of MDE algorithm is given in Fig. 2. Detailed information on differential evolution algorithm can be found in [59].

4 Problem Definition

In the scope of this study, vegetable—synthetic hybrid fiber laminated composites will be designed optimally in terms of high buckling resistance and low weight. Optimization problems will be solved with mixed-integer programming approach. In this study, he weight-buckling resistance performance of (i) non-hybrid vegetable, (ii) non-hybrid synthetic, and (iii) inter-ply hybrid vegetable-synthetic fiber-reinforced composites will be evaluated. Four kind of composite materials, kenaf/epoxy, flax/epoxy, sitka spruce and glass/epoxy are used. Properties regarding these materials are shown in Table 2.

Fig. 2 Flowchart of the MDE algorithm optimization [53]



The problems solved in this study are classified as single-objective and multi-objective. For all the problems, width/length ratio (aspect ratio) varies from 0.25 to 2 with 0.25 increment. In all problems, fiber angles with 15° increments are used. The detail description including objective, constraints and design variables about single and multi-objective problems are given as follows.

Single objective buckling problems	
Find	$\theta_k \quad \theta_k \in [0, 90]$ N_o and N_i (for hybrid structure)
Maximize	$\lambda_{cb}\ (\theta_1, \theta_2, \ldots.\theta_n)$
Such that	$\theta_k \in \left\{0^0, \pm15^\circ, \pm30^0, \pm45^\circ, \pm60^\circ, \pm75^0, 90^\circ\right\}$ $\gamma \leq 0.2, \delta \leq 0.2$
Design variables	$\theta_1, \theta_2, \ldots.\theta_k,$ N_o and N_i (for hybrid structure)
Multi objective buckling—Weight problems	
Find	$\theta_k \quad \theta_k \in [0, 90]$ N_o and N_i (for hybrid structure)
Minimize	$L = k_1 {l_1}^2 + k_2 {l_2}^2 + c_1 {g_1}^2 + c_2 {g_2}^2$
	$l_1 = \left(\frac{\lambda_{cbmax} - \lambda_{cb}}{\lambda_{cbmax}}\right)$
	$l_2 = \frac{weight}{weightmax}$
	$weight = ab\frac{h}{N}(\rho_0 N_0 + \rho_i N_i)$
	$g_1 = \delta - 0.2$ $g_2 = \gamma - 0.2$
Such that	$\theta_k \in \left\{0^0, \pm15^\circ, \pm30^0, \pm45^\circ, \pm60^\circ, \pm75^0, 90^\circ\right\}$ $\gamma \leq 0.2, \delta \leq 0.2$ $k_1 = k_2 = c_1 = c_2 = 1$
Design variables	$\theta_1, \theta_2, \ldots.\theta_k$ The numbers of the surface (N_0) and core layers (N_i)

The penalty function approach has been used to solve the multi objective problems. In this regard, the function L including the linear combination of the squares of the quantities "buckling" and "weight" are introduced. The parameters λ_{cb} and *weight*

Table 2 Material properties of the composite laminates

Parameters	Glass/Epoxy [44]	Kenaf/Epoxy [10]	Flax/Epoxy [14]	Sitka spruce [11]
Longitudinal modulus (GPa)	34	11.51	22.8	12.571
Transverse modulus (GPa)	8.2	2.15	4.52	0.833
In-plane shear modulus (GPa)	4.5	2.03	1.96	0.716
Poisson ratio	0.29	0.42	0.43	0.39
Material density (kg/m^3)	1910	1243.4	1310	404

correspond to the optimum values of critical buckling load and weight, respectively. λ_{cbmax} and *weightmax* terms are maximum critical buckling load and maximum weight for all layers consisting of glass/epoxy material, respectively. In the formulas, mass densities of the outer and inner layers are denoted by ρ_0 and ρ_i, respectively, and the parameters g_1 and g_2 correspond to penalty terms. The parameters k_i and c_i (for $\mathrm{i} = 1{,}2$) are sensitivity coefficients. These k_i and c_i coefficients are both assumed to be one since the importance of critical buckling load and weight are desired to be equal in the multi-objective function to be minimized.

5 Results and Discussion

In the scope of this study, three separate problems each involving different optimization scenarios are organized and solved. In Problem 1, critical buckling factor (λ_{cb}) values of 8- and 32-layered symmetric balanced kenaf/epoxy, flax/epoxy, sitka spruce and glass/epoxy composites are maximized for various aspect ratios, and optimum stacking sequences are obtained for all these design cases. Tables 3 and 4 show the results of the 8- and 32-layered composites, respectively. In Problem 2, multi-objective optimization is performed. Similarly, for the specified aspect ratios, critical buckling factors of 8-layered symmetric balanced hybrid glass-kenaf/epoxy, glass-flax/epoxy and glass/epoxy-sitka spruce composite laminates are maximized while weight is minimized at the same time. However, for the problems, the algorithm is constituted to determine the total number of glass plies to be placed at the bottom and top of the laminates. Tables 5, 6 and 7 show the optimization results of 8-layered glass-flax/epoxy, glass-kenaf/epoxy and glass/epoxy-sitka spruce laminates, respectively. Also, weight saving and reduction in critical buckling related to Problem 2 are evaluated together in Table 8 by comparing the non-hybrid glass/epoxy results. In Problem 3, considering the same optimization design cases as in Problem 2, critical buckling factors of 32-layered symmetric balanced hybrid glass-kenaf/epoxy, glass-flax/epoxy and glass/epoxy-sitka spruce composite laminates are maximized while weight is minimized. Tables 9, 10 and 11 show the optimization results of 32-layered glass-flax/epoxy, glass-kenaf/epoxy and glass/epoxy-sitka spruce laminates, respectively. Similar to Table 8, weight saving and reduction in critical buckling for the 32-layered hybrid laminates in comparison with non-hybrid 32-layered glass–epoxy laminates are presented in Table 12.

In Table 3, when we consider all the composites and their critical buckling factors for all aspect ratios, it is seen that maximum critical buckling strength is obtained for glass/epoxy as may be expected. Flax/epoxy, kenaf/epoxy and sitka spruce follows the glass/epoxy in terms of buckling stability, respectively. It may be also noted that a considerable change in critical buckling factor is not observed for all the composites when the aspect ratio increases from 1.25 to 2.

It can be seen in Table 4 that essentially similar behavior in the 32-layered composites compared to the 8-layered designs in Table 3 are found. The same optimum stacking sequences are found in some aspect ratios such as 0.25 and 1.25. Maximum

Table 3 Optimization results in terms of critical buckling factor for 8-layered symmetric-balance flax/epoxy, kenaf/epoxy, sitka spruce and glass/epoxy with 15° increment (Problem 1)

	Flax/epoxy		Kenaf/epoxy		Sitka spruce		Glass/epoxy	
a/b	Stacking sequence	λ_{cb}	Stacking sequence	λ_{cb}	Stacking sequence	λ_{cb}	Stacking sequence	λ_{cb}
0.25	$[0_4]_s$	113,401	$[0_4]_s$	61,220.10	$[0_4]_s$	57,403.4	$[0_4]_s$	172,402
0.5	$[\pm 15/0_2]_s$	27,667.80	$[0_4]_s$	15,305	$[\pm 15/\pm 45]_s$	13,330.1	$[0_4]_s$	43,100.60
0.75	$[\pm 30_2]_s$	13,082.90	$[\pm 15_2]_s$	6854.73	$[\pm 30/0_2]_s$	6197.32	$[\pm 30_2]_s$	20,030.20
1	$[\pm 45_2]_s$	9329.91	$[\pm 45_2]_s$	4647.08	$[\pm 45/0_2]_s$	4248.61	$[\pm 45_2]_s$	14,170.70
1.25	$[\pm 60_2]_s$	7602.93	$[\pm 60_2]_s$	3944.21	$[\pm 60/90_2]_s$	3562.82	$[\pm 60_2]_s$	11,652.10
1.5	$[\pm 60_2]_s$	6970.87	$[90_4]_s$	3821.87	$[\pm 60/90_2]_s$	3362.53	$[\pm 75_2]_s$	10,694.60
1.75	$[90_2/\pm 60]_s$	6905.72	$[90_4]_s$	3819.40	$[\pm 75/\pm 60]_s$	3352.64	$[90_4]_s$	10,678.90
2	$[\pm 75/90_2]_s$	6916.95	$[90_4]_s$	3826.25	$[\pm 75/\pm 45]_s$	3332.52	$[90_4]_s$	10,775.10

Table 4 Optimization results in terms of critical buckling factor for 32-layered symmetric-balance flax/epoxy, kenaf/epoxy, sitka spruce and glass/epoxy with 15° increment (Problem 1)

a/b	Flax/epoxy		Kenaf/epoxy		Sitka spruce		Glass/epoxy	
	Stacking sequence	λ_{cb}	Stacking sequence	λ_{cb}	Stacking sequence	λ_{cb}	Stacking sequence	Λ_{cb}
0.25	$[0_{16}]_s$	113,401	$[0_{16}]_s$	61,220.10	$[0_{16}]_s$	57,403.40	$[0_{16}]_s$	172,402
0.5	$[\pm 15/0_4/\pm 15_2/0_2/\pm 15_2]_s$	27,929.80	$[0_{16}]_s$	15,305	$[\pm 15_3/90_4/\pm 15/90_2/0_2]_s$	13,535.40	$[0_{16}]_s$	43,100.60
0.75	$[\pm 30_8]_s$	13,082.90	$[\pm 15_8]_s$	6854.73	$[\pm 30_8]_s$	6283.47	$[\pm 30_8]_s$	20,030.20
1	$[\pm 45_8]_s$	9329.91	$[\pm 45_8]_s$	4647.08	$[\pm 45_8]_s$	4248.61	$[\pm 45_8]_s$	14,170.70
1.25	$[\pm 60_8]_s$	7602.93	$[\pm 60_8]_s$	3944.21	$[\pm 60_8]_s$	3562.82	$[\pm 60_8]_s$	11,652.10
1.5	$[\pm 60_8]_s$	6970.87	$[90_{16}]_s$	3821.87	$[\pm 60_8]_s$	3362.53	$[\pm 75_8]_s$	10,694.60
1.75	$[90_6/\pm 75_4/90_2]_s$	6939.96	$[90_{16}]_s$	3819.40	$[\pm 75_3/\pm 60/\pm 75/\pm 60/90_2/\pm 75]_s$	3352.64	$[90_{16}]_s$	10,678.90
2	$[\pm 75/90_4/\pm 75_2/90_2/\pm 75_2]_s$	6982.44	$[90_{16}]_s$	3826.25	$[\pm 75_2/\pm 60/\pm 75_2/\pm 60/90_2/\pm 75]_s$	3332.52	$[90_{16}]_s$	10,775.10

Table 5 Optimization results of 8-layered symmetric-balance hybrid glass-flax/epoxy laminates for critical buckling factor, weight and index *L with* 15° increment (Problem 2)

a/b	Stacking sequence	N_o (Total glass ply)	λ_{cb}	Weight (kg)	*L*
0.25	$[0_4]_s$	2	147,511	0.2336	0.6051
0.5	$[0_2/\pm 15]_s$	2	36,585.90	0.4672	0.6072
0.75	$[\pm 30_2]_s$	2	17,099.30	0.7008	0.6057
1	$[\pm 45/\pm 15]_s$	2	11,874.30	0.9344	0.6106
1.25	$[\pm 60_2]_s$	2	9943.88	1.1680	0.6058
1.5	$[\pm 75/\pm 60]_s$	2	9107.41	1.4016	0.6063
1.75	$[90_4]_s$	2	9108.03	1.6352	0.6059
2	$[90_2/\pm 75]_s$	2	9146.46	1.8688	0.6072

Table 6 Optimization results of 8-layered symmetric-balance hybrid glass-kenaf/epoxy laminates for critical buckling factor, weight and index *L with* 15° increment (Problem 2)

a/b	Stacking sequence	N_o (Total glass ply)	λ_{cb}	Weight (kg)	*L*
0.25	$[0_4]_s$	2	125,497	0.2256	0.6190
0.5	$[0_4]_s$	2	31,374.30	0.4512	0.6190
0.75	$[\pm 15_2]_s$	2	14,058.80	0.6768	0.6339
1	$[\pm 75/\pm 45]_s$	2	8559.25	0.9024	0.7018
1.25	$[\pm 75/\pm 60]_s$	2	8005.40	1.1280	0.6430
1.5	$[\pm 75/90_2]_s$	2	7785.69	1.3537	0.6190
1.75	$[90_4]_s$	2	7785.03	1.5793	0.6184
2	$[90_4]_s$	2	7843.58	1.8049	0.6190

Table 7 Optimization results of 8-layered symmetric-balance hybrid glass/epoxy-sitka spruce laminates for critical buckling factor, weight and index *L with* 15° increment (Problem 2)

a/b	Stacking sequence	N_o (Total glass ply)	λ_{cb}	Weight (kg)	*L*
0.25	$[0_4]_s$	2	123,887	0.1249	0.2462
0.5	$[0_2/\pm 30]_s$	2	30,432.30	0.2498	0.2534
0.75	$[\pm 15/\pm 30]_s$	2	13,696.10	0.3746	0.2670
1	$[\pm 15/\pm 45]_s$	2	8262.62	0.4995	0.3408
1.25	$[\pm 75/\pm 60]_s$	2	7781.88	0.6244	0.2773
1.5	$[\pm 75/\pm 60]_s$	2	7599.31	0.7493	0.2508
1.75	$[90_4]_s$	2	7629.09	0.8742	0.2485
2	$[90_2/\pm 60]_s$	2	7608.09	0.9990	0.2534

Table 8 Weight saving and reduction in critical buckling factor for 8 layered composites (Problem 2)

a/b	Weight saving (%)			Reduction in critical buckling load (%)		
	Glass-flax/epoxy	Glass-kenaf/epoxy	Glass/epoxy-sitka spruce	Glass-flax/epoxy	Glass-kenaf/epoxy	Glass/epoxy-sitka spruce
0.25	23.5602	26.1780	59.1296	14.4378	27.2068	28.1406
0.5	23.5602	26.1780	59.1296	15.1151	27.2068	29.3924
0.75	23.5602	26.1780	59.1405	14.6324	29.8120	31.6227
1	23.5602	26.1780	59.1378	16.2053	39.5990	41.6922
1.25	23.5602	26.1780	59.1361	14.6602	31.2965	33.2148
1.5	23.5602	26.1726	59.1350	14.8410	27.1998	28.9426
1.75	23.5602	26.1733	59.1343	14.7100	27.0990	28.5592
2	23.5602	26.1739	59.1378	15.1148	27.2064	29.3919

Table 9 Optimization results of 32-layered symmetric-balance hybrid glass-flax/epoxy laminates for critical buckling factor, weight and index *L with* 15° increment (Problem 3)

a/b	Stacking sequence	N_o (Total glass ply)	λ_{cb}	Weight (kg)	*L*
0.25	$[0_{16}]_s$	2	123,787	0.2156	0.5772
0.5	$[0_4/\pm 15_2/0_2/\pm 15/0_4]_s$	4	32,958.50	0.4432	0.5811
0.75	$[\pm 30_8]_s$	2	14,305.80	0.6468	0.5794
1	$[\pm 45_8]_s$	2	10,182	0.8624	0.5770
1.25	$[\pm 60_8]_s$	2	8315.69	1.078	0.5797
1.5	$[\pm 75/\pm 60_7]_s$	4	8200	1.3296	0.5802
1.75	$[90_{16}]_s$	4	8184.44	1.5512	0.5804
2	$[90_2/\pm 75/90_4/\pm 75/90_2/\pm 75/90_2]_s$	4	8239.63	1.7728	0.5812

Table 10 Optimization results of 32-layered symmetric-balance hybrid glass-kenaf/epoxy laminates for critical buckling factor, weight and index *L with* 15° increment (Problem 3)

a/b	Stacking sequence	N_o (Total glass ply)	λ_{cb}	Weight (kg)	*L*
0.25	$[0_{16}]_s$	8	125,497	0.2256	0.6190
0.5	$[0_{16}]_s$	8	31,374.30	0.4512	0.6190
0.75	$[\pm 30_2/\pm 15_6]_s$	8	14,471.80	0.6768	0.6220
1	$[\pm 45_8]_s$	10	11,076	0.9291	0.6254
1.25	$[\pm 60_8]_s$	8	8400.36	1.1280	0.6229
1.5	$[\pm 75_2/90_{12}]_s$	8	7795.18	1.3537	0.6185
1.75	$[90_{16}]_s$	8	7785.03	1.5793	0.6184
2	$[90_{16}]_s$	8	7843.58	1.8049	0.6190

Table 11 Optimization results of 32-layered symmetric-balance hybrid glass/epoxy-sitka spruce laminates for critical buckling factor, weight and index *L with* 15° increment (problem 3)

a/b	Stacking sequence	N_o (Total glass ply)	λ_{cb}	Weight (kg)	*L*
0.25	$[0_{16}]_s$	8	123,887	0.1249	0.2462
0.5	$[0_2/\pm 15/0_8/\pm 15/\pm 30]_s$	8	30,671.40	0.2498	0.2501
0.75	$[\pm 30_8]_s$	8	14,230.80	0.3746	0.2508
1	$[\pm 45_8]_s$	8	10,071.70	0.4995	0.2507
1.25	$[\pm 60_8]_s$	8	8269.25	0.6244	0.2512
1.5	$[\pm 75_2/\pm 60_6]_s$	8	7605.98	0.7493	0.2504
1.75	$[90_{14}/\pm 60]_s$	8	7631.53	0.8742	0.2484
2	$[90_2/\pm 75/90_8/\pm 75/\pm 60]_s$	8	7667.86	0.9990	0.2501

Table 12 Weight saving and reduction in critical buckling factor for 32 layered composites (Problem 3)

a/b	Weight saving (%)			Reduction in critical buckling load (%)		
	Glass-flax/epoxy	Glass-kenaf/epoxy	Glass/epoxy-sitka spruce	Glass-flax/epoxy	Glass-kenaf/epoxy	Glass/epoxy-sitka spruce
0.25	29.4503	26.1780	59.1296	28.1986	27.2068	28.1406
0.5	27.4869	26.1780	59.1296	23.5312	27.2068	28.8376
0.75	29.4503	26.1780	59.1405	28.5788	27.7501	28.9533
1	29.4503	23.9938	59.1378	28.1475	21.8387	28.9259
1.25	29.4503	26.1780	59.1361	28.6336	27.9069	29.0321
1.5	27.4869	26.1726	59.1350	23.3258	27.1111	28.8802
1.75	27.4869	26.1733	59.1343	23.3588	27.0990	28.5364
2	27.4869	26.1739	59.1378	23.5308	27.2064	28.8372

critical buckling load factors are obtained in glass/epoxy laminates. As mentioned before, laminate thickness is kept constant in 8-layered and 32-layered composites. Thus, it has been investigated here whether the ply thickness change in the composite structure has a significant effect on the critical buckling load factor. It is seen that there is not any change in buckling stability with thinner layers except a few design cases in flax/epoxy and sitka spruce composites, which are slight increases.

In Tables 5, 6 and 7, critical buckling load factor and weight results of 8-layered composites obtained from the hybridization of glass fiber with natural fibers are given. *L* in the table is multi-objective function value to be minimized and involves critical buckling load factor and weight objectives together. As previously stated, glass layers are arranged to be placed in top and bottom of the laminates (outer surfaces) and be in equal numbers for the top and the bottom. There are natural composite plies in the inner layers. The number of glass layers (N_o) is determined by the algorithm to give the optimum result for each design case.

Accordingly, the optimization results of 8-layered hybrid composites state that N_o is found to be 2 in all the design cases of problem 2 as being one at the top and one at the bottom layer. It is also seen in all hybrid design cases that as the aspect ratio increases, the plate weight increases however the critical buckling load factor decreases. Considering all the cases, minimum weight and acceptable buckling strength compared to the others are obtained in the hybrid glass/epoxy-sitka spruce laminate optimization.

Table 8 showing weight saving and reduction in critical buckling load factor percentages for 8-layered hybrid composites compared to the non-hybrid glass/epoxy composites indicates that maximum weight saving is reached in the glass/epoxy-sitka spruce hybrid composite for all the aspect ratios. However, maximum buckling strength is obtained in the hybrid glass-flax/epoxy composite in which reduction in critical buckling load is minimum. Moreover, it can be said that specially selected designs cases could meet the desired requirements in pareto-optimal respect.

For the Problem 2 defined, optimization results of 32-layered hybrid glass-flax epoxy, glass-kenaf/epoxy, and glass/epoxy-sitka spruce composite laminates are presented in Tables 9, 10 and 11, respectively. When we evaluate all the results together, it can be said that number of total glass plies are mostly found as 8; however, it is obtained as 2 or 4 in the glass-flax epoxy optimization. When we compare the results in terms of critical buckling load factor, it is seen that maximum λ_{cb} values are obtained in glass-flax epoxy and glass-kenaf/epoxy composites for different aspect ratios. Namely, λ_{cb} values are maximum for the aspect ratios of 0.25, 0.75, 1 and 1.25 in the glass-kenaf/epoxy composites, and maximum for the remaining aspect ratios in glass-flax epoxy composites. Besides, relatively lower λ_{cb} values are obtained in all optimization cases of glass/epoxy-sitka spruce composite. With regards to weight, designs with the lowest weight are obtained in the all cases of glass/epoxy-sitka spruce composites.

Table 12 shows for the 32-layered optimization that maximum weight saving is achieved in all the cases of glass/epoxy-sitka spruce hybrid composite when compared to the non-hybrid glass–epoxy composites. However, maximum reduction in critical buckling load is typically obtained in the hybrid glass/epoxy-sitka spruce composites, which means that maximum buckling strength loss are in these cases. On the contrary, minimum reduction in critical buckling load occurs in the design case of a/b = 1 of glass-kenaf/epoxy composites, followed by the design cases of a/b = 0.5, 1.5, 1.75 and 2 of glass-flax epoxy composites.

When we compare the optimization results of the 8-layered and 32-layered same hybrid composites with each other, that there are significant outcomes can be seen. The first one is that the weights in the 32-layered glass-flax epoxy composites for all the aspect ratios are less than the 8-layered glass-flax epoxy composites. However, for the same hybrid composite optimization critical buckling load factor values in the 32-layered cases are slightly lower than the 8-layered cases. The second one is that weights in the glass-kenaf/epoxy composites are equal for almost all cases of 8- and 32-layered designs. Nonetheless, for some aspect ratios of the glass-kenaf/epoxy composites higher critical buckling load factor values are found in the 32-layered designs compared to the 8-layered designs. Optimum designs from a/b = 0.75 to 1.5 are the examples of this situation. The third and the last outcome is that higher critical buckling load factor values are obtained in the all design cases of the 32-layered glass/epoxy-sitka spruce composites compared to the 8-layered ones. However, the weights are obtained equal for all design cases of both.

As a result of the problems solved, it is seen that the glass/epoxy-sitka spruce hybrid composite laminate structure is to be more preferable in multi-objective critical buckling factor-weight problems than the other hybrid structures especially if multi-layered (more than 8 layers) composites are necessary for use. Therefore, the results of 32-layered symmetric-balanced hybrid glass/epoxy-sitka spruce composites have been evaluated in detail for six optimization cases involving different numbers of glass/epoxy and sitka spruce layers.

Comparison of critical buckling load factor of 32 layered symmetric-balanced hybrid glass/epoxy-sitka spruce for different aspect ratios is given in Fig. 3. As in the other problems, also here in the figure, N_o denotes the number of glass plies at the outer layers of the hybrid composite. N_i denotes the inner layers of the composite.

It can be seen from the Fig. 3 that critical buckling load factor increases for each aspect ratio as the number of glass/epoxy layers in the composite increases. This increase is more prominent in small aspect ratios such as 0.25 and 0.5. Besides that, critical buckling load factor values significantly decreases in all six optimization cases as the aspect ratio of the plate increases.

In Fig. 4, the change of critical buckling load factor values according to the number of glass layers is also presented for the same hybrid glass/epoxy-sitka spruce composite in 0.5, 0.75, 1, 1.25, 1.5. 1.75 and 2 aspect ratios. As seen in the figure, critical buckling load factor increases as the number of glass plies increases for all the aspect ratios. Maximum increase occurs in the aspect ratio of 0.5.

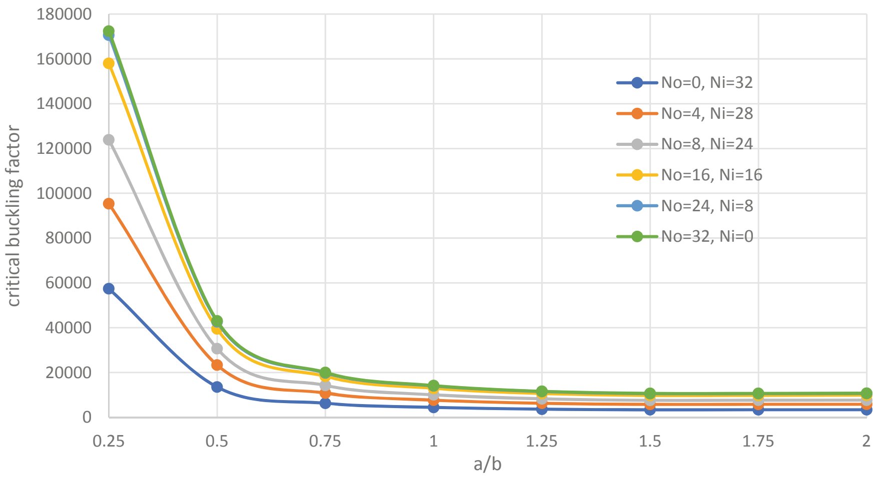


Fig. 3 Comparison of critical buckling factor of 32 layered symmetric-balanced hybrid glass/epoxy-sitka spruce for different aspect ratios and glass/epoxy ply number (problem 3)

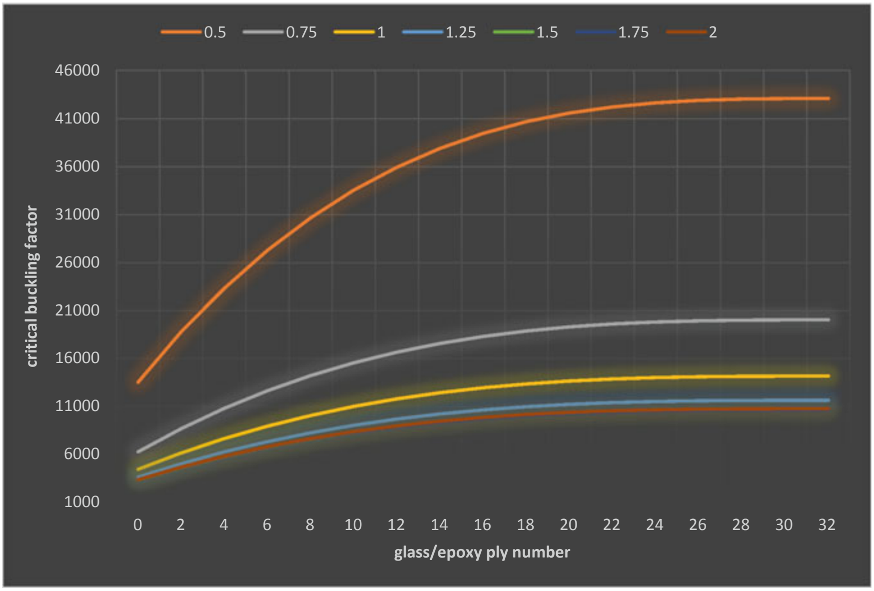


Fig. 4 Critical buckling factor versus the number of glass/epoxy ply for 32 layered symmetric-balanced hybrid glass/epoxy-sitka spruce considering different aspect ratios (Problem 3)

6 Conclusion

In the scope of this study, the usage of natural composites flax/epoxy, kenaf/epoxy and sitka spruce as non-hybrid structure and as hybrid structure including glass/epoxy has been presented taking into account weight saving and maximum buckling resistance.

Stacking sequences design and optimization of laminated composites based on Modified Differential Evolution (MDE) are considered. Single objective approach has been used in the problems including only maximum buckling strength as objective. Multi-objective approach has been preferred for solving of the problems where both the maximum buckling strength and the minimum weight are simultaneously selected as the objective.

Comparison of buckling resistance of natural composites flax/epoxy, kenaf/epoxy and sitka spruce has been carried out to assess whether these materials can be used or not with glass/epoxy in hybrid structures. For all hybrid structures, glass plies are placed at the bottom and top of the laminates and the optimization algorithm determines the number of glass/epoxy layers needed to gain optimum design. When an overall assessment is made, it is evident that among the non-hybrid and hybrid structures, maximum critical buckling strength is obtained for glass/epoxy. However, in this study, maximum buckling strength and minimum weight have been taken into account simultaneously and thus it is shown that the glass / epoxy-sitka spruce hybrid structure that best meets the mentioned requirements can be selected as the optimum design. Also, It can be seen from the results that.

(i) Among the non-hybrid structures, glass/epoxy composite provides highest buckling strength. Flax/epoxy, kenaf/epoxy and sitka spruce follows the glass/epoxy in terms of buckling stability, respectively.
(ii) When we examine the hybrid structures, it is clearly seen that 8 layered glass-flax/epoxy has the best result in terms of maximum buckling strength.
(iii) However, when buckling-weight factor (L) including the effect of both buckling and weight are considered as an objective function, the usage of 8 and 32-layered hybrid glass/epoxy-sitka spruce are appropriate to obtain maximum buckling strength and minimum weight.

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Recent Developments on Electrochemical Sensing Applications Using Vegetable Fiber Based Porous Carbon Materials

Libina Benny, Anila Rose Cherian, Anitha Varghese, and Gurumurthy Hegde

1 Introduction

Vegetables are the cornerstone to human nutrition, which is vital for healthy and balanced diet. Vegetable fibers are a power house of carbohydrates, vitamins, minerals and glycosides. In addition to the above-mentioned richness, various constituents of these vegetables like leaves, roots and stem possess some inherent porosity making them excellent candidates to synthesize porous carbon materials. Considering the diversity of vegetable fiber in our planet it is only fitting that there exists plenty of room for further advancements and exploration. Porous carbon material obtained from that of vegetable fibers showcased excellent electrical conductivity and numerous sites for analyte detection. This property of theirs was attributed due to the presence of high- edge plane like defective sites density, functional groups containing oxygen and most importantly because of the large surface area is provides [1]. This work will throw light on how these vegetable fiber stirred the hornets' nest brought scientists to thinking about the plethora of applications it found its way into electrochemical sensing.

L. Benny · A. R. Cherian · A. Varghese
Department of Chemistry, CHRIST (Deemed to be University), Hosur Road,
Bengaluru 560029, India
e-mail: anitha.varghese@christuniversity.in

G. Hegde (✉)
Centre for Nano-materials and Displays, B.M.S. College of Engineering, Bull Temple Road,
Bengaluru 560019, India
e-mail: murthyhegde@gmail.com

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_5

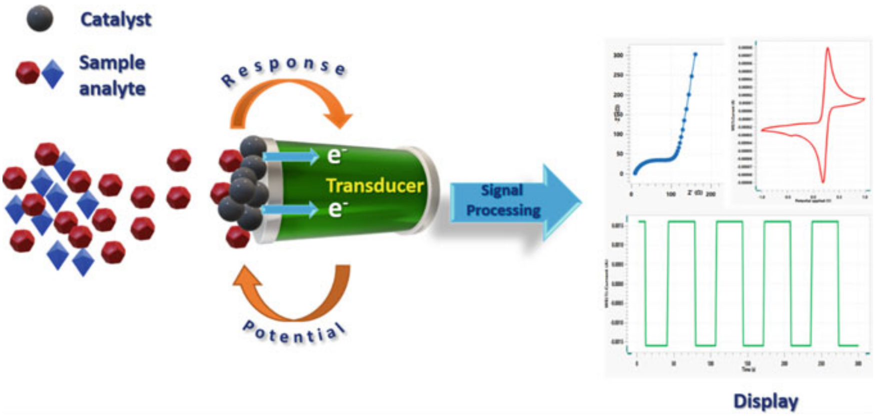

Fig. 1 General working principle of electrochemical sensors (Ref. [2])

2 Electrochemical Sensors

Electrochemical sensors have garnered prominence among the chemical sensors for over 100 years due to their simplicity, high sensitivity, selectivity and low cost of detection. They consist of a signal transducer which is encompassed by a recognition element which contribute to the properties such as rapidity and its facile and direct analysis. Electrochemical reactions basically involve the transfer of electrons which occur at the electrode- electrolyte interface, thereby enabling us to understand the electrical phenomena is various systems (Fig. 1). However electrochemical detection using bare electrodes show poor sensitivity due to electrochemical fouling and the presence of other interfering molecules. Development of novel, first of its kind electrode material is one of the most important as well as herculean task in order to achieve adequate sensing. Accordingly, electrochemical research is seen to be taking giant leaps and adding new colors to its canvas through the preparation of new sensor materials which possess excellent chemical and electrochemical property, stability and robustness [2]. Materials with the aforementioned properties are undoubtedly a need of the hour and has to be synthesized with abundant resources which are readily available. Hence over the past years one can see researchers devoting themselves to navigate through different materials which serve and fulfils these requirements.

3 Diverse Carbon Electrode Materials

Ever since the emergence of nano materials they have navigated their way and opened new avenues in fabricating nanomaterials modified electrodes for electrochemical sensing applications [3–6]. The most commonly used materials for working electrode are, metal/metal oxide, inorganic complexes [7], conducting polymers or salts

[8, 9] MOFs [10–15] and carbon materials [16, 17]. Among the materials mentioned carbon materials have been extensively used in the fabrication of electrodes owing to the wide potential window it provides in aqueous media, cost effectiveness and most importantly due to its inertness in most of the electrolyte solution. Variants of carbon-based material are subjected to research for their use in electroanalytical applications. In order to enhance and tweak its sensitivity and selectivity these materials are engineered with finesse to incorporate defects into them and also to modify them with functional groups and hetero atoms. Experimentation and advancements over electrode modification have taken place over the recent years owing to the introduction of graphene, carbon nanotubes (CNTs) and other nanoparticles. There was a rampant utilization of these particles which attributed to its high electronic conductivity, good catalytic activity and very large surface area. The making and commercial production of some of the carbon forms like carbon nanofibers, CNTs and fullerenes involves the usage of expensive instrumentation [18–21]. Graphene, which possess large surface area compared to that of single walled carbon nanotubes, involves multiple steps of chemical and mechanical exfoliation and chemical vapour deposition [22–24]. Graphene also showcases poor dispersion in aqueous media as a result of which in order to obtain a stable suspension, additional functionalization to graphene surface using dispersing agents such as, amphiphilic polymers, alkylamines, hydrophilic carboxyl groups, is a mandate [9]. One major setback of this material is that they could form close packed structures after they are assembled on electrode surface which would reduce the surface area and obstruct mass transfer. Hence there was a need for the emergence of a new material would bridge the gap which the above-mentioned materials innately possessed. Owing to their abundance lignocellulosic bio-mass, like vegetable fibers, agricultural and forest residues, are a promising resource which can be easily converted and processed into carbon materials. With this context, vegetable fiber derived carbon materials-based sensors are increasingly becoming popular due to their abundance and easier synthesis methods [25, 26], which altogether reduces the cost in development of novel electrochemical sensors.

4 Vegetable Fiber Based Porous Carbon Materials

Vegetable lignocellulosic fibers which are widely available in most developing countries possess diverse advantages, mainly their low real (1.3–1.5 g/cm^3) and apparent density (0.4–1.5 g/cm^3) biodegradability, renewability, requirement of low processing energy, and abundance [27, 28]. Generally, fibers from monocots possess average fiber lengths and width from 1.1 to 2.7 mm and 8–30 m respectively [29]. All these properties make the vegetable lignocellulosic fibers convenient materials for electrode modifications. Vegetable fibers can be classified according to their origin: from phloem or liber (e.g. jute and malva), from leaves (e.g. sisal and curaua), from seeds (e.g. cotton), from fruit (e.g. coconut), from grass and reed (e.g. palm trees, rice and corn) and from xylem or woody material. A prior knowledge of the morphology, chemical composition, and physical and mechanical properties of the vegetable fibers is essential for evaluation of their potential for different applications, of their capacity for a later industrial upscaling or for assessing the highest reinforcing potential of the fibers (e.g. improving their interaction with the composite matrix). These vegetable fibers when subjected to pyrolysis or carbonization yields porous carbonaceous materials. The aforementioned synthesis methods will be discussed below and the approaching sections in this chapter, will encompass the electrochemical sensing applications of vegetable fiber based porous carbon modified electrodes towards the detecting of diverse target analytes like heavy metal ions (Lead, Pb^{2+}), biomolecules (progesterone, ascorbic acid, dopamine and uric acid), pollutants (nitrite and hydrogen peroxide), and flavonoids (rutin).

4.1 Synthesis Strategies

Carbon material derived from carbon materials are prepared from mostly two methods namely Hydrothermal carbonization and Pyrolysis. Latter is carried out at temperature ranging from 180–250 °C in a completely closed system using water as the solvent [30]. While the latter is a technique which is carried out at temperatures ranging from 200 to 1000 °C [31, 32].

4.1.1 Hydrothermal Carbonization

In hydrothermal carbonization, hydrolyses of carbohydrates takes place and they are hydrolysed into simple sugars such as glucose and fructose which in turn are dehydrated into furfurals, hydro methyl furfurals and organic acids (Fig. 2). As the reaction time progress, it irks the furfurals to polymerize resulting in long chain humin and char. On analysing the decomposition of xylan, cellulose and lignin at

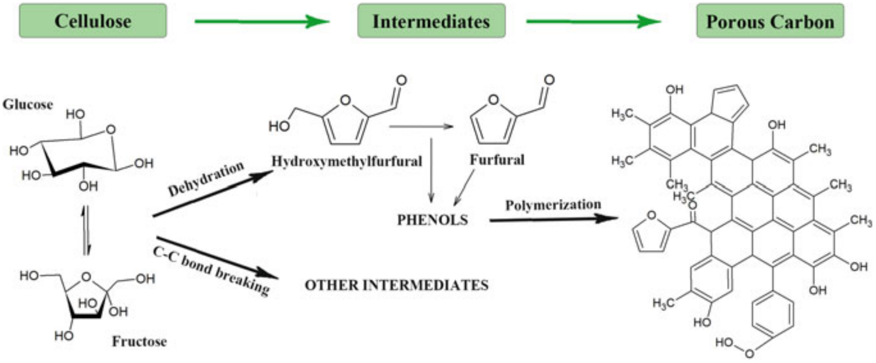

Fig. 2 A simplified reaction route of biomass conversion during Hydrothermal carbonization

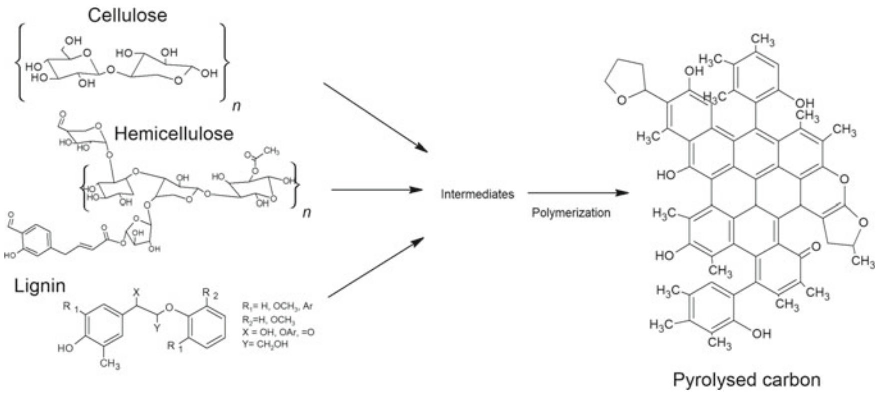

Fig. 3 A simplified plausible pathway of biomass conversion during pyrolysis (Ref. [37])

different HTC temperatures, Kim et al. determined the best or rather the optimum reaction temperatures for hemicellulose, cellulose and lignin and it was found to be 180, 200 and 220 °C respectively [33, 34].

4.1.2 Pyrolysis

Condensable and non-condensable volatiles and pyro char are produced by the complete decomposition of all the structural components of biomass during pyrolysis. Formation of low molecular weight compounds and levo glucosan takes place on depolymerisation of cellulose [35]. Decomposition of hemicellulose also follows similar pathway as that of cellulose [36]. Whereas lignin undergoes a physical transformation (softening and swelling), and later decomposes into oligomers, phenols, permanent gases and char. Also minerals influence pyrolysis reactions inside particles [35]. A possible pyroltic carbonization routes of biomass components are represented in Fig. 3.

4.2 Modification Strategies: Tuning of Surface Structures

Tuning the structural surface of vegetable fiber-based carbon materials can be highly advantageous for improving the electrocatalytic activity towards sensing applications. The sensing ability of such materials depend profoundly on their unique properties such as surface area, porosity, electrical conductivity and so on. Thus, rationalization of such properties is important in assessing the diverse applications of vegetable fiber based carbon material [38]. The selection of appropriate precursors such as vegetable fibers play an important role in the enhancement of the electrochemical activity. Moreover, control over the surface morphology or texture of vegetable fiber based carbon materials have been achieved by modifying the preparation methods i.e. activation [39] and their working conditions (temperature, time etc.) [40].

The influence of nitrogen, oxygen, sulphur or phosphorous containing functional groups on the surface is yet another route of tuning such carbonaceous materials [41]. These heteroatoms develop a synergistic effect with the carbon materials enhancing their exceptional properties. In addition to the afore-mentioned features it is well known that the magnitude of electrochemical activity depends on the carbonization temperature. Lee et al. investigated in a systematic way the impact of hydrothermal carbonization temperature and reaction time on the properties of resulting vegetable fiber based carbons [41]. Strikingly it was observed that a higher electrical property was attained for carbon materials from precursors which was treated at higher temperature and quicker reaction time [41]. Consequently, it becomes a necessity for optimizing the hydrothermal carbonization conditions with the intention to improve the electrocatalytic activity of the carbon materials obtained. Therefore, the surface chemistry, porosity and electrical properties of the resulting carbon materials can be tailored by controlled selection of suitable precursors and efficient synthesis conditions (reaction time and temperature of both carbonization and activation methods). This art of tuning of carbon-based materials various electrochemical parameters like sensitivity and limit of detection (LOD) can be enhanced [42].

5 Application: Electrochemical Sensing

5.1 Detection of Nitrite Using Banana Stem Based Porous Carbons

Banana stem *(Musa paradisiaca)* being a rice source of fiber is grown in most of the tropical areas of Asia and Africa. Conversion of banana stem waste into materials with practical application is eloquent as it is economically and environmentally benign. Moreover, Nitrite is an inorganic pollutant which is hazardous to the environment and poses threat to the human life and commonly used as food additives [43]. The high oxidation potential of nitrite ion prevents its detection when directly used with bare electrodes. Madhu et al. pioneered a facile and eco-friendly method to derive heteroatom enriched activated carbon (HAC) from banana stem for the first time to explore this material for the electrochemical nitrite sensor application [44]. HAC were prepared by carbonization at different temperatures 70, 800 and 900 ˚C and it was observed that HAC showed better performance. The highly ordered porosity of the HAC permitted fast electron transfer as it possessed high-energy adsorption sites, which promotes high sensitivity and selectivity. Additionally, large surface area (1465 m^2g^{-1}) of HAC with micropores and mesopores empowered the highly sensitive detection of nitrite. This proposed method was utilized to determine nitrite in various water samples [44]. Figure 4a, depicts the cyclic voltammograms of AC700,

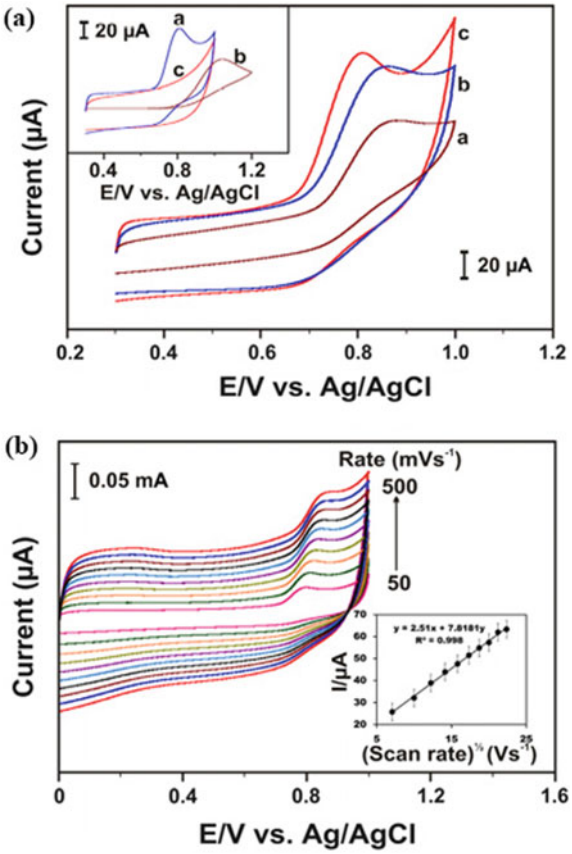

Fig. 4 **a** CVs obtained at AC700 **a**, AC800 **b** and HAC **c** modified GCEs in 0.1 M PBS (pH 4), which contained 50 mM nitrite, at the scan rate of 50 mVs^{-1}. Inset: CVs obtained at HAC towards absense **c**, presence of nitrite **a** and bare modified GCE **b**. **b** CVs obtained at HAC-modified GCE at different scan rates from 50 to 500 mV/s in 0.1 M PBS (pH 4), which contained 50 mM nitrite Ref. [44]

AC800 and AC900 modified electrodes at a scan rate of 50 mV/s in the potential range 0.0 to + 1.6 V in 0.1 M PBS (pH = 4.0) and 50 mM nitrite solution. However, for AC900 (curve c) the currents are greater than the other modified ones (AC700 and AC800). Figure 4b depicts the corresponding cyclic voltammogram of the HAC-modified electrode (AC900) with different scan rates in 50 mM nitrite in PBS buffer (pH 4) solution.

The voltammogram clearly exhibits that the oxidation peak current (Ipa) increases when the scan rates increase, whereas the peak potential positively shifts. Furthermore, the Ipa values also exhibited a linear dependence with the square root of the scan rates (inset) in the range of 50–500 mV/s. These results suggest that the kinetics of the overall process was controlled by a diffusion process [44]. Moreover, the obtained ultrahigh sensitivity of nitrite is 9 or 13.2 mAmM^{-1} cm^{-2} and low detection limit of 0.07 μM. A good linear relationship was observed in the nitrite concentration range of 1 to 127 μM, with the detection limit being at a signal-to-noise ratio of 3. All these results indicate commendable catalytic activity of the electrode towards nitrite oxidation.

5.2 Detection of Dopamine, Uric Acid and Ascorbic Acid Using Pumpkin Stem Based Porous Carbons

Electrochemically active neurotransmitters such as dopamine (DA) and uric acid (UA) present in the serum and central nervous system plays an important role in human metabolism [45]. DA is an organic catecholamine produced from the substantia nigra region of the central nervous system and it performs various neuropsychiatric functions such as human cognition, reward-motivated actions, motor nerve control, and hormonal balance [46]. UA is a natural antioxidant that reduces damage to neurons caused due to oxidative stress and DNA damage [47]. It is highly essential to detect UA and DA levels in human fluids for the diagnosis of various diseases caused due to dysfunctions in the human body. Ascorbic acid (AA), also known as Vitamin-C coexist along with DA and UA in the human body because AA is an essential nutrient for the enzymatic production of neurotransmitters and its deficiency can cause scurvy, bleeding, and infertility [48]. Microporous carbon materials possess high surface area and enhanced porous morphology, which promotes oxygen reduction, improves the electrocatalytic activities, and enhances the electrochemical properties. V. Veeramani et al. developed an electrochemical sensor based on the pumpkin stem -derived activated carbon for the simultaneous detection of AA, DA, and UA [49]. The developed electrode (AC-700) possesses a high surface area (793 m^2g^{-1}) and micro-mesoporous morphology, thereby promoting oxygen reduction and other electrochemical activities. The schematic representation of detection of DA, UA and AA is shown in Fig. 5d.

The representative FE-SEM, TEM, XRD, and XPS pattern of the as-synthesized AC is shown in figure below. Figure 5a depicts the SEM image of AC700 which displays a bundle-like porous morphology. Furthermore FE-TEM (Fig. 5 b) study revealed that AC700 contains the mesoscopic pores indicating the presence of multi-dimensional wormhole-like pore structure. The XRD pattern of AC700 illustrated two broad diffraction peaks at 23° and 43°, corresponding to the (002) and (101) plane reflection which reveals the amorphous behavior [49]. Additionally, Fig. 5c shows the XPS survey spectra of AC700 exhibits the peaks corresponding to carbon, and oxygen. Furthermore, elemental analysis was carried out to confirm the presence of heteroatoms like carbon, nitrogen, hydrogen and sulphur in AC surface. The foremost benefit of the AC is the presence of heteroatoms like nitrogen and sulfur in nature without incorporating any chemical dopants. This could be achieved due to the biowaste precursors contain small amounts of heteroatoms naturally, which may lead to the enhanced electrochemical performance.

AC-700 modified electrode provided high sensitivity and selectivity in the simultaneous detection of DA, UA and AA with a detection limit of 0.03, 0.51, and 2.3 μM respectively and sensitivity of 6.3, 6.1 and 7.6 $\mu A\ \mu M^{-1}\ cm^{-2}$ respectively. The modified electrode (AC-700/GCE), overwhelmed the several carbon-based modified electrodes [49]. Additionally, this reported biosensor provides a outstanding performance in snail hemolymph and human blood serum.

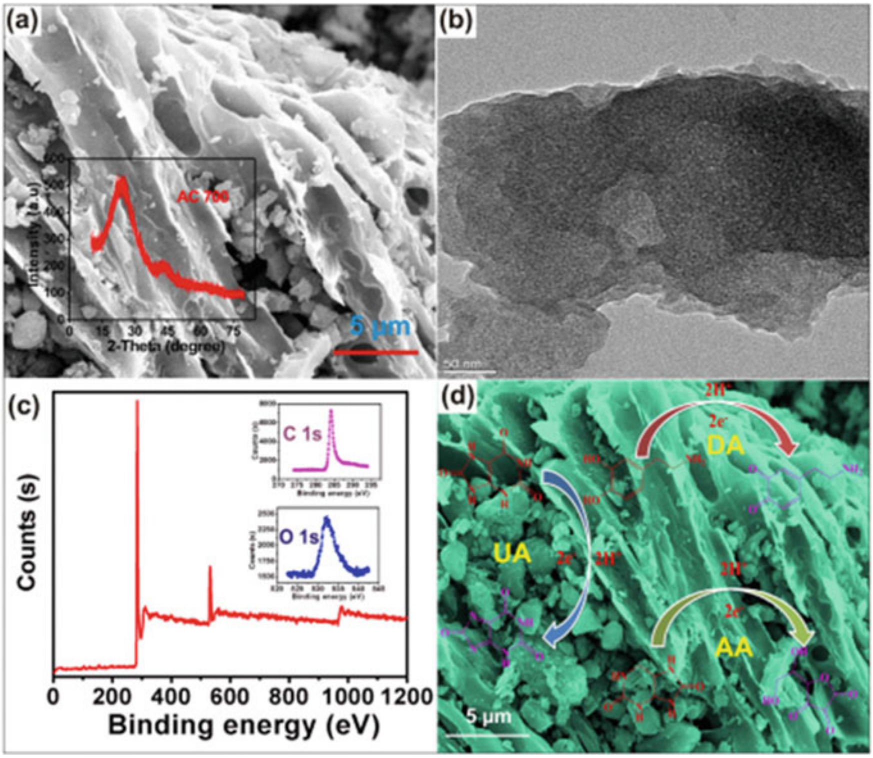

Fig. 5 **a** FE-SEM image of AC700; inset: XRD pattern of AC700. **b** HR-TEM image of AC700. **c** XPS spectra of AC700. **d** The plausible reaction mechanism of DA, UA and AA Ref. [49]

5.3 Detection of Rutin Using Peanut Shell Based Porous Carbons

Peanut shell wastes are generally the leftover after removing the nut from its pod. It is generally considered to be an abundant agro-industrial which possess a very slow degradation rate. However, these shells are enriched with different functional groups and utilized in biodiesel and bioethanol production [50]. Moreover, this has made its way even towards the field of electrochemical sensing. Pangfie Pang et al. chose six different types of bio-wastes, such as peanut shell (P), bagasse (B), corncob powder (C), straw powder (S), grapefruit skin (G), and walnut shell (W), as the precursors to synthesize activated carbons (AC) by high-temperature carbonization and activation with KOH [51]. The electrochemical features of synthesized ACs were assessed by cyclic voltammetry. It was observed that the activated carbon derived from peanut shell (P-AC) exhibits excellent electrochemical activity and is chosen as a model to synthesize electrochemical sensor with gold nanoparticles (P-AC/AuNP) as it showed higher BET surface area (2484 m^2g^{-1}) and BJH pore size (2.68 nm) [51]. The schematic representation for fabrication of the P-AC/AuNP is given in Fig. 6.

Moreover, Fig. 7a and b encompasses the FE-SEM images of the surface morphology of P-AC and P-AC/AuNP composite. P-AC showed a smooth morphology and uniform distribution of pore size. Consequently, excellent conductivity, high porous structure, rapid electron transfer, and large surface area of AuNPs and P-AC enhanced the electrochemical performance towards the detection of rutin. Rutin is an electroactive compound with four hydroxyl groups present in its molecular assembly. Two electron and proton redox process have been reported as the electrochemical reaction mechanism [52, 53]. Increased redox peaks were observed for AuNP/GCE and P-AC/GCE whereas smallest redox peak currents on bare electrode. Moreover, the composite P-AC/AuNP showed a well-defined peak with a remarkable increase in its current window which can thus be attributed to the synergistic effect between the P-AC and AuNPs (Fig. 7c and d). These results suggest that PAC/AuNPs composite could be a great platform for the sensitive detection of rutin as it acts as an effective mediator to enhance the elctrocatalytic activity [51]. Thus the P-AC/AuNP nanocomposite display excellent sensitivity and selectivity, long-term stability and reproducibility for the detection of rutin [51].

Differential pulse voltammetry (DPV) studies were performed for the determination of rutin due to its high sensitivity and selectivity. Furthermore, under the optimal conditions, the oxidation peak current of rutin was relative to its concentration in the range from 5.0 to 1.0 mM. The linear regression equation was calculated as Ipa (mA) = 9.06 log c (M) + 75.50 (R = 0.9985), with a sensitivity of 128.24 mA M^{-1} cm^{-2}. Similarly, the limit of detection (LOD) was found to be 2.0 nM which produce at the signal to noise ratio of 3 [51]. A comparable linear range and the detection limit exhibited by PAC/AuNPs/GCE is due to the synergistic effect of P-AC and AuNPs. Furthermore, rutin can be successfully led to a great potential application of the proposed method for biological and clinical analyses.

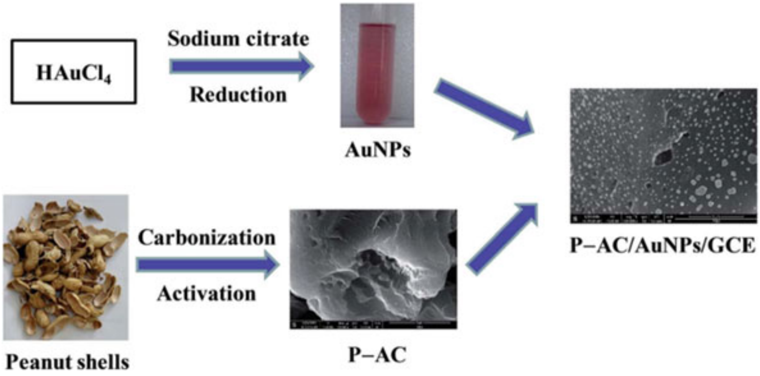

Fig. 6 Schematic representation for the fabrication of P-AC/AuNPs composite modified GCE Ref. [51]

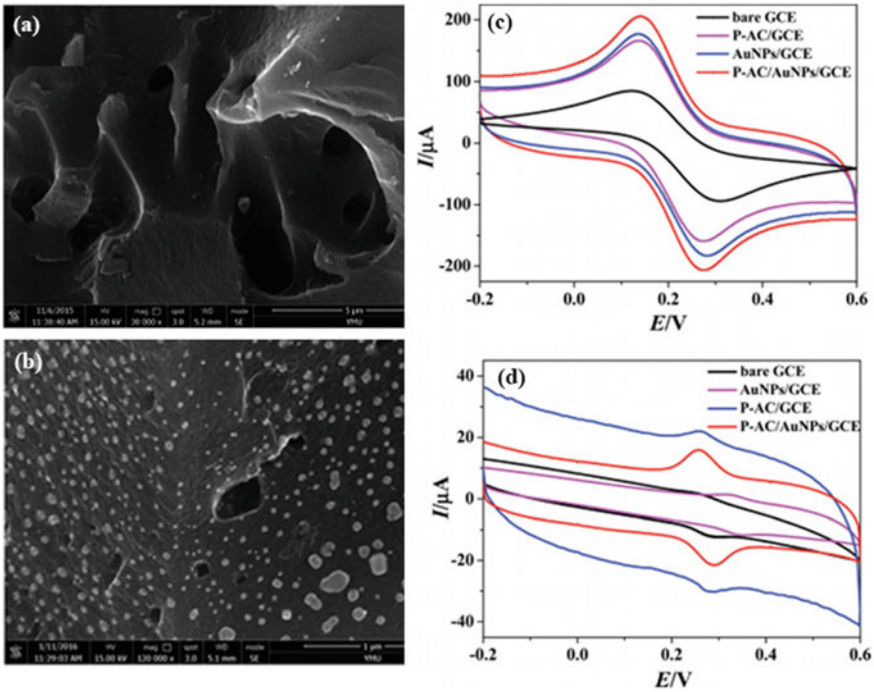

Fig. 7 **a** and **b** FE-SEM image of P-AC and P-AC/AuNPs nanocomposites. **c** CVs of different modified electrodes in 5.0 mM $K_3[Fe(CN)_6]$ containing 0.1 M KCl and in 0.1 M PBS (pH 6.0) in the presence of 1 mM rutin repectively Ref. [51]

5.4 Detection of Progesterone Using Onion Peel Based Porous Carbons

Onion peels which are rich in flavonoids are usually discarded after consuming the flesh within. The food waste value of natural food is often undervalued. Hence it is necessary to utilize it not only to recover its economic and nutritional value but also to employ in various analytical applications. Akshaya et. al., synthesized highly porous carbon nanospheres (CNSs) from onion peels by a single step pyrolysis method [54]. Further CNSs was coated on carbon fiber paper (CFP) which served as the working electrode (CNS/CFP) for the detection of progesterone [54].

This method avoided the need of biomarkers for the sensitive and selective determination of progesterone. The SEM images of the CNS/CFP electrodes agglomerated nanospheres are dispersed on the CFP substrate. The SEM images have displayed the porous nature of CNS and can be concluded that porosity plays a pivotal role in facilitating the electrolyte to sweep into the electrode (Fig. 8a and b). The surface parameters like surface area and pore size was calculated to be 692 m^2g^{-1} and 2.5 nm respectively.

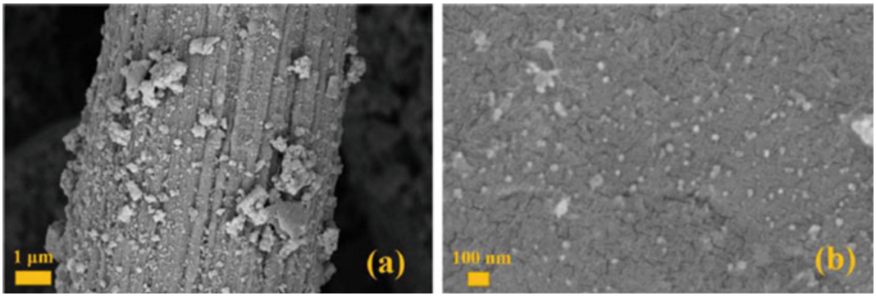

Fig. 8 **a** and **b** SEM images of CNS/CFP electrode (Ref. [54])

Because of the porosity of CNSs, the authors were able to achieve detection of progesterone at an ultra- nanomolar level with a detection limit of 0.012 nM. From the voltammograms obtained as seen in Fig. 9a, the modified electrode showed a better and higher current profile than the bare one for their response to the redox

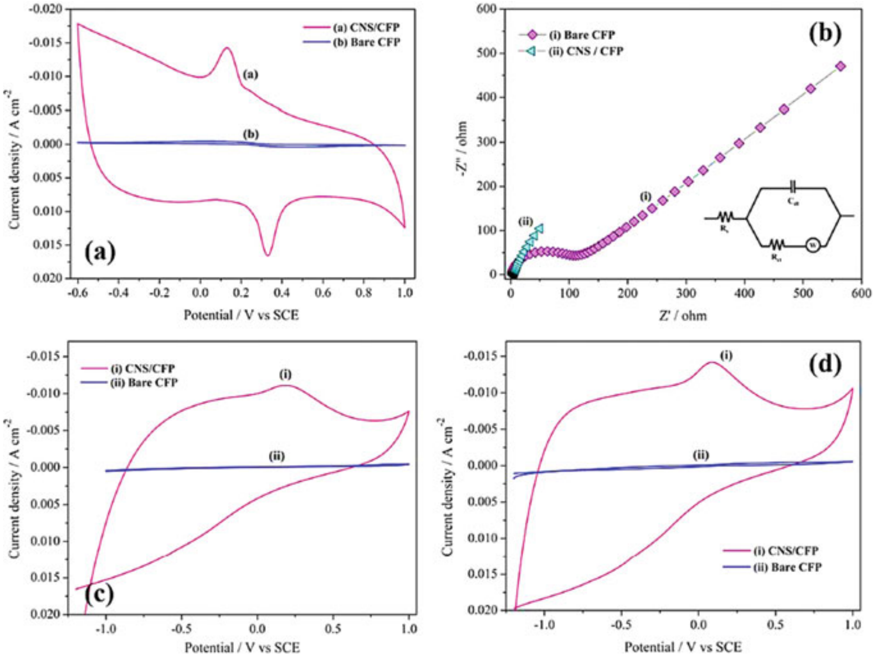

Fig. 9 **a** Cyclic voltammograms of 1 mM potassium ferrocyanide/ferricyanide at CNS/CFP (curve a) and bare CFP (curve b) electrodes in 1 M KCl. b Nyquist plots of bare CFP (curve (i)) and CNS/CFP (curve (ii)) electrodes in 5 mM $K_4[Fe (CN)_6]/K_3[Fe (CN)_6]$ solutions containing 0.1 M KCl**.** c Cyclic voltammograms of (i) CNS/CFP and (ii) Bare CFP electrodes without progesterone in PBS (pH 7.0) at a scan rate of 0.05 V/s. d Cyclic voltammograms of 0.15 nM progesterone at (i) CNS/CFP and (ii) Bare CFP electrodes in PBS (pH 7.0) at 0.05 V/s Ref. [54]

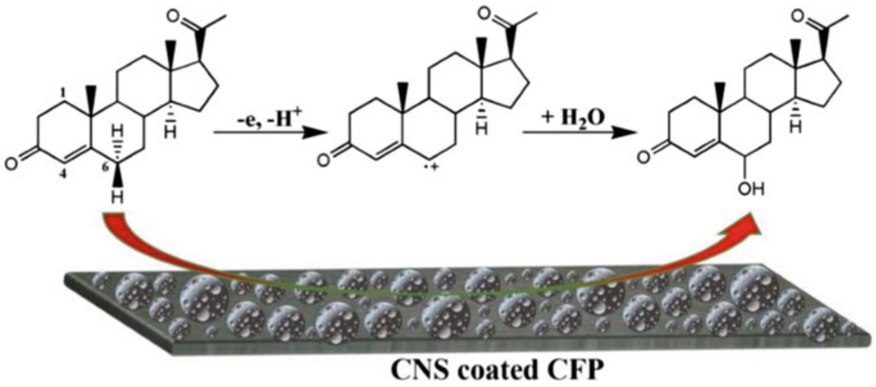

Fig. 10 Reaction mechanism proposed for oxidation of progesterone at CNS/CFP electrode Ref. [54]

couple of 1 mM potassium ferrocyanide/ ferricyanide in 1 M KCl. CVs of bare CFP and CNS/CFP in phosphate buffer solution (PBS) in pH-7 for progesterone analysis as shown in Fig. 9c, d. The impedimetric characterization from Fig. 9b, demonstrates that the modified CNS/CFP electrode exhibited significantly very low charge transfer resistance of 8.85 Ω with respect to the bare electrode which possessed a resistance of 93.68 Ω.

In order to gauge the kinetics of the process the electrochemical response 0.15 mM progesterone at CNS/CFP with varying scan rates from 0.01 to 0.1 V/s in PBS (pH 7.0) was recorded. The plausible mechanism of the proposed work is depicted below in Fig. 10. The applicability of the proposed method was evaluated in pharmaceutical progesterone injections, human blood serum and cow milk samples.

5.5 Detection of Hydrogen Peroxide Using Okra Based Porous Carbons

Okra (*Abelmoschus esculentus),* is a widely consumed vegetable in the subtropical and tropical regions as it possess excellent palatability [55]. Various studies have been reported which utilizes green synthesis to fabricate heteroatoms doped porous carbon as it is being environmentally benign but also remarkably enhances their performance [56, 57]. However, nitrogen and phosphorous atoms were additionally introduced in these works using different reagents. Sen Liu et. al., was successful in engineering one such heteroatom material via thermal treatment of freeze dried okra without the utilization of any chemicals and creating nitrogen, phosphorous co-doped hierarchical micro/mesoporous (N,P-MMC) carbon material for electrochemical H_2O_2 sensing [58].

A black carbon residue was obtained as the freeze-dried okra was pyrolyzed at 800° C for 3 h. The elemental composition of N, P- MMC which consist of C, N, P and O elements was revealed using energy dispersive X-ray spectroscopy (EDX). The modified material was used for the electrochemical detection of H_2O_2 by drop casting the porous carbon dispersion on glassy carbon electrode (GCE) with the aid of an inert binder Nafion. Cyclic Voltammetric studies was carried out in 0.1 M PBS at pH 7.0 in the presence and absence of 1.0 mM $H_2O_{2.}$ A strong reduction peak at -0.60 V for N, P-MMC/GCE was observed after addition of 1 mM H_2O_2 for the electrochemical reduction of H_2O_2 which accounts for good electrochemical activity of N, P-MMC [58]. The TEM and SEM images represents that this carbon material consist of nanobelts and irregular micropaticles, which can be credited to the various parts of okra.

Furthermore, using amperometric studies, the response of H_2O_2 at N, P-MMC/GCE was carried out in a N_2-saturated 0.1 M PBS (pH 7.0) at the applied potential of -0.60 V in the presence of H_2O_2. The electrochemical parameters such as linear detection range and detection limit was found to be from 0.1 to 10 and 6.8 μM respectively [58]. Additionally, anti-interference study was also carried out to confirm the strong selectivity and electrochemical catalytic activity of N, P-MMC. One can conclude that, the incorporation of such heteroatoms has enhanced the conductivity in comparison with the bare mesoporous carbon material. This particular work highlights an effective method for the synthesis of heteroatom doped porous carbon using vegetable fibers.

5.6 Detection of Heavy Metal (Lead) Using Wax Gourd Based Porous Carbons

There has been a desire to synthesize activated carbon framework from vegetable fibers as they surpass the requirement of multiple synthesis methods and tedious instrumental set-up. The fast-growing, ubiquitous and long-season vegetable, wax gourd (*Benincasa hispida*) is widely grown in most of the Asian countries [59]. The wax gourd has made its way in the application of electrochemical sensing of toxic heavy metals specifically lead (Pb). Trace amounts of metal ions like manganese, iron, copper, zinc, and selenium which are also known as heavy metals are highly significant for the metabolism of the living organisms [60]. However, exposure to other heavy metals like lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), and antimony (Sb) can be a serious threat to the environment. It is highly dangerous because they tend to bio accumulate and can affect the central nervous system, skin, kidneys, bones, and teeth [61]. Hence, detection of these heavy metals is imperative to save the human race [62].

Cuixing Xu et al. [63] developed the worm-like nitrogen-doped-carbon framework (WNCF) using natural wax gourd as the main carbon precursor and milk as the nitrogen precursor Fig. 11. The WNCF was utilized to design a highly sensitive

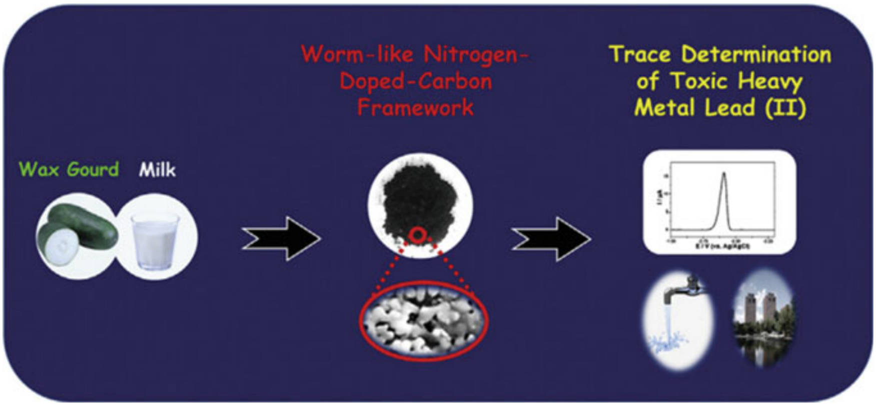

Fig. 11 A graphical representation for the detection of toxic heavy metal lead utilizing wax gourd derived carbon framework Ref. [63]

electrochemical sensor for the trace determination of toxic heavy metal Pb^{2+} by the DPV. Certain key factors including calcination temperature of WNCF, pH of the buffer solution, concentration of bismuth (Bi^{3+}), deposition potential and time were optimized for the analysis of Pb^{2+}. The electrochemical parameters of different electrodes were investigated in 10 mM $K_3Fe(CN)_6$ containing 0.1 M KCl by CV. A well-defined CV curve with both anodic and cathodic peaks was observed at bare GCE (Fig. 12 a).

However, compared to bare GCE, higher peaks currents were obtained at the modified electrodes. Among them, the nitrogen doped electrode exhibited more favorable electrocatalytic activity with high peak current because the nitrogen doping in the WNCF is capable of facilitating electron transfer [64–66]. The improved electron-transfer property of modified GCE was further proved by electrochemical impedance spectroscopy (EIS) analysis [63].

Table 1 summarizes the determination of various analytes at different vegetable fiber derived carbon modified electrodes.Under the optimum experimental condition, the finally modified GCE displayed a wide linear range from 0.5 to 100 mg L^{-1} and a low detection limit of 0.2 mM (S/N = 3) for detecting Pb^{2+}. This green and cost-effective proposed method was used to detect Pb^{2+} in different tap water and lake water samples. The detection of Pb^{2+} in real samples of tap water and lake water were achieved to evaluate the practical application of modified GCE by using the standard addition method [63]. The DPV curves of the samples with different spiked Pb^{2+} concentrations of 0, 10, 20 and 30 mg L^{-1} A is depicted Fig. 12b and c.

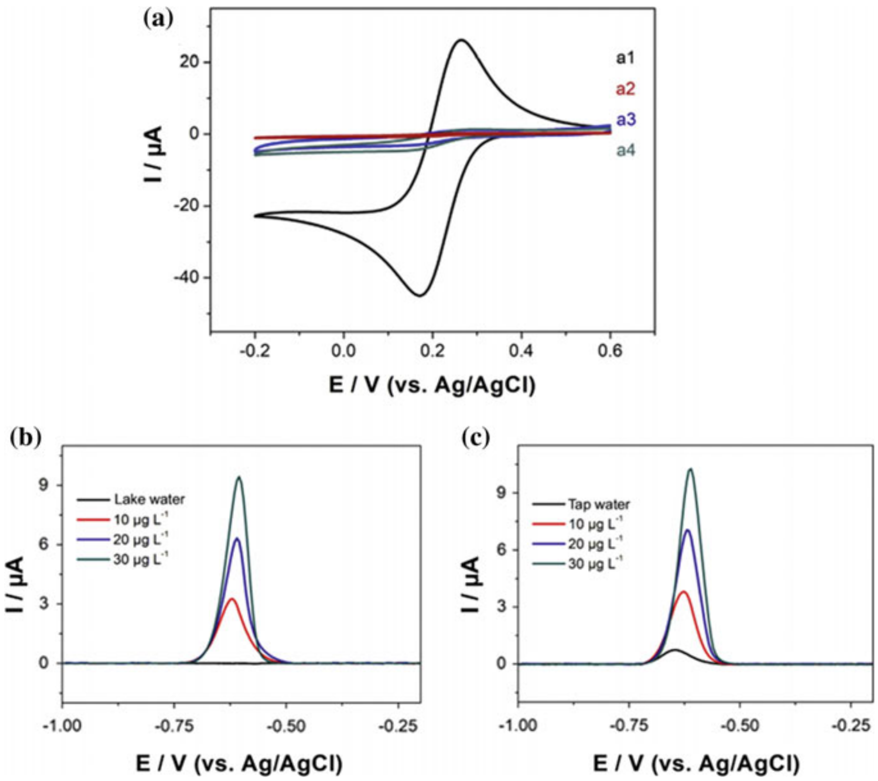

Fig. 12 **a** CV curves of GCE (a1), Nafion/GCE (a2), Nafion-WCF/GCE (a3) and Nafion-WNCF/GCE (a4) in 10 mM $K_3Fe(CN)_6$ containing 0.1 M KCl with the scan rate of 10 mV s^{-1}. **b** and**c** DPV responses for Pb^{2+} detection in lake water and tap water by using standard addition method at finally modified electrode respectively Ref. [63]

6 Conclusion and Future Trends

This work enlightens the reader to a whole new realm of biomass material obtained from vegetable fibers and how these serve as an excellent platform for electrochemical sensing. This is mainly attributed to its large surface area; it is very evident from of the works described in the chapter how the surface area of the material employed as a working electrode had a direct correlation to the electrode analyte interaction. Being a potential candidate as a noble material, it has unleashed its unlimited opportunity in the area of electro sensing, thereby nudging the researchers and the scientists to exploit their usage. These carbon nanoparticles have been utilized by the researchers effectively for the determination of various biomolecules mainly due to it sensitivity, avoidance of the fouling effect, and better peak resolution. However, one set back which is worth mentioning is that no reports has been found on simultaneous determination of a mixture of analytes threading a path for a novel method for the fabrication

Table 1 Comparison of the electrochemical measurements obtained from diverse vegetable fiber derived modified working electrodes

Vegetable fiber	Electrode material	Analyte	Linear range (μM)	Limit (μM)	Sensitivity μA μM^{-1} cm^{-2})	Ref
Banana stem	HAC	Nitrite	3–90	0.13	–	[67]
Pumpkin stem	AC	AA DA UA	– – –	2.3 0.03 0.51	7.6 6.3 6.1	[51]
Peanut shell	P-AC/AuNPs/GCE	Rutin	5 nm–1 μM	2 nm	–	[53]
Onion peel	CNS/CFP	Progesterone	39.39×10^{-5} -25.0×10^{-5}	$1.2*10^{-5}$	19,590	[56]
Okra	N,P-MMC	Hydrogen peroxide	$100–10^{4}$ $20 \times 10^{3}–200 \times 10^{3}$	6.8	–	[60]
Wax gourd	WNCF	Heavy metal (Pb)	0.5–100	0.2	–	[65]

of carbon nanoparticles-modified electrodes to serve this purpose. In spite of this we can anticipate them to emerge as premier electrode material mainly because of its biocompatibility, wide potential window, its abundance on the planet earth, large surface area and its interaction with several analytes.

However, there are a few hurdles that should be overcome for effective usage vegetable fiber derived carbon nanoparticles as working electrode material. Also, the synthesis of carbon material, the size and uniformity should be controlled in order to obtain reproducible results which are top notch priorities while designing a sensor. The modification of electrodes with carbon nanomaterials is undoubtedly a herculean task. Though drop cast electrodes show superior electro catalytic activity and have low detection limits toward various analytes and biomolecules, the reproducibility and the stability of the electrode still faces challenges which needs to be looked upon.

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Vegetable Fiber Pre-tensioning Influence on the Composites

Mahesh M. Hombalmath, Arun Y. Patil, Anirudh Kohli, and Anish Khan

1 Introduction

In the present-day scenarios, most of the time a single material cannot fulfill the demands that are required for the particular application [1]. The single material may not be physically or chemically stable for that particular application [2]. To overcome this, different materials are combined together in order to enhance their properties to make suitable for an application. Considering the Composite materials wherein two or more different materials in various forms are combined together, another important aspect comes into picture i.e. the biodegradability of the material [3]. The non-biodegradable materials pollute environment in various ways wherein the main concern is the amount of waste that is being deployed in the environment since they do not degrade to the soonest [4]. The waste dumped also includes organic waste which is biodegradable and is available in very large amounts across the globe [5]. The food waste which is a type of organic waste can be biologically treated and then used for experimentation purposes [6]. But when considered, in major of the applications non-biode802gradable materials are preferred over biodegradable materials in concerned with their strength and other factors [7]. To satisfy the biodegradability and the strength or physical properties bio-composite materials are developed for wide range of applications [8]. One advantage can be achieved from bio composites is that they can have high strength to weight ratio and hence can be used in automotive, aerospace industries [9].

M. M. Hombalmath · A. Y. Patil (✉) · A. Kohli
School of Mechanical Engineering, KLE Technological University, Vidya Nagar, Hubballi 580031, India

A. Khan
Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_6

In composites wide range of reinforcements can be added to the matrix to get suitable results. Fibers are classified into two types namely natural and synthetic [10]. Natural fibers can be extracted from either plants or animals. Synthetic fibers include glass, nylon etc. [11]. Here, natural fiber reinforced polymer matrix composites are taken into consideration [12]. A certain polymer will be embedded with the natural fibers. The natural fibers can be placed in the matrix in the form of long fibers, short fibers and particulate fibers [13]. In order to yield better results the natural fibers are placed in the form of long fibers. The cost involved in manufacturing these fiber reinforced composites is usually on the lower side [14]. It has been studied that pre-tensioning of the fibers will lead to better results than without pre-tensioning in the fiber reinforced composites [15]. In pre-tensioning the fibers are initially subjected to a certain value of tensile load and then is taken into manufacturing process [16–18]. However, in this case the fibers are not subjected to pre-tensioning. This study involves formation of a fiber reinforced composite and subjecting the composite specimen to various tests like tensile, compressive and flexural test.

2 Materials and Methods

2.1 Materials

Natural fibers embedded in the polymer matrix–lemon peel, onion peel and potato peel. These are the organic waste and are available abundantly. The natural fibers are embedded into the polymer matrix in three different volume fractions i.e. 10, 20 and 30%. Polylactic acid (PLA), a biopolymer opted as substrate. PLA is procured from Nature works, Chennai unit (A subsidiary of USA).

Outermost peels of onion, potato and lemon were extracted from respective fresh vegetables. These fibres subjected to 24 h natural sun shine to remove moisture content and were ground to make fine particles. After crushing to a 300-micron size particle, sieved for exact shape and size to maintain uniformity across the particles. The sieved cluster of raw material tested for their constituents at ESSAR Laboratories, Hubballi. The composition details were illustrated in Table 1.

The material properties of Polylactic acid shown in Table 2.

2.2 Fabrication of Composites

Hand lay-up method preferred to develop a bio-polymer based composites. Six specimens of bio-composites fabricated with reinforcement of fillers in a range of 10–30% in steps of 10%. The biopolymer composites dried for 24 h at ambient temperature. Coupons of ASTM dimensions developed for generic mechanical testing properties and measurements were carried out to make uniformity and dimensional stability

Table 1 Chemical composition of potato, onion and lemon filler particles [19, 20]

Sl. No.	Parameter	Unit	Potato fibre	Onion fibre	Lemon fibre
1	Moisture	%	4.26	4.81	7.13
2	Total ash	%	5.34	6.5	6.23
3	Crude fibre	%	33.82	32	33.15
4	Cellulose	%	42.60	41.54	41.8
5	Specific gravity	–	1.075	0.847	0.781
6	Lignin	%	44.13	43.11	43.51
7	pH	–	6.9	6.6	6.8

Table 2 Material properties of constituents [19, 20]

Material	Density (g/cm^3)	Elastic modulus (GPa)	Poisson's ratio
PLA	1.25	3	0.27
Lemon peel	0.7	1.2	0.18
Onion peel	0.847	9.71	0.25
Potato peel	1.075	0.2	0.26

Tensile Test Values (Load Applied = 1000 N):

among the samples. The composites fabricated using each fibre is shown in Fig. 1 along with sample of lemon.

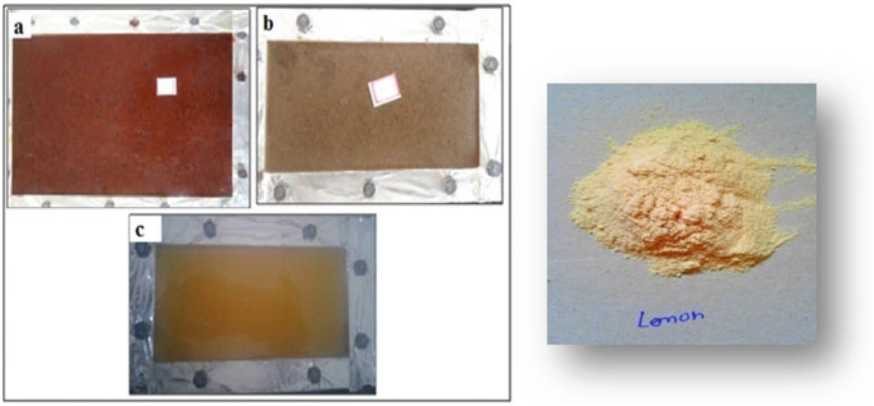


Fig. 1 Mould with composites using fillers of **a** onion/epoxy **b** potato/epoxy **c** carrot/epoxy composites **d** lemon [19, 20]

2.3 Physical Testing

Density Test

The density test of the coupons carried out using distilled water according to Archimedes principle and ASTM D792**.** The actual density of each specimen is measured by using cantilever set up and weighing machine [19].

Density is determined by using the Formula,

$$\rho = \frac{W_a}{W_a - W_w} \tag{1}$$

where,
ρ = actual density of specimen (g/cm^3).
W_a = weight of specimen in air (gms).
W_w = weight of specimen in water (gms).

Water Absorption Test

Water absorption is carried out for 11 days and the specimens under ASTM D5229 [19].

2.4 Mechanical Testing

Tensile Test

Tensile test is executed with Universal Testing Machine (UTM) by Enkay Enterprises, Bangalore of capacity 10Tonne. The coupons developed under ASTM D-3039. The coupons built with size 250× 25× 3 mm. An uni-axial load is applied at one end and other end is constrained with knurled gripper [19].

Flexural Test

The flexural test carried out with a machine as shown in Fig. 2 for 3-point bending test. The specimens followed with ASTM D-7264. The specimen with 154× 13× 3 mm and the support span of 100 mm and crosshead speed of 3 mm/min were fixed [19].

Hardness Test

Hardness test executed with Rockwell Hardness Tester made from Saroj Udyog Pvt. Ltd., Bangalore as shown in Fig. 3. The steel ball indenter of diameter 1/16″. The coupon prepared as per ASTM D785. The specimen is placed on the horizontal surface and a load of 60 kg is applied for a dwell time of 15 s on the each specimen and the hardness value was recorded [20].

Fig. 2 Flexural test performed on the specimen

Fig. 3 Rockwell hardness tester

Scanning Electron Microscopy

The micro study of fractured surfaces of tensile tested specimens carried out with ZEISS Supra Scanning Electron Microscope (SEM) having accelerating voltage of 2 kV. Six coupons of 10% volume fraction of natural fibre reinforced composites considered for SEM analysis. The specifications of coupons built with 10 × 10×

2.5 mm. The coupons coated with gold palladium for electrical conductivity as PLA is a insulator [19].

3 Results and Discussions

This section presents the results obtained on the testing of the different bio-composites developed using varied filler materials.

3.1 Density

The density of the onion/epoxy, potato/epoxy and carrot/epoxy composites were measured using Archimedes principle and is shown in Table 3. From the Table it follows that density decreases with increase in fibre loading in all the composites developed [19].

The density is determined using Eq. 2,

$$\rho_{onion/epoxy} = \frac{8.2}{371.6 - 364.3} = 1.138\ \text{g/cm}^3 \tag{2}$$

Table 3 Density of onion/epoxy, potato/epoxy and carrot/epoxy composites [19, 20]

Sl. No.	Composite	%NF	Density (g/cm^3)
1	Onion/Epoxy	10	1.138
		20	1.128
		30	1.04
2	Potato/Epoxy	10	1.153
		20	1.149
		30	1.139
3	Carrot/Epoxy	10	1.121
		20	1.08
		30	1.039
4	Epoxy resin	100%	1.3

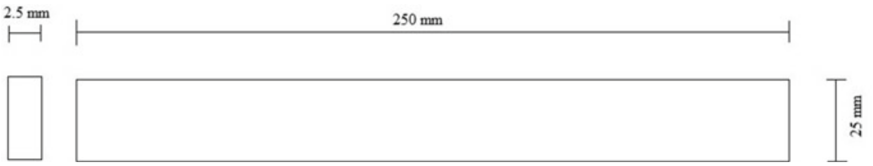


Fig. 4 Tensile test specimen dimensions as per ASTM D3039

3.2 Tensile Test

The flat specimens were used for tensile testing. The specimen dimensions and the testing procedure are as per the ASTM D3039 [19]. The dimensions for the tensile specimen are as below:

Overall length	250 mm
Gauge lengt	138 mm
Width	25 mm
Thickness	2.5 mm

The tensile test was conducted using Universal Testing Machine (UTM). The test was carried out at the cross head speed of 3 mm/min. Four samples were tested for each natural fibre and the average value was taken. Figure 4 shows the specimen dimensions as per ASTM, specimen images and the machine used for the testing.

3.3 Flexural Test

The UTM was used to check the flexural strength of the specimens. The three-point bending test was carried out with the help of UTM as per ASTM D7264 [20]. The specimen dimensions are as given below:

Overall length	154 mm
Gauge length	100 mm
Width	13 mm
Thickness	4 mm

The test was carried out at the cross head speed of 3 mm/min. Four samples were tested for each natural fibre and the average value was taken. In three point bending test, the flexural stress is calculated using the Eq. 3

$$\sigma = \frac{3PL}{2bh^2} \tag{3}$$

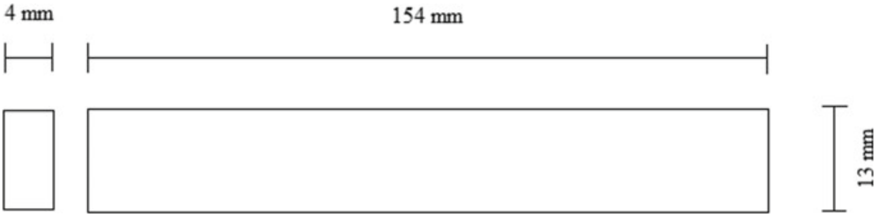


Fig. 5 Flexural test specimen dimensions as per ASTM D7264

Here, P is load, L is gauge length, b is width and h is the thickness of the specimen.

The specimen dimension as per ASTM, specimen images and the loading arrangement on UTM is as shown in Figs. 5.

4 Simulations with ANSYS Workbench

The simulation packages have come of age in recent days to reduce the error percentage with respect to experimental or analytical calculations. In today's environment, Simulation is pick of the tools for Industry Internet of Things(IIOT) [21, 22].

4.1 Geometric Modeling

As per ASTM standard for tensile and flexural strength the solid model developed in design modeler of ANSYS 18.2 Version [23]. The geometrical model created with layer by layer based on the volume fraction of the model [24]. One typical case is for 10% inclusion of vegetable peels in poly lactic acid. Vegetable peel is sandwiched between two layers of polylactic acid as shown in Fig. 6.

4.2 Mesh Generation

The coupons meshed with Hexa dominant element with second order mid side node kept condition having 20 node [25]. The specimen meshed with 2015 nodes and 208 elements as shown in Fig. 7.

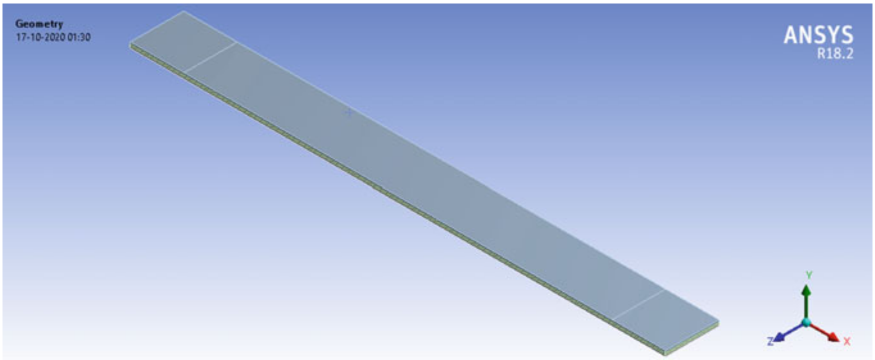
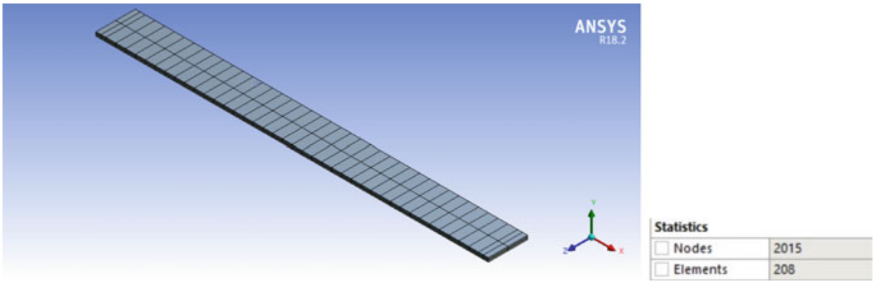


Fig. 6 Tensile test specimen



Statistics

☐ Nodes	2015
☐ Elements	208

Fig. 7 Tensile Test specimen with mesh generation and Element and node statistics [26]

4.3 Loads and Boundary Conditions

Experimental set up conditions were matched similar and one end of specimen fixed with all six degrees of freedom and other side is scoped with force of 1000 N. Figures 8 and 9 discuss on the loads and boundary conditions. The test carried out with uni-axial loading one end fixed with micro gripper [27].

4.4 Tensile Strength Test

The specimens built using lemon peel, onion peel and potato peels in range of 10–30% inclusion in steps of 10 with PLA.

Case-1:

a. **PLA_LemonPeel_10%**
   From Fig. 10 , defines about how the stress and strain carried out [28].
b. **PLA_LemonPeel_20%**

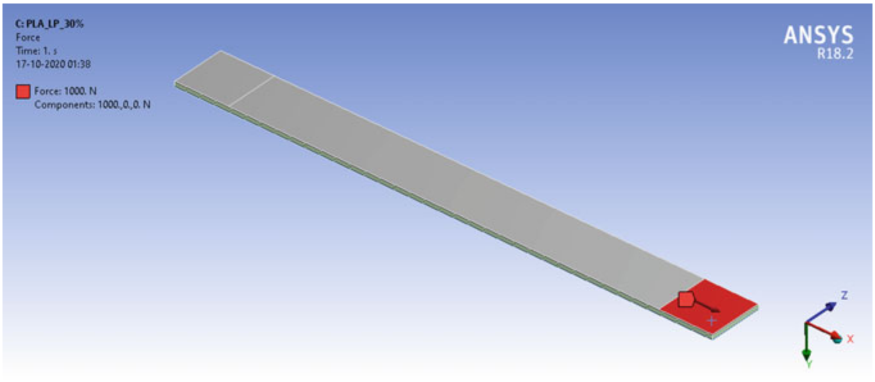


Fig. 8 Application of load at free end

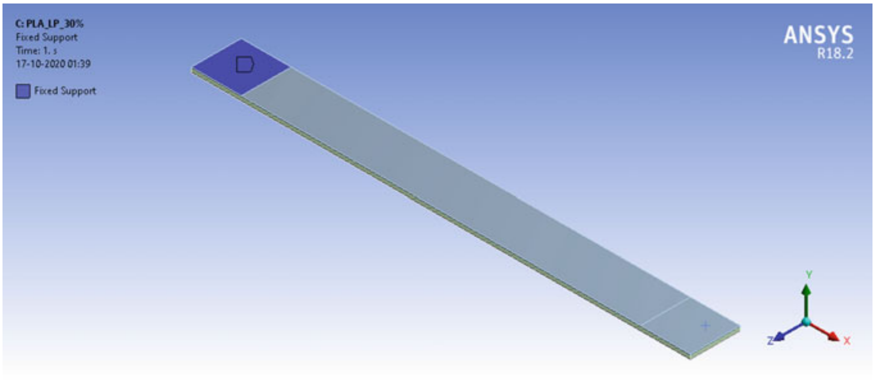


Fig. 9 Fixed support

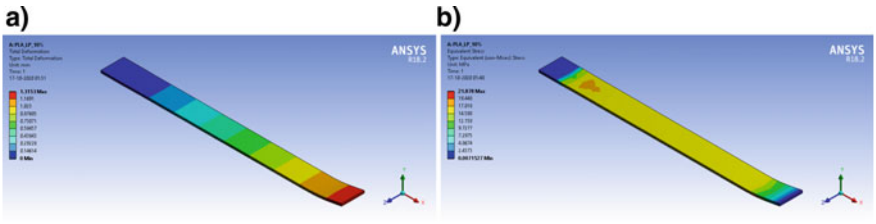


Fig. 10 **a** Von mises stress. **b** Total deformation

From Fig. 11, defines about how the stress and strain carried out [28].

c. **PLA_LemonPeel_30%**

From Fig. 12, defines about how the stress and strain carried out [28].

d. **PLA_OnionPeel_10%**

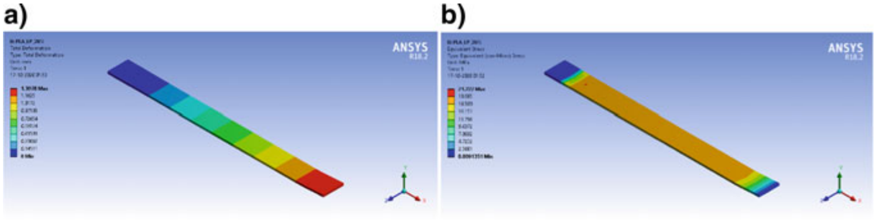


Fig. 11 **a** Von mises stress. **b** Total deformation.

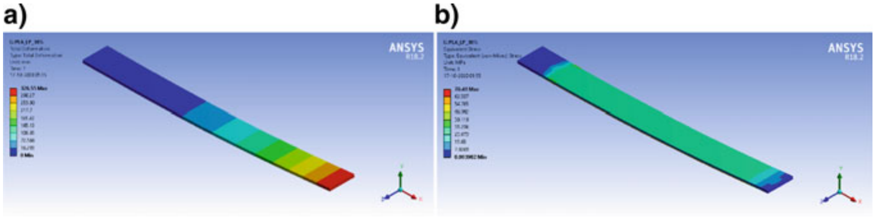


Fig. 12 **a** Von mises stress. **b** Total deformation

From Fig. 13, defines about how the stress and strain carried out [28].

e. **PLA_OnionPeel_20%**

From Fig. 14, defines about how the stress and strain carried out [28].

f. **PLA_OnionPeel_30%**

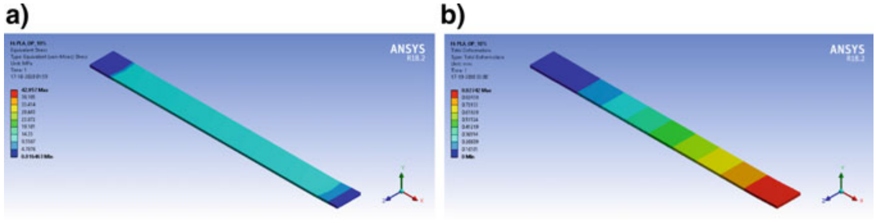


Fig. 13 **a** Von mises stress. **b** Total deformation

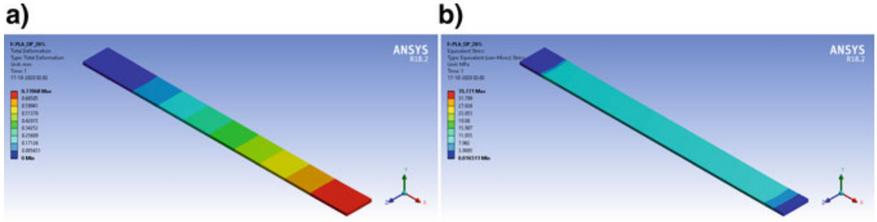


Fig. 14 **a** Von mises stress. **b** Total deformation

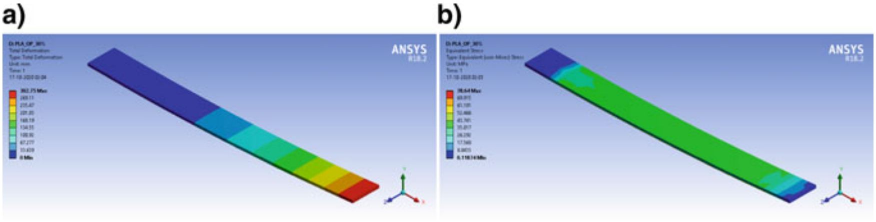


Fig. 15 **a** Von mises stress. **b** Total deformation

From Fig. 15, defines about how the stress and strain carried out [28].

g. **PLA_PotatoPeel_10%**

From Fig. 16, defines about how the stress and strain carried out [28].

h. **PLA_PotatoPeel_20%**

From Fig. 17, defines about how the stress and strain carried out [28].

i. **PLA_PotatoPeel_30%**

From Fig. 18, defines about how the stress and strain carried out [28].

Case-2:Tensile Test (Fibre Pretension)

Geometric model built with continuous fibers embedded in the substrate subjected to prior pretension as shown in Fig. 19 [29].

Figure 20 infers tetrahedron mesh generation with Solid 187, 10-noded second order element [30]. The entire model turns out with 201,500 nodes and 60,816 elements.

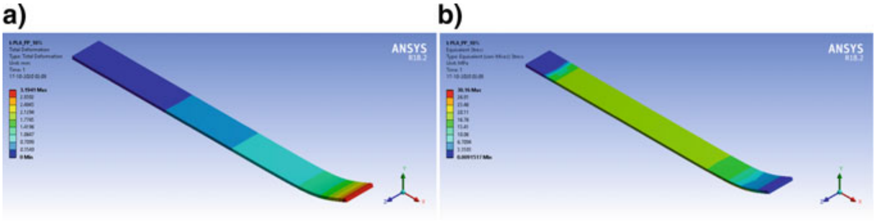


Fig. 16 **a** Von mises stress. **b** Total deformation

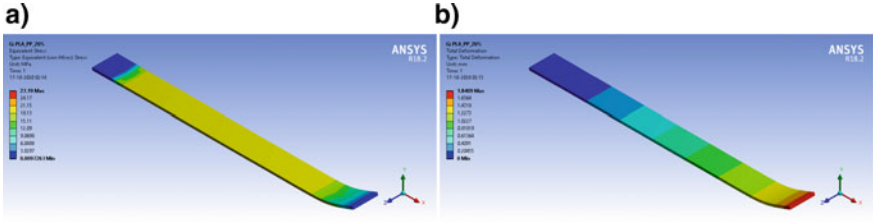


Fig. 17 **a** Von mises stress. **b** Total deformation

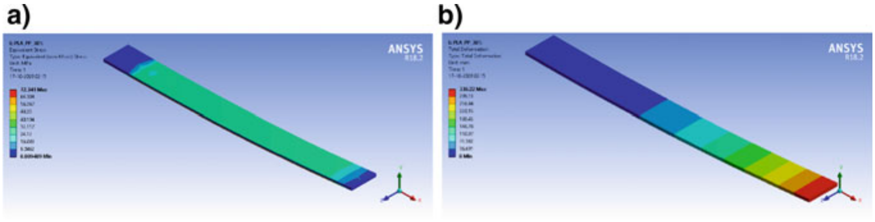


Fig. 18 **a** Von mises stress. **b** Total deformation

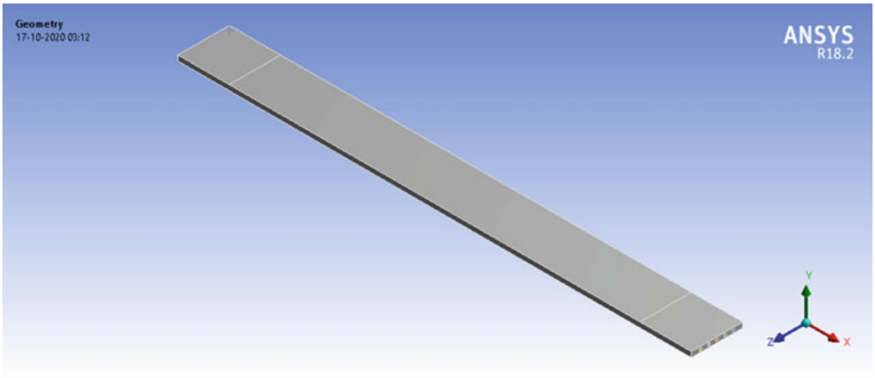
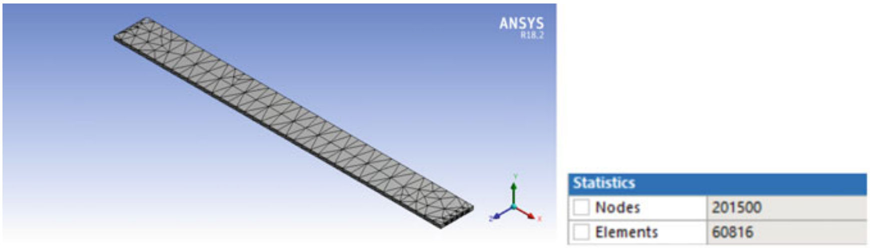


Fig. 19 Geometry model



Statistics	
☐ Nodes	201500
☐ Elements	60816

Fig. 20 Mesh generation

Figure 21 illustrate the boundary conditions applied to the coupon with all six degrees of freedom constrained.

Figure 22 depicts the pre-tension applied to the continuous fibers formed as strands and embedded in the substrate using Vacuum Assisted Resin Transfer Molding(VARTM) [21].

Figure 23 illustrate the strands subjected to pre-tension [22]. The pre-tension behavior will give provision for higher elongation and strength in comparison to earlier.

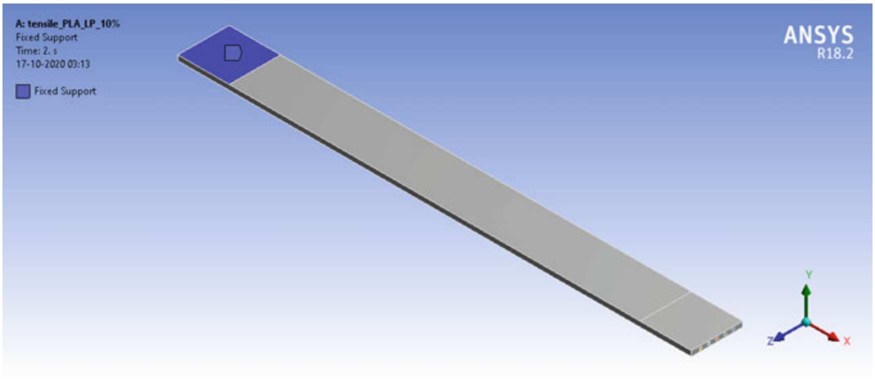


Fig. 21 Boundary condition

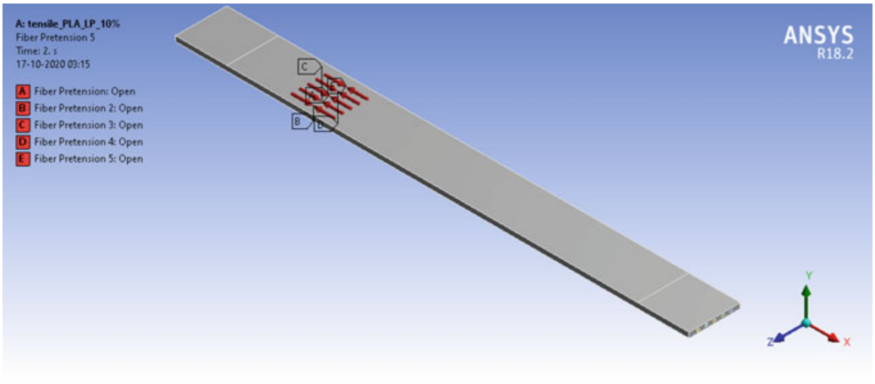


Fig. 22 Pre-tension behavior

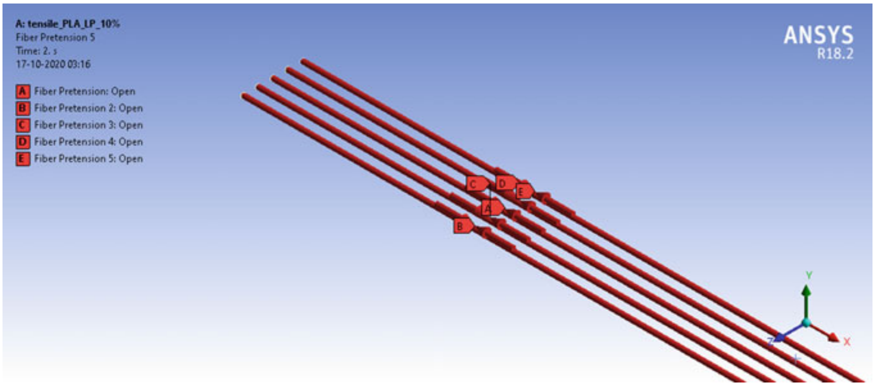


Fig. 23 Pre-tension of strands

From Fig. 24 it is clear that the same amount of load applied for the tensile strength test resulting in the stress and deformation results.

Further the results for lemon peel case were considered with respect to peers. The 10% peel results shown in Fig. 25.

a. **PLA_LemonPeel_10%**

b. **PLA_OnionPeel_10%**

Figure 26 illustrate the onion peel inclusion in PLA with 10 percentage result in stress and deformation behavior.

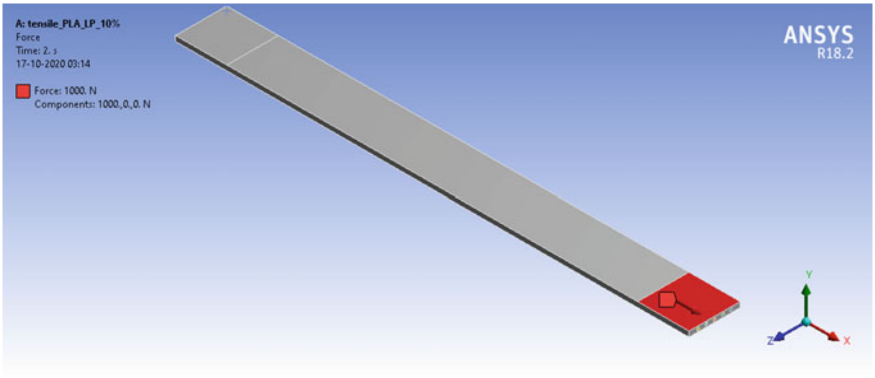


Fig. 24 Force applied on the coupon

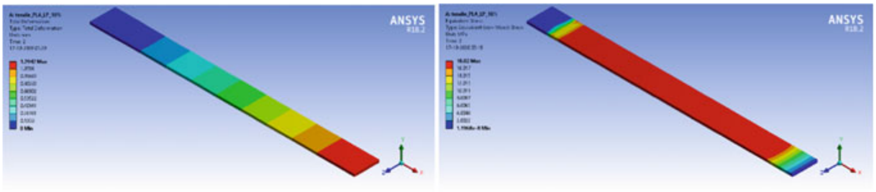


Fig. 25 Deformation and stress

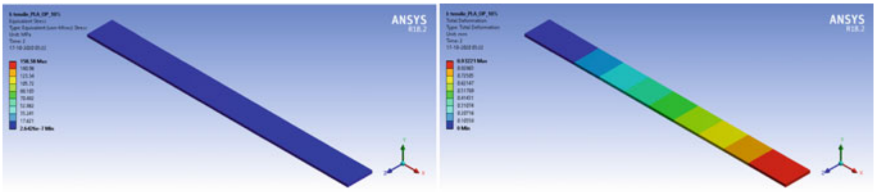


Fig. 26 Stress and deformation

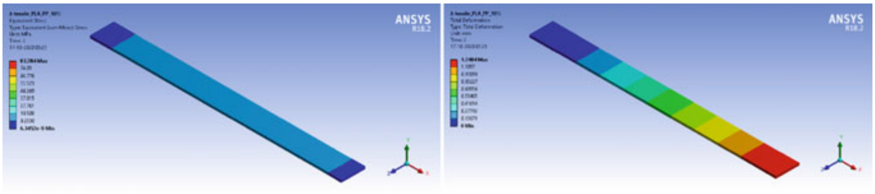


Fig. 27 Stress and deformation

c. **PLA_PotatoPeel_10%**

Figure 27 illustrate the potato peel subjected for testing.

4.5 *Flexural Strength Test*

Case-1: Laminated

The coupons built with laminated layer by layer method. Figure 28 depicts the vegetable peels sandwiched between top and bottom substrate as PLA.

However, mesh generation is carried out with Hexa-dominant 20 noded mid side node kept condition. Solid 186 is used for element selection under the ANSYS library. The details were shared along with element and node numbers in Fig. 29.

From Fig. 30 it can be infer that Three point bend test is applied with two roller supports, on which a coupon is mounted and a load in the form of roller applied on top at exactly midspan of the it. The details are as shown in Fig. 31 (Figs. 32, 33, 34, 35, 36, 37, 38, 39 and 40).

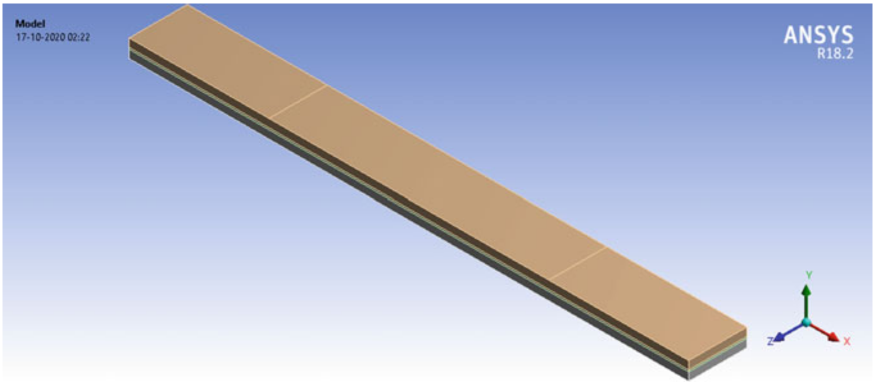
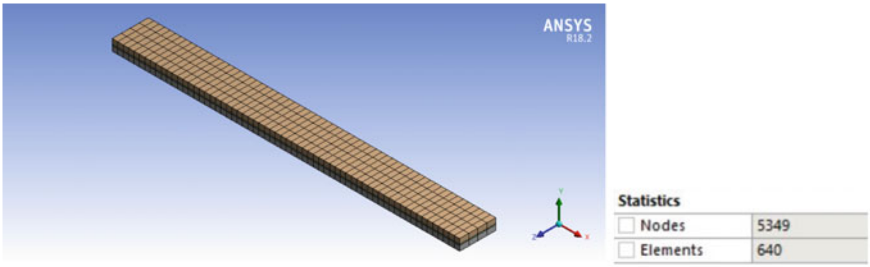


Fig. 28 Geometry model



Statistics

☐ Nodes	5349
☐ Elements	640

Fig. 29 Tensile test specimen with mesh generation and element and node statistics

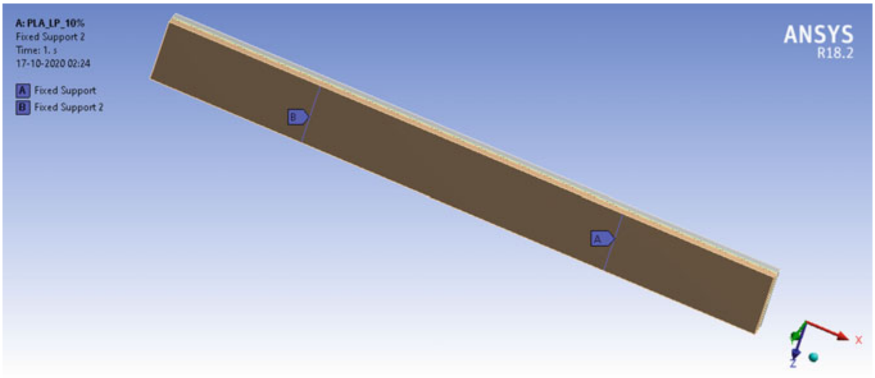


Fig. 30 Three point bend test simulation setup

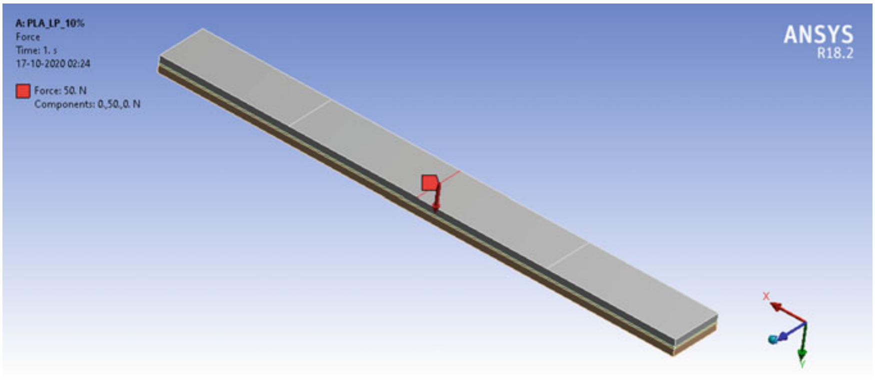


Fig. 31 Three point bend test simulation setup

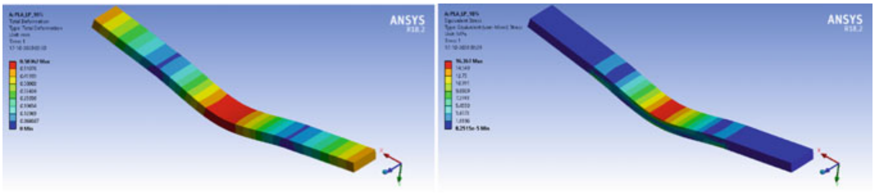


Fig. 32 PLA_LemonPeel_10%

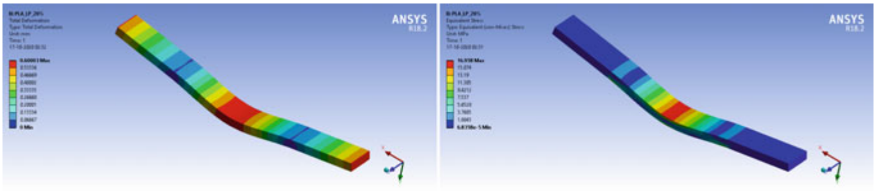


Fig. 33 PLA_LemonPeel_20%:

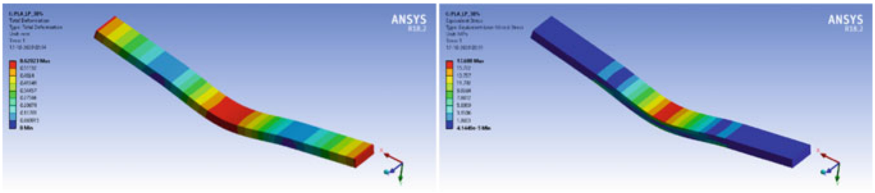


Fig. 34 PLA_LemonPeel_30%:

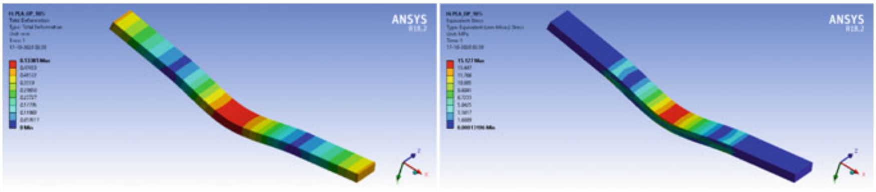


Fig. 35 PLA_OnionPeel_10%

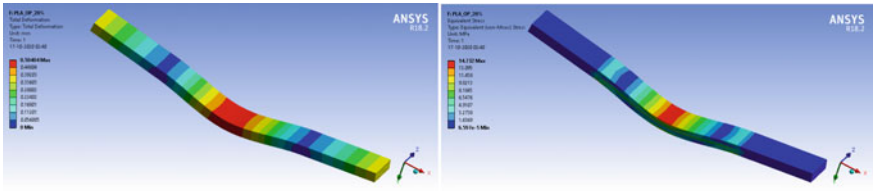


Fig. 36 PLA_OnionPeel_20%

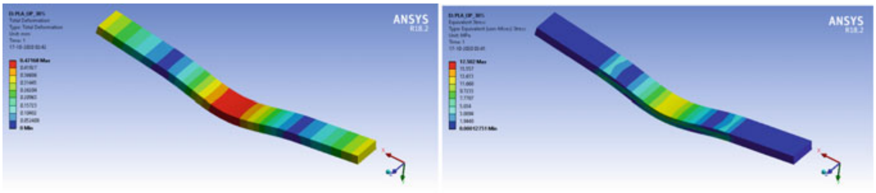


Fig. 37 PLA_OnionPeel_30%

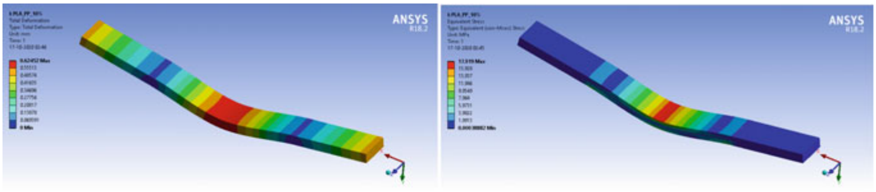


Fig. 38 PLA_PotatoPeel_10%

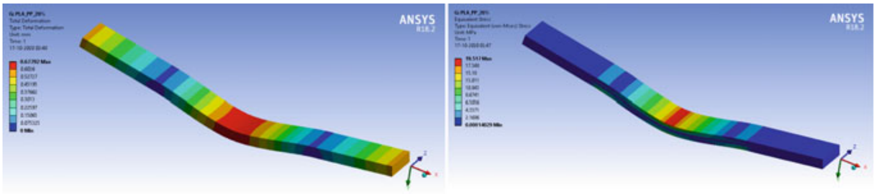


Fig. 39 PLA_PotatoPeel_20%:

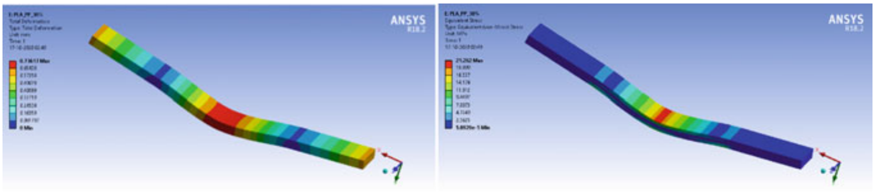


Fig. 40 PLA_PotatoPeel_30%:

Case-2: Fiber Pre-tension

Fiber pre-tension will yield better bonding along with volume shrinkage of PLA will result in reduction of overall dimension to cope up with this similar to thermo mechanically treated(TMT) rods these will also have pre-tension effect. The built model is shown in Fig. 41.

Figure 42 depicts the mesh generation of model with Hexa dominant second order polynomial Solid 186.

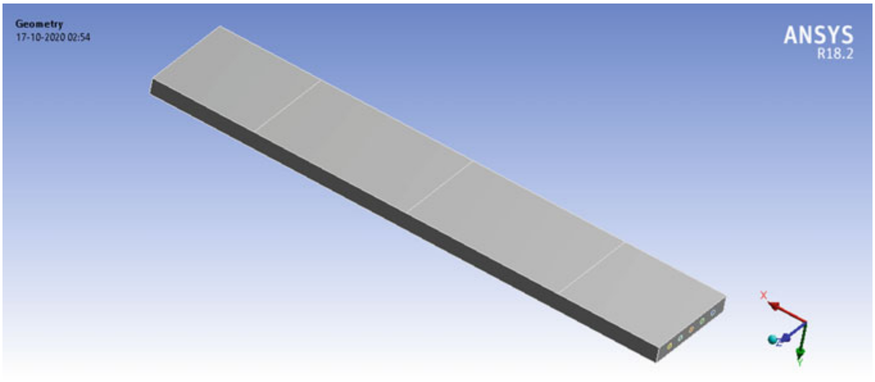
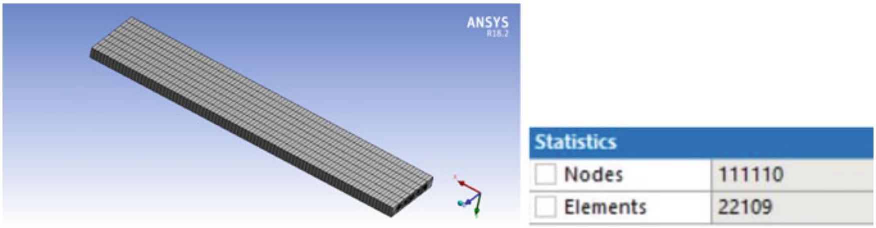


Fig. 41 Geometry model



Statistics	
☐ Nodes	111110
☐ Elements	22109

Fig. 42 Mesh generation [31]

Figure 43 illustrate the constrain location for coupon. Figures 44 and 45 infers pre-tension effect on the vegetable fibers under strand form.

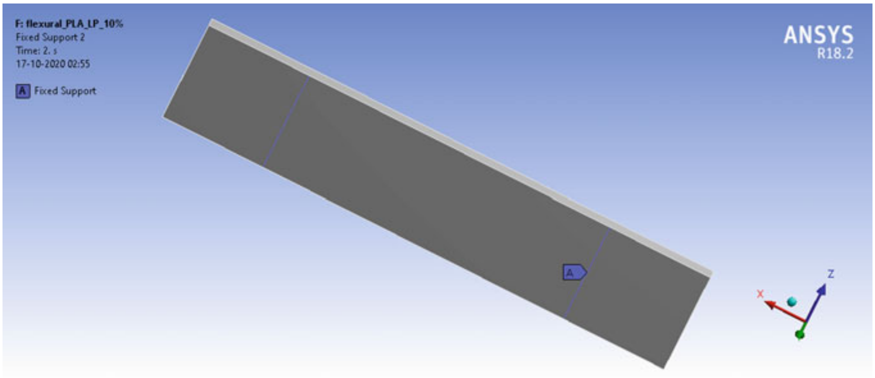
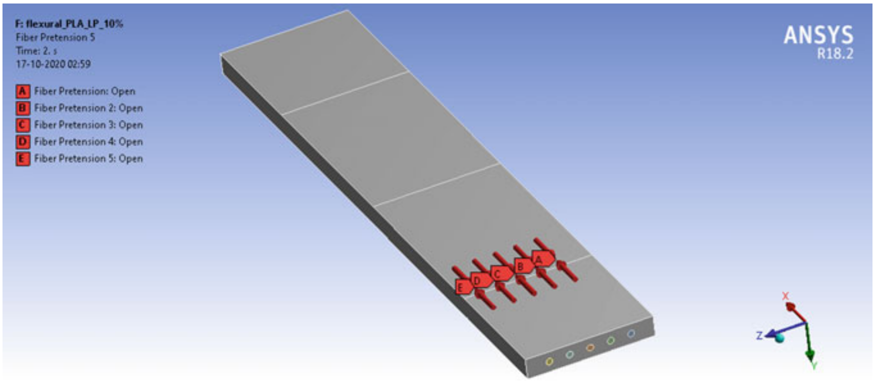


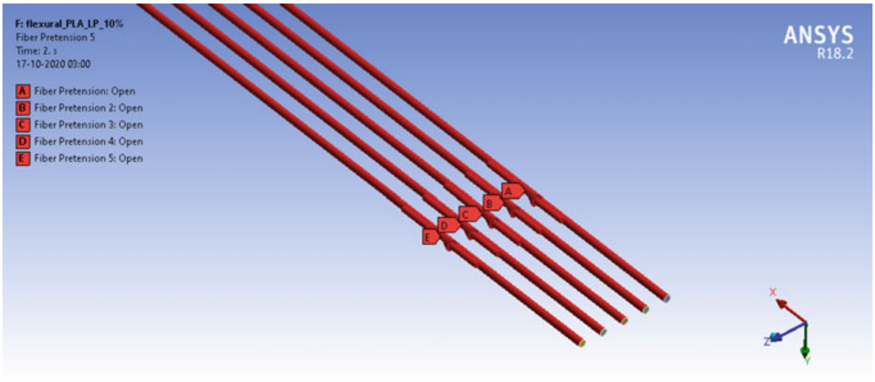
Fig. 43 Constrain in the form of boundary condition [31]



F: flexural_PLA_LP_10%
Fiber Pretension 5
Time: 2. s
17-10-2020 02:59

A Fiber Pretension: Open
B Fiber Pretension 2: Open
C Fiber Pretension 3: Open
D Fiber Pretension 4: Open
E Fiber Pretension 5: Open

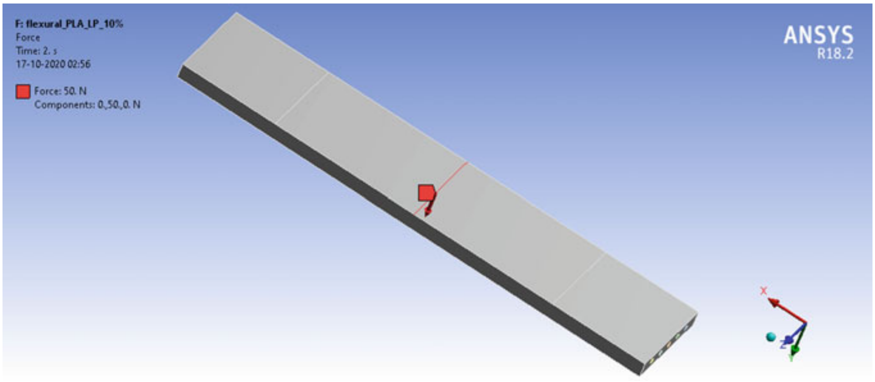
Fig. 44 Pre-tension [31]



F: flexural_PLA_LP_10%
Fiber Pretension 5
Time: 2. s
17-10-2020 03:00

A Fiber Pretension: Open
B Fiber Pretension 2: Open
C Fiber Pretension 3: Open
D Fiber Pretension 4: Open
E Fiber Pretension 5: Open

Fig. 45 Pre-tension strands



F: flexural_PLA_LP_10%
Force
Time: 2. s
17-10-2020 02:56

Force: 50. N
Components: 0.,50.,0. N

Fig. 46 Force acting at mid span

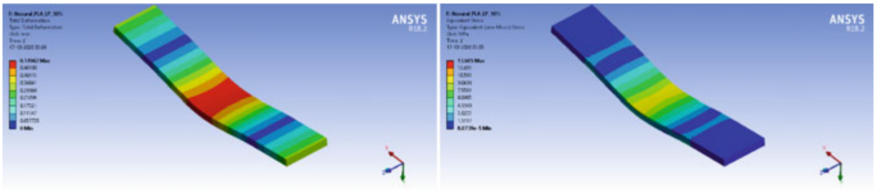


Fig. 47 PLA_LemonPeel_10%

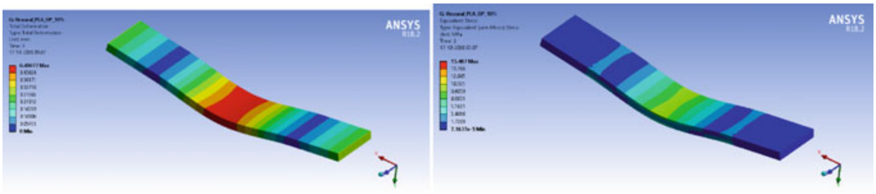


Fig. 48 PLA_OnionPeel_10%

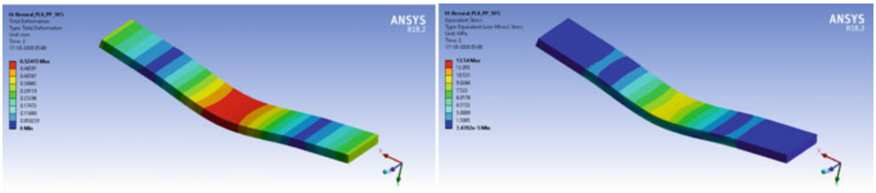


Fig. 49 PLA_PotatoPeel_10%

Figure 46 illustrate about the force acting at the mid span for the specimen. Figures 47, 48 and 49 shows the behavior of total deformation and stress for lemon, onion and potato peels respectively.

4.6 Comparative Study

The comparative study for tensile strength with laminated and pre-tension based conditions were discussed in Tables 4 and 5. Further, flexural strength related to laminated and pre-tension based conditions for bio composites discussed in Tables 6 and 7.

a. **Tensile Test (Fibre Pre-Tensioning) Values:**

(Load Applied = 1000 N).
Fibre Pre-Tension = 1000 N.

b. **Flexural Test Values (Load Applied = 50 N):**

Table 4 Comparative study for laminated composite specimen for tensile strength

Sl. No. Composite	NF%	Stress (MPa)	Deformation (MPa)
1. Lemon peel/PLA	10	21.878	1.3153
	20	21.222	1.3078
	30	70.41	326.55
2. Onion peel/PLA	10	42.957	0.92742
	20	35.771	0.77068
	30	78.64	302.75
3. Potato peel/PLA	10	30.16	3.1941
	20	27.19	1.8409
	30	72.341	330.22

Table 5 Comparative study for laminated composite specimen for pre-tension tensile strength

Sl.No. Composite	NF%	Stress (MPa)	Deformation (MPa)
1. Lemon peel/PLA	10	18.02	1.024
2. Onion peel/PLA	10	158.58	0.93221
3. Potato peel/PLA	10	83.284	1.2484

c. Flexural Test (Fibre Pre-Tensioning) Values:

(Load Applied = 50 N).
Fibre Pre-Tension = 1000 N.

Table 6 Comparative study for laminated composite specimen for flexural strength

Sl.No. Composite	NF%	Stress (MPa)	Deformation (MPa)
1. Lemon peel/PLA	10	16.367	0.58362
	20	16.958	0.60003
	30	17.688	0.62023
2. Onion peel/PLA	10	15.127	0.53385
	20	14.732	0.50404
	30	17.502	0.4718
3. Potato peel/PLA	10	17.919	0.62452
	20	19.517	0.67792
	30	21.262	0.73617

Table 7 Comparative study for laminated composite specimen for pre-tension tensile strength

Sl.No. Composite	NF%	Stress (MPa)	Deformation (MPa)
1. Lemon peel/PLA	10	13.605	0.51962
2. Onion peel/PLA	10	15.487	0.49077
3. Potato peel/PLA	10	13.54	0.52415

5 Conclusion

The exhaustive experimental and simulation work can be summarized into following conclusions

- The entire work focus on usage of waste kitchen peels into a fruitful product. The experimental tests conducted with epoxy were result in lower strength rate compare to PLA based bio composite along with that its eco environmental material compare to epoxy.
- Tensile strength with laminated condition for lemon peel at 20% inclusion gave comparatively better result of stress 21.22 MPa and deformation of 1.3 mm were as 24 MPa and deformation of 1.5 mm for epoxy resin.
- Flexural strength with laminated condition for lemon peel at 30% inclusion result in better values for PLA as substrate than epoxy with stress 17.68 MPa and deformation 0.62 mm were as 20.8 MPa and deformation of 0.81 mm for later condition.
- Pre-tension effect of lemon peel for 10% inclusion in PLA has resulted in stress value of 18.02 MPa in comparison to 21.87 MPa and deformation of 1.02–1.31 mm.
- Pre-tension has given additional bonding to the specimen and this is clearly resembled in the results as volume shrinkage of PLA once it solidifies it will have the effect on fiber strands as well.

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Improvement of Fiber-Matrix Adhesion of Vegetable Natural Fibers by Chemical Treatment

Fatima-Zahra Semlali Aouragh Hassani, Zineb Kassab, Mounir El Achaby, Rachid Bouhfid, and Abouelkacem Qaiss

1 Introduction

A composite is a heterogeneous material obtained by a combination of two or more materials with different chemical structures. These basic materials retain their intrinsic characteristics, but their combination gives rise to different properties. A composite consists mainly of a continuous phase called a matrix and a reinforcement which is used to improve or modify the properties of the matrix [1–3]. As mentioned before, fiber reinforcements have high strength and stiffness, but in the absence of a matrix, the structural potential of fiber bundles cannot be exploited in load sharing applications [4]. Combining fiber bundles with a matrix results in a material in which the fibers are the main load-bearing elements while the surrounding matrix maintains them in the desired position and orientation. In addition, the matrix acts as a charge transfer medium, protects the fibers against damage caused by the surrounding environment (temperature, humidity, etc.) and gives the composite its shape and surface appearance [1, 5, 6].

Most of the composites properties strongly depend on the type of interaction between groups or molecules which ensures their cohesion; several studies have demonstrated this dependence by studying the behavior of several composite materials with a polymeric matrix reinforced by different types of natural fibers. Scientific literature has raised a low affinity of these fibers with hydrophobic matrices which generates poor adhesion between the two materials. This interface problem

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F.-Z. Semlali Aouragh Hassani · R. Bouhfid · A. Qaiss (✉)
Composites and Nanocomposites Center, Moroccan Foundation for Advanced Science, Innovation and Research (MAScIR), Rabat, Morocco
e-mail: a.qaiss@mascir.com

Z. Kassab · M. El Achaby · A. Qaiss
Materials Science and Nano-engineering Department, Mohammed VI Polytechnic University, Ben Guerir, Morocco

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_7

can be overcome by chemical or mechanical treatment of the natural fiber. The main objective of this treatment is to replace the polar hydroxyl groups on the surface of cellulosic substrates by groups capable of strengthening interactions with generally hydrophobic polymeric matrices, and even allowing the preparation of composites based solely on cellulosic fibers (composites continuous) [7]. There are many ways of chemically modifying cellulosic fibers, namely acylation, etherification, grafting by copolymerization, alkali treatment, treatment with silane, treatment with isocyanates, etc. [8]. This chapter firstly presents the state of the art on plant fibers as well as the composite structure, details the importance of fibers chemical modification for the fiber-matrix adhesion improvement, and then depicts the effect of chemical treatment on the composites mechanical and thermal properties.

2 Vegetable Natural Fibers

Regardless of the anatomical variations specific to each species, plant fibers from multiple botanical sources share cellulose as a common component [9]. The fiber performance in a specific application depends on several factors such as: the chemical composition, the surface properties and the chemical treatment. These factors affect the fiber performance in a given application [9].

2.1 Description

Natural plant fibers are cell walls having a fibrillar structure, consisting essentially of cellulose, hemicellulose and lignin in addition to compounds in small proportions, namely waxes, lipids, minerals and water-soluble compounds [10]. The proportions of these different constituents depend greatly on the species, age and organs of the plant [11–13]. However, most of the vegetables properties are governed by the three main polymeric components (cellulose, hemicellulose and lignin) [14]. Taking into account these three main organic constituents, the plant fibers are therefore collectively referred to lignocellulosic fibers, lignocellulosic materials, or simply lignocellulose. Also, one of the great challenges in the industrial use of lignocellulosic materials is to understand the highly variable composition and the attributes resulting from differences between species, as well as the often considerable variation between individuals of a species and even within individual plants [9].

2.2 Classification

The classification of plant fibers is quite complex. According to the literature, vegetable fibers can be classified into three categories according to [15]:

- The origin of the fibers: stem (kenaf, jute, flax, ramie, etc.), leaves (sisal, abaca, grass straw, etc.), fruits (coconut) or seeds (cotton, kapok, etc.).
- The length of the fibers: it depends on the technological process used for its extraction. Most bast fibers and fibers from leaves, considered long fibers, have lengths greater than 120–150 mm. In contrast, fibers with a fiber length between 20 and 60 mm, for example cotton, are considered to be short-staple fibers.
- Functional criteria: (i) low stiffness fibers, generally derived from annual plants poor in lignin (cotton, hemp, jute, flax), are characterized by a soft feel; (ii) coarser fibers exhibiting greater torsional and bending stiffness, are harder and are characterized by a greater lignin content. Typical examples are wood, sisal and abaca.

Despite these justifications, the fiber classifications remain somewhat arbitrary although often are quite useful.

2.3 Chemical Composition and Structure

The chemical composition varies from one plant to another and in different parts of the same plant [9], depending on the degree of maturity of the plant [11, 12, 16], the geomorphology of the latter [12, 16] and the origin organ of the fiber. Also, the chemical composition as well as the fibers structure is quite complicated.

Plant fiber is a composite material designed by nature. Most, with the exception of cotton, are composed of cellulose, hemicellulose, lignin, waxes and some water soluble compounds, where cellulose, hemicellulose and lignin are the main constituents [17].

2.3.1 Cellulose

As early as 1838, Anselme Payen established that the main component of most plant fibers is characterized by a unique chemical structure called “cellulose". The macromolecular nature of cellulose was demonstrated around the 1930s. Subsequently, cellulose was shown to be a polymer of carbohydrate units [18, 19]. Cellulose is made up of D-anhydroglucose units linked together by β(I-4) bonds. However, the basic repeating unit of cellulose is the “cellobiose” dimer which comprises two glucose units linked by the β(I-4) bond [18, 19]. A typical cellulose structure is shown in Fig. 1.

The way in which glucose units are linked in the linear polymer determines the properties of cellulose [20]. Cellulose, which is made up of thousands of units of glucose, can stack to form crystalline forms with intramolecular hydrogen bonds providing a stable polymer with high tensile strength. Hydroxyl groups and their ability to form hydrogen bonds play a major role in the orientation of the crystal lattice and govern the physical properties of cellulose [20]. In addition to the ordered

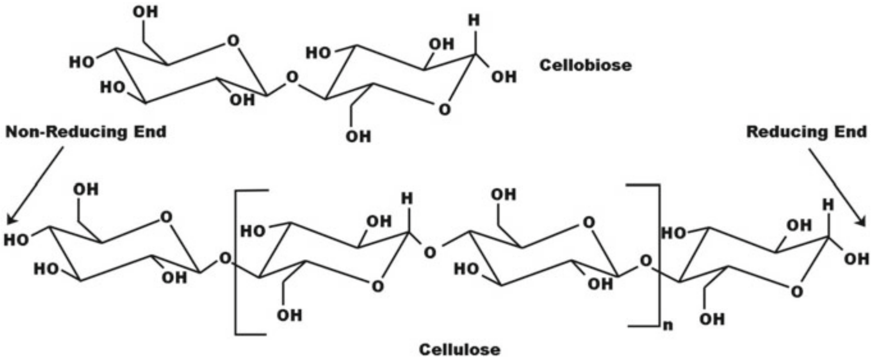


Fig. 1 Cellulose structure

or crystalline regions of cellulose, there are other less ordered regions, or amorphous regions. These differences can have a huge influence on the characteristics and functionality of the fiber [9, 20].

2.3.2 Hemicellulose

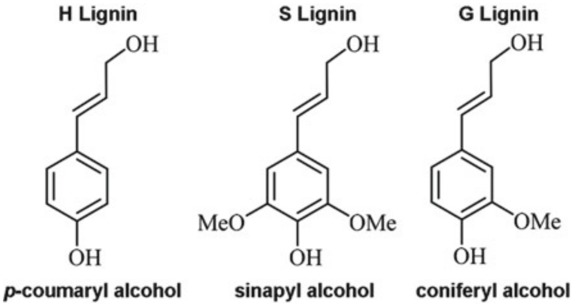
After cellulose, hemicellulose is considered to be the most abundant carbohydrate in the cell walls of plants. Hemicellulose is composed of an association of very heterogeneous groups of polysaccharides, differing in structure and composition according to their origins. Non-cellulosic polysaccharides such as glucans $(C_6H_{12}0_6)_n$, mannans $(C_6H_{12}0_6)_n$, galactans $(C_6H_{12}0_6)_n$, arabinans $(C_5H_{10}O_5)_n$ and xylans $(C_5H_{10}O_5)_n$ represent hemicellulose [20]. The non-linear hemicelluloses are associated with pectins, aromatic constituents and cellulose in plant cell walls [20]. They represent the support matrix for the cellulose microfibrils. Unlike cellulose, the hemicellulose chains are branched and much shorter (DP = 50–300) compared to cellulose [9, 21].

2.3.3 Lignin

Lignin is a complex three-dimensional copolymer made up of aromatic and aliphatic compounds with very high molecular weight. It is made up of three different units of the phenylopropane type, namely p-coumaryl, coniferyl and sinapyl alcohols (Fig. 2) [12, 20]. It is an amorphous and hydrophobic material in nature. Its chemistry has not yet been precisely established, but most of its functional groups and structural units of the macromolecule have been identified. It is characterized by high carbon content but low hydrogen content [9, 21].

Lignin confers strength and rigidity to cell walls in addition to protection against microbial pathogens. The content of lignin in plants is very varied as it often depends on the method of analysis. Lignins are intimately associated with hemicellulose and

Fig. 2 Elementary patterns of lignin



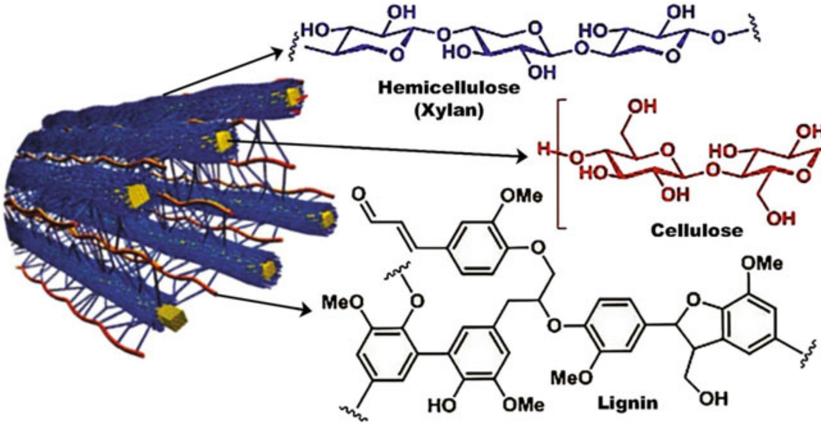


Fig. 3 Structure of lignocellulose

cellulose in the cell walls of plants (Fig. 3) [20]. It acts as an agent embedded in the cellulose/hemicellulose matrix, for this reason, lignin is often referred to the plant cell wall adhesive [17].

In addition to cellulose, hemicellulose and lignin, the cell walls of plants contain other organic molecules like proteins, tannins, pectins, waxes, aromatics and low molecular weight carbohydrates.

2.3.4 Extractables

These materials are considered non-structural, that is, although present within the cell wall, they do not form the basic structure of the wall like cellulose, hemicellulose and lignin. Nevertheless, they have a considerable effect on lignocellulosic materials. These naturally occurring chemicals can be removed or extracted from plant material using a relatively mild chemical treatment, as they are generally soluble in water and/or organic solvents, hence their name. The extractable composition varies depending on the species considered and influences the color and odor [9].

Table 1 Chemical composition of some vegetable fibers

Fibers	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Oil palm	14.3–65.2	12.5–38.7	17.3–26.5
Bamboo	20.3–61.5	19.3–21.4	11.1–32.2
Bagasse	55.6–57.4	23.9–24.5	24.35–26.3
Rattan	35.6–52.9	22.8–34.7	21.0–22.0
Bast Kenaf	44.3–57.8	15.6–19.2	22.0–23.2
Core Kenaf	37.5–49.6	15.1–21.4	18.0–24.3
Jute	61–71.5	12–13	13.6–20.4
Flax	71	2.2	18.6–20.6
Hemp	70.2–74.4	3.7–5.7	17.9–22.4
Ramie	68.6–76.2	0.6–0.7	13.1–16.7
Sisal	67–78	8–11	10–14.2
Cotton	82.7	–	5.7
Coir	36–43	41.45	0.15–0.25
Henequen	77.6	13.1	4–8

Table 1 shows the chemical composition of some vegetable fibers [22, 23].

2.4 Physical and Mechanical Properties

The physical and mechanical properties of vegetable fibers are of crucial importance in determining the fibers potential in various industrial applications.

2.4.1 Physical Properties

As previously described, the fibers physical properties such as strength, size, structure, crystallinity, and fiber variability are the critical parameters to consider when using fibers in a given application for the production of a high performance material [22]. Indeed, the fiber dimensions (length, width, aspect ratio (length/width), thickness and density) are important for comparing the different types of natural fibers.

Most plant fibers have a maximum density of 1.5 g/cm^3 and high porosity. The variability in cell wall thickness [13] results from the fibrils porosity (lumen diameter/total fiber diameter). The latter determines the hygrophilic character of the plant fiber [24] which can diverge in large proportions. For example, flax has a porosity of 6.8%, and palm fiber, a porosity of 10%, while that of cotton can be greater than 90% [24]. It has been proven that the degree of openness of a fibrous material has a major impact on the properties of the material, with respect to mechanical, physical and chemical aspects. The degree of openness depends on factors such as the number of fibers per unit weight, length, thickness and branching of the fibers [25].

2.4.2 Mechanical Properties

Natural fibers have very variable mechanical properties due to their physical form and chemical composition, thus giving each type of fiber a very specific use [26, 27]. It should be noted that the fibers generally undergo deformations of traction, compression, flexion, torsion and shear, in the plant itself or in use [28–30]. Physical properties such as morphology, smoothness or irregularity along and across the main axis, moisture content, degree of crystallinity and chemical composition show a remarkable effect on the plant fibers mechanical properties [31]. As previously argued, plant fibers are composites in nature with cellulose microfibrils as reinforcement in a lignin and hemicellulose matrix [5]. The great constitutive and anatomical variability of plant fibers implies variability in their mechanical properties [5, 22, 31].

Indeed, if the low density of lignocellulosic fibers gives these materials interesting specific mechanical properties, according to Lilholt and Lawther [32], long fibers have lower tensile stresses than short fibers, because the former have greater chances of containing training defects. In addition, the fibers size, and mainly the aspect ratio, influences the materials mechanical properties [33, 34]. In addition, a low fibrillar angle, small fiber diameter and high form factor lead to high mechanical properties [23, 25]. In general, the tensile strength and Young's modulus of plant fibers increase with the fibers cellulose content, while the cellulose microfibrils orientation with respect to the fiber axis determines the fibers stiffness. Plant fibers are more ductile if the microfibrils have a spiral orientation with respect to the fiber axis. Fibers are less flexible and stiffer with greater tensile strength if the microfibrils are oriented parallel to the fiber axis [5]. Due to the low density and relatively good strength of plant fibers, they are preferred as reinforcements in several applications [35].

Plant fibers can also develop structural defects as a result of the various stresses that the plant may undergo during the different stages of its life, for example scallops and twists (folds) that can form during the transformation process, which considerably affects the rigidity and strength of the final product [5, 32, 36]. In addition, natural fibers are hydrophilic in nature and contain a substantial moisture content which affects mechanical properties. The moisture content of natural fibers could be related to the pore volumes in the fibers, the relative humidity, the chemical composition and the crystallinity of the fibers. In general, high cellulose content, relative humidity and pore volume in addition to low fiber crystallinity tend to cause high moisture contents [35]. Some physical and mechanical properties of different plant fibers are reported in Table 2 [6, 23, 37–39].

Table 2 Physical and mechanical properties of different vegetable fibers

Fibers	Length (mm)	Diameter (μm)	Density (g/cm^3)	Young modulus (GPa)	Stress at break (MPa)	Strain at break (%)
Agave	0.8–8	100–300	1.3–1.5	9–28	507–855	2–2.9
Diss	–	–	0.89	9.3	149	1.70
Linen	10.65	5–38	1.38	27–80	343–1035	1.2–3
Typha	80	66.7	1.25	27	450	1.70
Pennisetum	0.70	70–400	0.82	7.4	185	2.50
Hemp	5–55	10–51	1.35	3–90	580–1110	1.6–4.5
Kenaf	1.4–11	12–36	1.20	22–53	295–930	2.7–6.9
Halfa	0.2–3.3	6–22	1.40	13–21.5	134–247	1.5–2.4
Cotton	15–56	12–35	1.21	5.5–12.6	287–597	2–10
Jute	0.8–6	5–25	1.23	3–55	187–773	1.5–3.1
Bagasse	0.8–2.8	10–34	1.20	2.7–17	20–290	0.90
Ramie	40–250	18–80	1.44	44–128	400–938	2–4
Wood (spruce)	2.7–4.6	32–43	0.46–1.5	11–40	112–1000	–
Wood (birch)	0.7–3	20–40	0.67–1.5	30–80	300–1500	–

3 Structure of Composites

Since the middle of the twentieth century, reinforcements of lignocellulosic origin have been used to develop composite materials that are technically and economically efficient while respecting the environment [10]. These materials find many applications in areas where light and strong structures are required [4, 40].

The effective and efficient use of composite materials reinforced with natural fibers requires a thorough knowledge of the materials properties. Based on the properties and configurations of the constituents one can predict the properties of the resulting composite [28]. The following axis is devoted to the composite materials description; the types of matrices used and their compatibility with vegetable fibers while detailing the effect of the modified fibers incorporation on the composite materials properties.

3.1 Fibrous Reinforcements

From various origins, reinforcements are marketed in the form of fibers, particles, flakes, whiskers, etc. However, most reinforcements are fibers because the materials are stronger and more rigid in the fibrous form than in any other form [41, 42]. Fibrous reinforcements can be classified into three categories: polymeric fibers, carbon fibers and mineral fibers [2]. Polymeric fibers can be synthetic or natural.

Of course, synthetic fibers offer excellent properties to the resulting composite. However, the negative impact on the environment and the excessive use of the non-renewable material represent the main disadvantages of the use of these reinforcements. To overcome these problems, several scientists have conducted studies to develop composites reinforced with natural fibers. These natural reinforcements have many advantages, in particular their low density, their robustness and their biodegradable nature. It should be noted that natural fibers can be used in their native state or after processing to another form with greater added value, such as continuous strands of rayon, which are made from wood pulp [41, 43]. Cellulosic fibers spun from liquid crystal solutions prepared by dissolving cellulose in phosphoric acid have also been used. The strength of these cellulose fibers is about 1700 MPa; which is by far the highest value for strength of cellulose-based fibers [44]. Natural fibers can also be combined with synthetic or mineral fibers to reinforce polymeric matrices in order to develop composites with particular properties. Several combinations have been studied in the scientific literature such as linen/glass [45], linen/polypropylene [46] and linen/polyester [47].

One of the primary goals of any design of a fiber reinforced composite material is to place the fibers in positions and orientations that allow the material to resist load in all directions, as in the case of isotropic materials such as metals and unreinforced polymers. Generally, the effectiveness of fiber reinforcement depends on the type, length, volume fraction and orientation of the fibers in the matrix. The appropriate choice of these parameters is very important because it influences one or more of the following characteristics of a composite namely: density, tensile strength and modulus, compressive strength, fracture and performance in fatigue, shock response, electrical and thermal properties as well as cost [2, 48, 49].

3.2 Matrices

The matrix can be polymeric, metallic or ceramic. Different chemical compositions and microstructural arrangements are possible in each category [2, 48]. Usually the matrix can take the form of almost any material. However, polymeric matrices are the most widely used since they represent more than 99% of composite materials [41]. These matrices are divided mainly into two main classes: thermoplastics and thermosets. The nature of the matrix dictates the fields of composites application with polymeric matrices. In fact, thermoplastics are used mainly in non-structural applications while thermosetting matrices find their application in the manufacture of structural materials [41, 50].

3.2.1 Thermoplastics

In a thermoplastic polymer, the molecules are linear or branched in structure and held by weak secondary bonds (intermolecular forces), such as Van der Waals forces and hydrogen bonds. Under the effect of heat and pressure, these intermolecular bonds can be broken temporarily, which entails a displacement of the molecules which will tend to occupy new positions. After cooling, the molecules freeze in their new positions, thus reestablishing secondary links between them which gives rise to a new solid form. The strength and rigidity of thermoplastics are linked to the intrinsic properties of the monomer units and their very high molecular weight [6, 51].

3.2.2 Thermosets

Unlike thermoplastics, the molecules of a polymer thermosets are chemically linked by crosslinks (crosslinking), forming a tightly consolidated three-dimensional network. This change in the structure of the polymer occurs during the formation of the composite. Once these crosslinks are formed, the thermosetting polymer cannot be melted or reshaped under heat and pressure [6, 51]. Compared to thermoplastic polymers, thermosets are more thermally stable and exhibit high chemical resistance. In addition, these polymers are much more resistant to creep and relaxation [6, 51]. It should be noted that the thermal and mechanical properties of thermosets depend on the molecular units that form the network, on the length and density of the crosslinks [9, 52]. The most commonly used resins are epoxy, unsaturated polyester, and vinyl ester. These cover a very wide class of chemicals and a wide range of physical and mechanical properties can be obtained [9, 52].

3.3 Cohesion of Composites

The combination of two different materials (matrix and reinforcement) gives rise to an interface, which is an essentially two-dimensional area. At the level of this zone the important parameters such as the crystal structure, the modulus of elasticity, the density, and the thermal expansion coefficient differ from one face to the other [5, 6, 53]. The interface plays an essential role in determining the mechanical properties of composites as stress transfer occurs at the matrix-fiber interface. As a result, much research has been carried out in order to understand the interfacial bond and to evaluate its effect on the mechanical behavior of composites. In this regard, different methods are used to evaluate the interface in order to obtain good fiber-matrix adhesion.

In general, the bond between a polymer and a solid surface (fiber) can be provided by three types of interfacial bonds: mechanical, physical and chemical. These interactions can be evaluated by analytical techniques such as nano-indentation, nano-scratch tests and atomic force microscopy [2, 5, 6].

3.3.1 Mechanical Connection

The mechanical bond is ensured by an attachment of the polymer at the level of the pores and irregularities of the fibers surface after the polymer has hardened. The mechanical bonding is thus improved by increasing the porosity and/or the roughness of the surface. It should be noted that roughness is only a positive factor if the fiber is perfectly wetted by the liquid polymer. Indeed, if the liquid cannot penetrate the roughness of the fiber, the hardening of the resin will be accompanied by the formation of interfacial cavities which are liable to initiate the failure of the interfacial bond [9, 53].

3.3.2 Physical Connection (Electronic Attraction)

The cohesion between two materials is provided by bonding forces which are divided into two broad categories: chemical bond (short-range force) and physical or intermolecular bond (long-range force). The energy of these bonds is largely a function of the distance separating the two materials. It exist several intermolecular interactions, commonly called Van der Waals forces and hydrogen bonds [9, 53].

3.3.3 Chemical Bond

Fiber and matrix can also be linked by high energy covalent bonds. The chemical groups that give rise to such bonds are rarely present on the surface of the material in the native state, but they must be created by chemical treatment [9, 53].

4 Improvement of Fiber-matrix Adhesion by Chemical Treatment

The functionalization of cellulosic substrates has been widely exploited, even before the determination of the polymeric nature of cellulose, as shown by the discovery of nitrocellulose in 1846 [44]. Over the years, several types of fibers chemical treatment have been developed. This made it possible to obtain products with varied characteristics depending on the type and uniformity of the substituent groups distribution, thus opening up a wide field for the new materials design [10, 54]. In this regard, many research teams have been particularly interested in improving the fiber-matrix compatibility by chemical modification. This treatment uses reagents ranging from small molecules, making it possible to reduce the fiber hydrophilicity, to macromolecules aiming to create covalent bonds between the reinforcement and the matrix, thus ensuring efficient transfer of stresses. It is important to point out that the chemical modification of plant fibers often calls for complex mechanisms imposed by the macromolecular structure of its basic constituents.

4.1 Alkaline Treatment

Natural fibers treatment with sodium hydroxide (NaOH) is widely used to modify cellulosic molecular structure. It changes the orientation of the cellulose crystalline areas (Cellulose I–Cellulose II) [55, 56] and forms more amorphous regions. This increases the accessibility of chemicals. In the amorphous region, the cellulose chains are separated and water molecules fit between these chains. The alkaline treatment decreases the level of –OH groups in cellulose and forms $–O^{-}\ Na^{+}$ groups between the molecular chains of cellulose [57]. Thus, the moisture sensitivity of the fibers decreases. This treatment also removes some of the hemicelluloses, lignin, pectin, wax and oils [58–60]. As a result, the surface of the fiber becomes clean and more uniform. It also reduces the diameter of the fiber and thus increases the length/diameter ratio of the fiber. This increases the effective fiber surface for good adhesion to the matrix [61]. The mechanical and thermal behaviors of composites are significantly improved by this treatment. If the solution is too concentrated, it causes excessive delignification of the fiber resulting in deterioration of the fibers [58, 62].

Ray et al. [63] applied the alkaline treatment to jute fibers using a 5% NaOH solution at 30 °C for times ranging from 2 to 8 h. The crystallinity of the fibers increased after 6 h of treatment. The Young's modulus of jute fibers increased by 12% after 4 h of treatment, and by 68% and 79% when treated for 6 and 8 h respectively. The tenacity of the fibers increased by almost 46% after 6 and 8 h of treatment, and the elongation at break was reduced by 23% after 8 h of treatment.

Roy et al. [64] applied the alkaline treatment to jute fibers using solutions of different concentrations and for different times at room temperature. The fibers were immersed in the alkaline solution, then washed and dried. This treatment gradually eliminated the hemicelluloses and lignin. According to the authors, the alkaline treatment breaks the hydrogen bonds between the hydroxyl groups (–OH) of cellulose, the hemicelluloses and the lignin and leads to defibrillation i.e. breaking down the fiber bundle into smaller fibers. The moisture content of jute fibers decreased with increasing concentration of the alkaline solution and increasing duration of processing. The moisture content of the untreated jute fiber was 15.51%. It reached 4.08% when the jute fibers were treated with 1% alkaline solution for 48 h. In the latter case, the water contact angle of the treated fibers increased from 63.9° to 96.2°. Thus, these fibers have become more hydrophobic and more compatible with a matrix. The surface roughness of the jute fiber increased with the concentration of the alkaline solution and the duration of the treatment. This is due to the removal of surface impurities, non-cellulose materials, inorganic substances and waxes. The fiber diameter has been reduced by 39%. The mechanical properties have been improved. The alkaline treatment increased the tensile strength of the fibers by 82% and the elongation at break by 45%.

4.2 Acetylization Treatment

Acetylation is a technique for esterifying natural fibers. The fibers are acetylated with acetic acid or acetic anhydride in the presence or absence of an acid catalyst to graft acetyl groups onto the cellulose. The acetyl group (CH_3CO) replaces the hydrophilic hydroxyl (OH) group of the fiber. Thus, the hydrophilic nature of the fiber decreases [56].

Kalaprasad et al. [65] followed this technique to acetylate sisal fibers. For this, the fibers were kept immersed in glacial acetic acid for 1 h at room temperature. The acid was then decanted and the immersion was continued in acetic anhydride containing two drops of concentrated sulfuric acid for 10 min. The change in the chemical structure of sisal fiber following acetylation was analyzed by Fourier transform infrared spectroscopy. The intensity of the band bound to the –OH group is reduced after acetylation as a result of esterification of hydroxyl groups. These fibers were incorporated into a low density polyethylene matrix to prepare composites (20/80). The authors observed an improvement in the tensile properties of the composites after acetylation of the fibers. This is attributed to the presence of $–CH_3$ groups in acetylated sisal fiber, which enhances the interaction with polyethylene. Even though there is no covalent chemical bond between the acetylated sisal fiber and the polyethylene, it is the increased hydrophobicity of sisal after processing that is responsible for the improvement in tensile properties.

4.3 Stearic Acid Treatment

Another technique for esterifying natural fibers is treatment with stearic acid [66]. Stearic acid with the formula $CH_3(CH_2)_{16}COOH$ is used to modify the fibers surface. The carboxyl –COOH group of stearic acid reacts with hydrophilic hydroxyl groups in the fiber and reduces its sensitivity to moisture [56]. This treatment can give natural fibers an extremely hydrophobic character [67, 68]. However, it eliminates certain constituents of the fiber structure (pectin, wax oil, etc.). As a result, the fiber bundles break down and defibrillation phenomena occur [66, 69]. For composite applications, this treatment promotes better bonding to the fiber-matrix interface and provides better properties of the composites.

Paul et al. [66] treated the banana fibers with stearic acid. First, the fibers were alkali treated with a 10% strength solution for one hour. After washing and drying, the treated fibers were immersed in a solution of 1% stearic acid in ethanol for 1 h. The treated fiber/Polypropylene (50/50) composites show an improvement in mechanical properties compared to composites containing untreated fibers. The tensile strength and Young's modulus of the composite increased by 7% and 8.4% respectively. The same tendency is also observed during 3-point bending tests.

Kalaprasad et al. [65] modified sisal fibers with different concentrations of stearic acid in ethanol. The results indicate that the fiber surface becomes more hydrophobic with increasing concentration of stearic acid. The treatment with stearic acid increases the contact angle between the surface of the fiber and the water and therefore decreases the wetting of the fiber with the water. This hydrophobic character conferred on the sisal fiber makes it more compatible with polyethylene which is also hydrophobic. The tensile strength and Young's modulus of these composites (20/80) were improved with this treatment. Maximum tensile strength (+13%) and maximum Young's modulus (+12%) were obtained at a concentration of 4%. According to the authors, the increase in tensile strength is due to the higher degree of dispersion of sisal fibers treated with stearic acid.

5 Effect of Chemical Treatment on the Composites Properties

Polymers reinforced with natural fibers can have very different mechanical and thermal performances due to environmental influences, depending on their interphase properties. The main function of the interphase is to facilitate the transfer of stress from one fiber to another through the matrix. As the interfacial bond between the reinforcement fibers and the resin matrix is an important element in obtaining the mechanical properties of composite materials. Since the poor quality of the interface between the fibers and the polymeric matrix is the first and most important problem in composites reinforced with natural fibers, the modification of the fibers surface by chemical treatments is one of the most important research areas nowadays in improving the materials properties. Several authors have focused their studies on the treatment of fibers to improve their bond with the resin matrix. Fiber modification can increase or decrease fiber strength, so it is important to understand what happens structurally [70].

5.1 Mechanical Properties of Composites

Mechanical properties are the main properties studied for composites reinforced with natural fibers. These properties include strength, stiffness, toughness, shear, compression, fatigue and creep [28–30]. The composite materials strength is assessed by a number of test methods which are conceptually mechanically simple but are extremely sensitive to sample preparation and the procedure for performing the test. Mechanical tests mainly include tensile, compression, shear, bending and fatigue tests. These test methods are governed by standards developed by the American Society for Testing of Materials (ASTM), the International Organization for Standardization (ISO) and the Association of Advanced Composite Materials (SACMA). In the present study, we limit ourselves to the study of the tensile properties of composites. Tensile tests are performed to determine the uniaxial tensile strength, Young's modulus and elongation at break of the material [71].

5.1.1 Failure of Composites Under Tensile Load

On a macroscopic scale, a composite under tensile load can exhibit ductile or brittle failure. These two terms describe the degree of macroscopic plastic deformation preceding failure.

- Ductile rupture occurs by the coalescence of micro voids which cause an internal crack by normal rupture. This mode of failure is accompanied by a sudden plastic deformation which leads to a fibrous appearance of the fractured surface.
- Brittle fracture is characterized by a rapid propagation of cracks without sudden plastic deformation; the behavior of a brittle material is almost exclusively elastic until it breaks. In this type of material, the fracture surface is characterized by the presence of radial ridges at the fracture surface which are parallel to the direction of propagation of the crack. Note that a streak is produced when two cracks, which are not coplanar, become connected by tearing the intermediate material. Brittle fracture in tension has a granular appearance with little or no necking [71, 72].

At the microscopic scale, two failure mechanisms can take place depending on the properties of the interface, namely a detachment at the fiber/matrix interface or a loosening of fibers from the matrix (Fig. 4). If the interface peels off easily, the crack propagation is interrupted by the peel process and instead of the crack going through the fiber; it propagates along the surface of the fiber, allowing the fiber to withstand higher loads. Fiber loosening occurs as the fibers break at random locations away

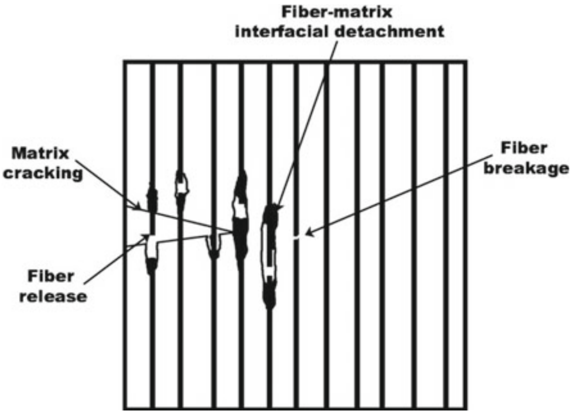


Fig. 4 Fiber-matrix rupture mechanism

from the plane of the crack. One of the ends of the broken fibers loosens from the matrix when the crack opens with the increase in the applied load [2].

5.1.2 Effect of Chemical Treatments of Fibers on the Mechanical Resistance of Composites

The long and short term mechanical performance of short-fiber reinforced composites depends mainly on three factors: the strength and modulus of the fiber, the strength and chemical stability of the resin, and the efficiency of the interfacial bond that ensures the transfer of the load from the matrix to the fiber. However, the quality of the fiber-matrix interface remains the key factor to be optimized in order to provide a high-performance composite. Due to the strong dependence between the polarity of the fibers and the interfacial adhesion, the research teams were interested in the chemical modification of the fibers by several treatments such as acylation, etherification, grafting by copolymerization, treatment alkali, silane treatment and isocyanate treatment to improve the performance of composites. These treatments have been successful in achieving varying levels of success in improving the fiber-matrix adhesion of composites based on lignocellulosic fibers.

Acetylation is the most studied treatment to improve the quality of the plant fiber/polymer matrix interface [73, 74]. As mentioned before, acetylation is based on the substitution of hydroxyl groups of polymers of the cell wall of fibers by less polar acetyl groups exhibiting better affinity with nonpolar matrices [57, 75]. Previous studies have shown that acetylation affects not only the chemical structure of fibers, but also their surface morphology [76, 77]. Indeed, studies conducted by Kabir et al. [56] and Li et al. [58] revealed that acetylation increases the roughness of the fibers surface thus leading to better mechanical bonding with the matrix. Ismail et al. [78] observed an improvement in Young's modulus, stress and elongation at break of the kenaf/soybean powder/HDPE composite of 9%, 19% and 34% respectively. An improvement in the interfacial shear strength of cotton/polystyrene and wood/polystyrene fiber composites has been observed thanks to the improvement in the wettability of acetylated fibers to molten polystyrene [79]. An 18% improvement in the tensile strength of the flax/polypropylene composite was observed by Bledzki et al. [80]. This increase was attributed to the elimination of lignin and extractables as well as a slight increase in the content of acetylated cellulose and hemicelluloses. Similarly, an increase in Young's modulus and tensile strength of the flax/biopolyester composite by 31% and 45%, respectively, and a 21% reduction in elongation at break were noted thanks to an improvement in l interfacial adhesion [81]. It should be noted that the research teams were mainly interested in studying the effect of acetylation on the properties of composites with a thermoplastic matrix. On the other hand, few studies have focused on the reinforcing power of acetylated fibers in composites with a thermosetting matrix [80]; probably due to the weak interaction between acetylated fibers and this type of matrix. Indeed, Khalil et al. [82] studied the variation in the reinforcing power of acetylated palm and coconut fibers depending on the nature of the polymer matrix. The results showed that the polystyrene matrix composites exhibit the highest degree of improvement in interfacial shear strength, followed by epoxy and polyester. This behavior has been linked to the improvement in the wettability of the acetylated fibers to the polystyrene matrix.

To further improve the mechanical properties of composites, research teams have carried out an alkaline treatment of lignocellulosic fibers before reacting them with acetic acid derivatives. Indeed, previous studies have shown that this combination improves the adhesion between sisal and polystyrene [83], sisal and epoxy [84] as well as flax and unsaturated polyester [85] and this due to the strong modification of the topology of the fibers which promotes mechanical attachment as well as adhesion by interdiffusion between the fibers and the matrix.

It should be noted that the mechanical resistance of materials increases with the rate of acetylation [76, 86]. However, from a specific degree of substitution, the composite strength decreases due to the fibers degradation and the creation of internal cracks in the fiber [80]. In fact, acetylation not only modifies the interface between the fibers and the polymeric matrices but also the physical and mechanical properties of natural fibers. These properties are influenced by the chemical composition and structural parameters of the fibers, mainly the orientation of the chains (of nanocrystalline cellulose and of crystalline fibrils), the supramolecular structure (degree of crystallinity), the degree of polymerization and the structure of the crystal (pore content, specific interface and pore size). These parameters are modified after chemical treatment of the fiber.

Most chemical treatments reduce the mechanical strength of the fiber due to the breaking of bonds and the extraction of amorphous components, which act as cement in the structure of the fibers. As for the elongation at break, it is increased after chemical treatment. In fact, in their native state, the fibers exhibit a crosslinked three-dimensional structure which reduces their elongation at break. Chemical treatment breaks this network structure giving the fiber higher elongation and lower strength properties [87]. A study by Gassan et al. [88] showed the strong dependence between the mechanical properties of flax/epoxy composites and the structure of flax fiber.

Due to the fibers damage after acetylation, the mechanical strength of the composites reinforced by these fibers is reduced. Indeed Mwaikambo et al. [89] have shown that acetylation reduces the crystallinity of cotton and kapok fibers, thus leading to a deterioration of the tensile properties of composites with a polypropylene matrix. The negative effect of fiber acetylation on the mechanical strength of certain composites may also be linked to a weak fiber-matrix interface. Indeed, Taib et al. [90] reported in their study that the acetyl groups present on the surface of Acacia Mangium fibers are probably too short to diffuse and form entanglements with the HDPE matrix. This leads to poor fiber-matrix adhesion and subsequently lower tensile strength of the resulting composite. Furthermore, the substitution of hydroxyl groups by acetyl groups can reduce the resistance of composites with a thermosetting matrix such as phenolics, due to the reduction in chemical interactions at the level of the hydrophilic sites of the phenol/formalin resin [91]. In addition, Luz et al. [77] attributed the decrease in tensile strength of bagasse/polypropylene composites to the reduction in fiber size after acetylation.

Moreover, the acylation of the fibers by reagents other than the acetic acid derivatives also provides new properties to the plant fibers, thus inducing an improvement in the mechanical properties of the composites reinforced by these fibers. In addition, the silane and isocyanate treatment of the fibers has shown a positive effect on the tensile strength of various fiber/matrix combinations. Furthermore, previous studies have shown that overall the alkaline treatment of fibers also improves the mechanical strength of composites due to the elimination of intra and intercrystalline lignin and other waxy substances. This produces a rough surface which greatly increases the possibility of mechanical entanglement between the fibers and the polymeric matrices [92–94]. The positive effect of alkaline treatment on the mechanical properties of composites at different types of matrices has been mentioned by Bisanda (sisal/epoxy) [94], Moyeenuddin et al. (hemp/polylactide) [95], Shinoj et al. (palm fibers/natural rubber) [8] and several research teams (linen/epoxy) [93, 96, 97]. It should be noted that the alkaline treatment has been combined with other chemical treatments to further improve the quality of fiber/matrix adhesion. These treatments include acylation [98, 99], treatment with silanes [10], treatment with isocyanates [92] and treatment with peroxide [62]. In addition, various specific treatments have been studied in order to improve the adhesion between the flax fibers and the ‘epoxy matrix such as the impregnation of the fiber with the polymeric resin, the latex modification and the epoxidized natural rubber [96]. The pre-impregnation of fibers has also been reported by other research teams [100, 101]. Recently, special attention has been paid to the formation of continuous covalent bonds between fibers and polymeric matrices using coupling agents such as silanes, maleates, titanates and zirconates [58, 100, 102].

5.2 Thermal Properties

The interaction of thermal energy with the material atoms determines some of its most important physical properties. The properties describing this interaction are called thermophysical properties which include heat capacity, thermal diffusivity and thermal conductivity [44]. In the case of composites reinforced with lignocellulosic fibers, thermal stability is the property most studied by research teams. Among the main methods used for the composites thermal analysis we cite the temperature difference between a sample and a reference “Differential thermal analysis” (DTA), the weight loss measured by thermogravimetry “Thermogravimetric analysis” (TGA), its derivative “Thermogravimetric derivative” (TGD) and determination of heat flux by differential scanning calorimetry (DSC). However, TGA/TGD analysis remains the most widely used technique to characterize the thermal stability of composites reinforced with plant fibers [103]. The degradation of lignocellulosic fibers under the effect of temperature is the main parameter which governs the composite materials thermal stability reinforced with natural fibers. The thermal behavior of fibers depends on the cell wall polymers degradation temperatures (cellulose, hemicelluloses and lignin). The thermal decomposition of cellulose begins with dehydration at a temperature between 210 and 260 °C followed by depolymerization between 310 and about 450 °C. As for hemicelluloses, they decompose at 290 °C, while lignin decomposes between 280 and 520 °C [103, 104]. The quality of the fiber-matrix interface also influences the thermal behavior of the composites. Indeed, a good fiber-matrix adhesion makes it possible to have thermally stable composites. As mentioned previously, chemical treatments of fibers can improve interfacial adhesion and therefore increase both the mechanical and thermal resistance of the resulting composites. In this regard, the research teams have tested several chemical treatments such as acetylation, silanes and isocyanates.

Nair et al. have shown that acetylation improves thermal stability of sisal/polystyrene composites not only due to high thermal stability of acetylated fibers but also improved interfacial adhesion [83]. In addition, acetylation improves thermal stability of sisal/polypropylene and sisal/polypropylene/high density polyethylene composites still due to the better quality of the fiber-matrix interface [105]. A similar behavior was observed for the kapok/cotton/polypropylene composite [89].

Due to the dependence between the quality of the interface and the thermal stability of the composites, one should expect an improvement in this stability by any treatment capable of enhancing the fiber-matrix interactions. In fact, previous studies have shown that the silane treatment increases the degradation temperature of the pineapple/polyethylene, sisal/epoxy and linen/epoxy composites. Identical behavior was obtained by an isocyanate treatment of the flax fibers reinforcing the epoxy matrix and by the benzoylation of sisal fibers combined with a polystyrene matrix. The grafting of polyethylene treated with maleic anhydride and glycidic methacrylate also had a positive effect on the thermal stability of the hemp/polypropylene and jute/high density polyethylene composites. In addition, the alkaline treatment can have a positive as well as a negative effect depending on the concentration of the alkaline medium used [89, 96, 103]. It should be noted that any chemical treatment of fibers can increase or decrease the thermal stability of composites depending on the effect of the treatment on the crystalline order of the fibers [87].

In addition, several research studies on the thermal stability of composites with a polymer matrix reinforced with lignocellulosic fibers have shown that these materials degrade at temperatures between 240 and 355 °C which is attributed to the decomposition of lignocellulosic fibers [104]. According to previous studies and independently of the used fibers state (native or treated), composites generally degrade at temperatures lower than those of the degradation of polymeric matrices, due to the fibers low degradation temperature. Such behavior has been observed for kenaf/epoxy, linen/epoxy, cotton/phenolic matrix, sisal/phenolic matrix and hemp/polypropylene composites [103]. The TGD curves of the composites also show peaks at temperatures between 422 and 463 °C, which correspond to the polymer matrix degradation. However, for the determination of the thermal stability of composites, this temperature range is of less importance compared to the temperature of the onset of degradation [104].

6 Conclusion

In this chapter, the renewable and biodegradable material takes on all its originality. Particular interest has been focused on vegetable fibers which is a fundamental source of biomass. Its structure, its reactivity as well as the modifications likely to give it new properties (hydrophobicity, compatibility, etc.) were studied. Our study not only focused on natural fibers, but also on composite materials and the use of these fibers as light reinforcement, biodegradable, renewable, recyclable and at relatively moderate cost. The compatibility between the fiber and the matrix is of major importance in the synthesis of high performance composite materials.

As natural fibers are seldom compatible with polymeric resins (especially thermoplastics), modifications of one of the components are necessary to improve the quality of the interface. Indeed, good adhesion is required to have high performance composites. Generally, the modifications relate more to the fibers than to the matrix. These different treatments, particularly those of chemical origin, most often provide fairly advantageous properties to natural fibers.

Acknowledgment This work was supported by MAScIR; Moroccan Foun-dation for Advanced Science, Innovation and Research, MESRSFC and CNRST, Morocco Grant no.1970/15.

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Thermal Degradation of a Phenolic Resin, Vegetable Fibers, and Derived Composites

Ashvinder K. Rana, Vijay K. Thakur, and Anish Khan

1 Introduction

Although synthetic fibers reinforced thermosetting composites have higher mechanical strength than vegetable fibers reinforced composites, however latter one has several benefits over synthetic fibers reinforced phenolic composites as they are recyclable, biocompatible, modest and biodegradable [1]. Regardless of alluring properties, hydrophilic vegetable fibers (VFs) find their role partly in industrial applications because of poor wettability with matrix and higher moisture absorption. However, through surface functionalization the wettability/compatibility of these VFs with matrix can be enhanced. There are numerous techniques reported in literature such as physical, chemical and enzymatic techniques for surface tailoring of the VFs, which have been utilized by analyst to upgrade the mechanical as well as thermal strength of resulted bio-composites [2]. Surface modification enhances the hydrophobic character onto fibers surface and thus prompts better compatibility with hydrophobic matrix. No doubt, surface modification has pronounced effect on manufacturing cost; but it also enhances the quality of resulted composites and thus diminishes the economical competitiveness of the VFs reinforced composites. The development in VFs reinforced polymer composites markets have also been supported by Lucintel [3], who estimated compound annual growth of 8.2% in last five years.

A. K. Rana (✉)
Department of Chemistry, Sri Sai University, Palampur 176061, India

V. K. Thakur
Agriculture and Biorefining and Advanced Materials Research Centre, Parkgate, Barony Campus, DG1 3NE, Dumfries, UK

A. Khan
Center of Excellence for Advanced Materials Research , King Abdulaziz University, Jeddah 21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_8

The choice of VFs is still area of broad exploration and requires unique considerations by specialists throughout. Since VFs are very different from each others in terms of amount of constituents, thus their properties vary significantly from region to region and with atmospheric conditions [2]. So, scientists ought to completely investigate VFs constituents, its properties as well as its hydrophilic/hydrophobic behaviour before preceding its utilization as reinforcement. During fabrication of VFs fortify polymer composites, researchers basically concentrate on temperature of curing and softening temperature of respective matrix. Since neat matrix typically has particular and specific type of compound structure, so in contrast to VFs, comparable essential properties expected for virgin resin. The future prospects of VFs reinforced polymer composites depends on the in-depth investigation of high explicit solidarity to-weight and specific stiffness-to-weight proportions of resulted composites [3]. Aside from mechanical, phys-chemical, topographical and dielectric properties [4], other fundamental points, which should be focused is thermal attributes of the polymer composites as it is the major constrain in their application. Since VFs undergoes degradation at higher temperature and thus controls the overall performance of composites. The appropriateness of VFs for a specific matrix and thermal strength of VFs reinforced thermosetting composites had been a subject of enthusiasm for many years. The VFs reinforced thermoset matrix finds their use vastly in automobile sectors for manufacturing of door panels, seats, package trays, dashboards, inside parts, etc. [5–7]. Different specialists have assessed the stability of single VFs reinforced phenolic composites as well as different VFs fortified polymer composites [8–10]. So, in this chapter we will look at the impact of different surface modification strategies on thermal stability of resulted fibers and their phenolic composites.

1.1 World Consumption of VFs

The world consumption of VFs as a bolstering in polymer composites totalled 4.3 billion dollars in 2018, inholding a compound annual Growth rate (CAGR) of 3.3 percent from 2010 to 2018. No doubt their consumption has elevated from 2010 to 2018 however boom rate is gradual and it indicates that market isn't developing as fast as expected. Rogers (1995) has explained the cause for low boom rate; he concluded that there are five elements i.e. relative advantage, compatibility, complexity, trialability and communicability which are causing diffusion in innovation. Figure 1 indicates the relative production of VFs by way of different nations with China topping the list.

Further world consumption of natural fibers has been represented in Fig. 2. It can be analysed from figure that Flax fibers has highest consumption followed by jute, coconut, other vegetables, sisal and hemp. Since, Flax has highest cellulosic contents and thus possess high strength which may be the reason for its higher consumption.

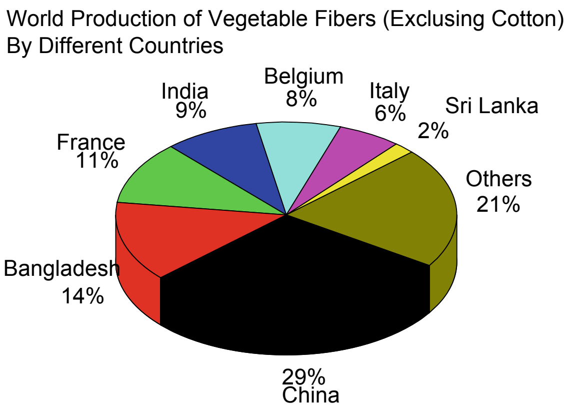

Fig. 1 Showing the relative percent production of VFs by different nations. Information has been founded on UN COMTRADE insights

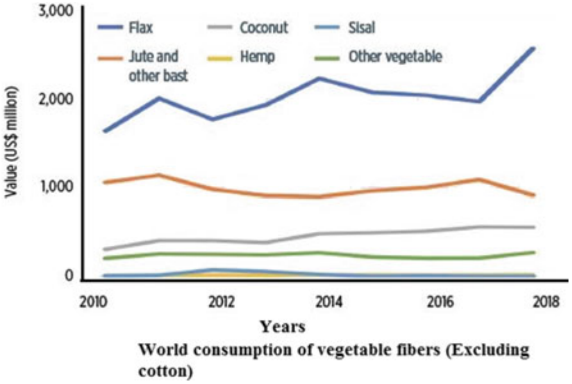

Fig. 2 World consumption of natural fibers (Data have been founded on UN COMTRADE statistics)

1.2 *Structure of Natural Fibers*

The primary chemical constituent of plant cell is cellulose and other constituents are hemicelluloses, lignin, pectin, glycan and waxes (see in Fig. 3a) [11]. Cellulose, a bio- polymer, is formed by several alpha glucose units having empirical formula $(C_6H_{10}O_5)n$ linked end to end and forms bundles via organization of parallel chains of glucose, called microfibrils. Hemicellulose is made up by heterogeneous group of polysaccharides and is a short and highly branched one. The most crucial biological **function** of **hemicelluloses** is to reinforce the cell wall via association with cellulose and with lignin. Additionally, coexistence of pectins and cross-linked glycans, made up through corporations of highly branched polysaccharides, supply the necessary compressive strength and tensile strength to the cellulose respectively. The secondary cell wall (which lies within primary wall), in addition to constituents of primary cell wall, also contains an additional substance known as lignin. Lignin, which is a polymer of propyl phenol groups, is rigid and provides noticeably quality to fibers structure. In addition lignin also supply structural support to plant and protects cell

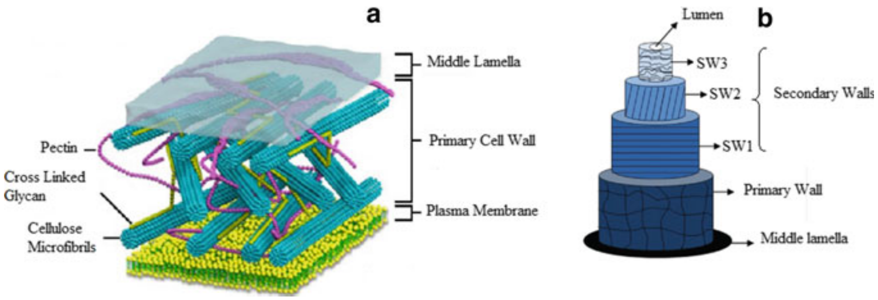

Fig. 3 Figure showing the **a** plant cell wall structure. Reprinted with permission from Ref. [12, 13, 13], **b** schematic representation of plant fiber structure [14, 15]. Reprinted with permission from Polímeros: Ciência e Tecnologia Pereira et al. [15]

wall from fungi and bacteria attacks. The constituents found outside in plant cell wall are cutin, suberin, and other waxy materials. The middle lamella **made** up of calcium and magnesium pectates, is the outermost layer of cell wall and is highly rich in pectins. Its main function is to cement the cell walls of adjacent plant cells and in doing so it forms plasmodesmata type connections.

The cell wall structure has been depicted in Fig. 3b [12]. It is observed from figure that cell wall is organized into layers and is non homogenous membrane. Cell fibers carries four layers of microfibrils with outermost layer known as primary wall, and internal layer that is comprised of three layers (External secondary layer (SW1), centre secondary layer (SW2) and internal secondary layer (SW3)] is known as secondary wall. Inside the SW2, the microfilaments are oriented at an angle θ with respect to vertical axis of the cell [16].

The inner layer (SW1) is of no technological importance as it is not well developed; SW2 layer, composed of microfibrils formed by helical shaped long chains cellulose molecules, provide mechanical strength and has high elasticity modulus [17] whereas outermost SW3 is comprised of several lamellae spiral runs in anti parallel directions. Further, mechanical properties of fibers are defined by middle lamella of fibers which incorporates long lengthy chain cellulose molecules shaped by aid of several cell microfibrils and pectin serves as cementing materials between fibers. The cellulose content, density, aspect ratio, thermal stability, fiber dimensions and crystallinity are some factors which must be taken into consideration before selecting the particular fibers for desired applications. Also angle of helix determine the mechanical behaviour of VFs and has been reported that as the angle of helix diminishes, the tensile strength increases. Further when cellulose content expands, rigidity/tensile strength of the filaments additionally increases.

1.3 Chemical Composition and Physic-Mechanical Properties of VFs

After assessment of table 1 it has been observed that high cellulose contents in the cell wall lets in a growth in tensile strength of the VFs. Amongst diverse fibers, Hemp fiber has excessive cellulose proportions and as a consequence, it can be utilized in the manufacturing of items that demand high tensile strength. However, if one wants to develop a product with better resistance towards micro organism or fungi, than he can use the high lignin content containing kapok fibers.

2 Different Surface Modification Techniques

Despite the attractive properties, VFs finds its utility to a limited extent in industrial practice because of their hydrophilic nature which causes poor dispersion in hydrophobic matrix and thus leads to poor mechanical and thermal stability. However through functionalization, thermal strength, mechanical strength and compatibility of VFs with polymer matrix can be enhanced. Various surface tailoring techniques which can be employed have been listed below (Table 2).

2.1 Thermal Stability of VFs

The difference in thermal stability of VFs is because of the chemical compositions of the fiber. Cellulose, hemicellulose and lignin are prime constituents and their ratio in VFs depend upon the type of fiber, their method of extraction, region of their collections, seasons, etc. Degradation of cellulose occurs in between 260 and 350 °C, and produces char and flammable and non combustible gases. On the other hand, hemicellulose decomposes in between 200 and 260 °C and delivers more non-combustible gases than cellulose. Lignin deterioration occurs at a wide temperature range (160–400 °C) and produces major char residue. Thermal stability of different raw VFs and impact of surface modification have been discussed below.

2.2 Thermal Stability of Bamboo Fiber

Nahar and co-workers [23] studied thermal stability of raw bamboo fiber, gamma radiation irradiated fibers, basic chromium sulphate (BCS) and BCS + $NaHCO_3$ treated bamboo fibers by employing thermal gravimetric analysis (TGA)/differential thermal analysis (DTA) techniques. Two steps degradation process have been reported for raw and treated bamboo fiber, in between 150–300 °C and 300–450 °C. On evaluating

Table 1 Physico-chemical properties of various VFs [18, 19]

Fiber's name	Density (g/cm^3)	Tensile strength (MPa)	% Elongation	Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)	Ashes (%)	Waxes (%)
Abaca	1.5	980	–	63–68	19–20	0.5	5.1–5.5	3	0.2
Flax	1.50	88–1500	1.2–1.6	62–71	16–18	1.8–2.0	2.0–2.5	–	1.5
Hemp	1.48–1.49	550–900	1.6	62–75	16–18	0.8	2.9–3.3	0.8	0.7
Henequen	1.40	430–580	3–4.7	74.6	4–8	13.1	–	1.2	–
Kenaf	1.2	295	2.7–6.9	44–57	–	–	15–19	2.5	–
Banana	1.35	353	53	60–65	6–8	5–10	–	1.2	–
Cotton fibers	1.52–1.56	400	3–10	92–95	5.7	1.2	0.0		0.6
Pineapple	1.44	413–1627	1.6	68	15–20	2–4	8–12		4–7
Ramie	1.51–1.55	500	2	68–76	13–14	1.9–2.1	0.6–0.7	–	0.3
Sisal	1.2	600–700	2–3	67.73	12–13	0.8	9.9	3	0.3
Coir Fiber	1.2	220	15–25	36–43	0.2	3–4	41–45	–	–
Kapok	0.37	80.3	1.75	50.7	49.3	–	13.4	–	–
Bhimal (*Grewia Optiva fiber*)	–	–	–	55–65	20–25	3–4	15–25	–	–

Table 2 Various chemical Treatments which can be employed for surface functionalization of VFs [20–22]

Type of methods	Classifications	Explanation/possible action
Chemical methods	Mercerization	Mercerization involves alkali treatment with NaOH solutions and it leads to removal of hemicelluloses, lignin and waxes present in cell wall and thus produces a rough surface topography
	Acetylation	Acetylation reaction introduces an acetyl functional group onto VFs backbone and it is usually carried out by nucleophilic addition of an organic acid anhydride or acid chlorides in basic medium
	Benzoylation	Benzoylation reaction involves the substitution of OH group present on cell wall by benzoyl groups and is accompanied by treatment with benzoyl chloride in basic medium
	Isocyanate treatment	It involves the reaction of isocyanate (–N=C=O) groups with the OH groups of lignocellulose. The isocyanate group reacts nicely and forms a string covalent bonds with the hydroxyl group present on VFs
	Peroxide treatment	Organic peroxides (compounds Containing O–O single bond) undergoes decomposition easily in acetone to form $RO^{\cdot}$ which then subsequently react with the VFs
	Sodium Chlorite treatment	Sodium chlorite ($NaClO_2$) is used for bleaching of VFs and it acts as oxidizing agent and tends to remove natural waxes and pectin found in cellulose fibers. In addition it also makes the fiber smooth, more even and workable
	Permanganate treatment	It is carried out by dipping VFs (raw/mercerized) in $KMnO_4$ solution in acetone. This treatment leads to the formation of cellulose radical which further brings about graft copolymerization

(continued)

Table 2 (continued)

Type of methods	Classifications	Explanation/possible action
	Silane treatment	This treatment involves the reaction of VFs with silane coupling agent solution prepared in ethanol/water (60/40) mixture. The general formula of the various silane coupling agents, which can be employed for coupling, is X3Si-R, where X is either Cl or -OCH_3 or–OC_2H_5 and R may be vinyl or γ-aminopropyl or γ-methacryloxypropyne etc
	Graft copolymerization	Graft copolymerization can be carried out via different initiation methods inclusive of chemical initiation, radiation, photochemical and enzymatic induced graft copolymerization. Further for grafting, one can employ single principal monomer or binary monomers mixtures
	Triton treatment	Triton ($C_{14}H_{22}O$ $(C_2H_4O)n$) is a surfactant having polyethylene oxide hydrophilic group and a long chain hydrocarbon hydrophobic group; and during treatment it is the hydrophilic groups which forms the covalent bond with the OH group of VFs
Physical methods	Stretching/calendaring/thermal treatment/electric discharge treatment (corona, cold plasma	Physical methods do not affect the chemical properties of VFs, however they control the surface and structural properties of fibers

the data, they found that thermal strength of fibers increased after treatment. Further, BCS grafted samples confirmed higher stability followed by BCS + $NaHCO_3$ treated fiber, gamma irradiated fiber and raw bamboo fiber. The better thermal stability of BCS and BCS + $NaHCO_3$ treated samples has been assigned because of the formation of octahedral complexes of grafted BCS and BCS + $NaHCO_3$ with cellulose, which causes reduction in free rotation of C–O–C link in glucose chain. Additionally, in case of BCS + $NaHCO_3$ treated fiber, each Cr atom got surrounded by $NaHCO_3$ molecules and forms rigid three dimensional network due to hydrogen bonding between adjacent chain. Thus proyltic decomposition of cellulose requires higher temperature [24]. Increment in thermal strength after alkali treatment has additionally been noticed by Zhang et al. [25] Effect of different % NaOH concentrations (6, 8, 10, 15 and 25% w/v) on thermal stability (T_{max} and T_{onset}) of bamboo fibers was also evaluated by employing TGA/DTG techniques. It has been reported that with growth in alkali concentration up to 10%, the thermal stability of treated bamboo fibers increases and thereafter a steep decrease in thermal strength was discovered [26]. Wan et al. [27] evaluated the thermal strength of methylmethacrylate (MMA) graft copolymerized bamboo cellulose through TGA technique. They found a considerable increase in thermal strength after graft copolymerization and reported Initial mass loss temperature (T_i) and maximum decomposition temperature (T_{max}) for raw and grafted bamboo cellulose to be 208 and 331 °C; 251 and 353 °C respectively.

2.3 Thermal Properties of Banana Fibers

The TGA curve of raw banana fibers (BFs) shows a three step degradation process [28]. First step degradation with a weight loss of 9.8% occurs in between 80 and 100 °C due to evaporation of moisture contents [29]; second step degradation occurs in between 200 and 400 °C with a weight loss of 70% due to degradation of cellulose, hemicelluloses and lignin [30] and third step degradation occurs in range 400–600 °C because of removal of volatile contents which leaves behind the residual char. After surface functionalization of fibers thermal strength has been noticed to improve. Indira and co-workers employed different chemical techniques, for example mercerization, formic acid, $KMnO_4$, silane, acetylation and benzoylation onto BFs and reported increment in thermal stability after studying the TGA and DTG curves of samples. The stability was found in the order of: alkali treated fibers (IDT = 290 and FDT = 385 °C) > formic acid (285 and 370 °C) > $KMnO_4$ (280 and 363 °C) > Silane (270 and 364 °C) > benzoylated (270 and 363 °C) > acetylated (269 and 346 °C) > raw fibers (270 and 340 °C) [28]. Higher stability of alkali treated fibers is because of the partial elimination of hemicelluloses, lignin and cementing materials which causes better stuffing of cellulose chain and thus shows better thermal stability. Formic acid and $KMnO_4$ treatment decreases the moisture absorption of banana fibers just like alkali treatment thus shows better stability. However, after silane, acetylation and benzoylation, there is slight increase in thermal stability with respect to raw fibers because of doping of bulkier groups onto cellulose surface. Joseph and co-workers [31] evaluated the impact of numerous techniques such as mercerization, vinyl silane, amino silane, heat, cyanoethylated and latex treatment on thermal stability of resulted BF samples. After comparing the weight loss, shown by different samples during TGA analysis, for distinct temperatures they concluded that treated fibers have better thermal stability than raw one. Further, among different treated fiber samples, highest thermal stability was found for amino silane treated fiber followed by vinyl silane, latex heated, mercerized and cyanoethylated fibers. Aseer et al. [32] evaluated the thermal strength of bleached BFs through TG analysis and stated decrease in thermal stability after treatment. The IDT and FDT values for raw and bleached fibers reported by them are 252 and 386 °C and 245 and 360 °C**,** respectively. Further, TGA results were additionally upheld by DTG examination. Two peaks for both raw and bleached fibers were found at 51 and 360 °C and 50.6 and 310 °C, respectively which further confirms better stability of former one.

There is poor effect of glycidyl methacrylate graft copolymerization on the thermal strength of BFs graft copolymerized fibers, as it causes increased weight loss of graft copolymerized fibers [33]. No doubt, raw fibers showed vigorous weight loss at initial stage, due to their hygroscopic nature, however overall strength of untreated fibers is best. The poor strength of treated one is attributed to rapid decomposition of grafted polymer chains. Effect of methaacrylic acid graft copolymerization under distinctive reactive situations such as via beta irradiation, microwave irradiation and by traditional method on thermal stability was also evaluated through TG analysis and was stated to be enhanced [34]. The stability order of different samples was found to be: BF-g-poly[acrylic acid (AAc)]-under gamma irradiation (IDT = 213 °C and FDT = 476 °C) > BF-g-poly(AAc) (236 and 429 °C) > BF-g-poly(AAc) under-MWR irradiation (236 and 423 °C) > untreated fibers (238 and 399 °C). Dielectric barrier discharge (DBD) plasma treatment showed bad effect on thermal behaviour of BFs and had been confirmed through Differential scanning calorimetry, which clearly indicates how BFs decomposition peak decreases from 333.9 to 328.2 °C after functionalization [35].

Selambakkannu et al. [36] compared the impact of Glycidyl methacrylate (GMA) grafting onto BFs through electron beam irradiation approach and their subsequent modification via imidazole group (IM) on thermal strength of resulted fibers. Three samples particularly: BFs, BFs-g-poly(GMA) fibers and IM functionalized BFs-g-poly(GMA) have been characterized through TGA/DTG techniques and found that IM functionalized BFs-g-poly(GMA) fibers have better stability than other samples. This may be because of introduction of –NH_2 group after IM treatment on the fiber surface, which act as radical scavenger and thus resist the decomposition of the sample [37].

2.4 *Thermal Stability of Coir Fibers*

Saw et al. [38] studied the thermal strength of raw and furfuryl alcohol treated coir fiber by utilizing TGA/DSC/DTA technique. After TGA study they found a minor weight reduction for both raw as well as treated one at the initial stage due to moisture (Fig. 4a). However two huge weight reductions have been reported in middle of 200–250 °C and 412–466 °C. Further, TGA data has been additionally supported through DTA analysis. In addition, Saw et al. also studied DSC curves (Fig. 4b) and reported shift in endothermic peaks for raw fibre from 91 °C to 108 and 117 °C for chlorite tailored and furfuryl alcohol functionalized fibres, respectively. They reported different peaks for raw fibers at 230 °C (endothermic peak), 350 °C (endothermic peak) and 400 °C (exothermic peak) because of degradation of cellulose, aliphatic moiety and aromatic rings (present in lignin), respectively. However, after furfuryl alcohol treatment a shift in lignin decomposition peak, which generally occurs above 300 °C, to lower temperature has been affirmed by them, which states poor stability of grafted fibers.

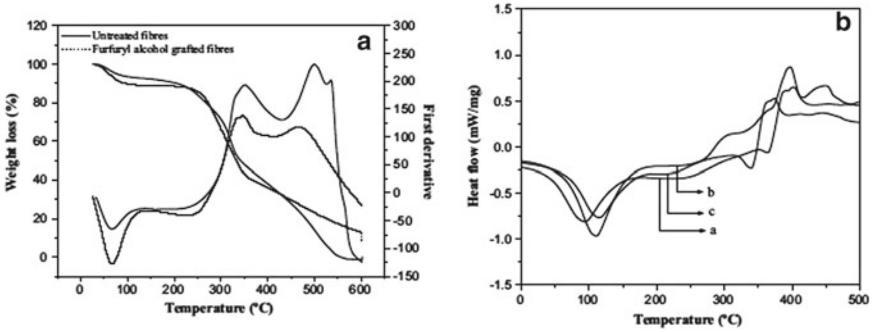

Fig. 4 **a** TGA/DTA curves of raw and grafted fibers and, **b** DSC curves for, **a** raw, **b** chlorite treated and, **c** grafted fibers [38]. Reprinted from Saw et al. [38], Copyright 2011, with permission from Elsevier

2.5 Thermal Stability of Flax Fibers

Wang et al. [39] evaluated the impact of chemical techniques including silane, benzoylation and dicumyl treatment on thermal stability of flax fibers. They pronounced growth in melting point of fibers after chemical treatments and was reported maximum for silane treated fibers (153.15 °C) followed by benzoyl chloride (149.33 °C), dicumyl peroxide treated fibers(147 °C) and virgin fibers (146.92 °C). Velde and Baetens [40] have studied thermal stability of four different Scutched flax fibres samples, coded as VC001, VC002, VC003 and VC007, which corresponds to scutched long green, scutched long under retted, scutched long normal retted and scutched long green respectively, under air and nitrogen atmosphere. Three peaks have been observed in the DTA curve of all samples. The first peak is assigned to the water evaporation, second and third peaks correspond to the degradation/decomposition of cellulose and hemicelluloses, and of non-cellulosic materials respectively. They reported that thermal stability of fibers depends upon retting process and also atmosphere medium for TGA. Seghini et al. [41] reported positive impact on thermal behaviour of flax yarns after its treatment with Peclyve enzyme solutions. After comparing the temperature for 10% weight loss for different samples they found that flax yarns handled with Peclyve 10 wt% for 6 h have highest thermal stability (325.5 °C) followed by flax yarns handled with Peclyve 10 wt% for 4.5 h (322.8 °C) and neat flax yarn (311.3 °C). In addition Seghini et al. [42] also mentioned increase in thermal stability of flax yarns after its modification through super critical carbon dioxide. FDT and temperature at 10% weight loss for flax yarn and functionalized fibers have been stated to be 357.2 and 363.4 °C; and 311.3 and 313.9 °C respectively.

Kaith and Kalia [43] made a comparative study of thermal stability of flax fibers-g-poly MMA samples synthesised beneath distinctive reaction conditions i.e. in air (IA), under reduced pressure (UP) and in microwave radiations (MWR). A decrease in thermal stability has been stated by them after graft copolymerization. The IDT and FDT of flax fiber, fibers-g- MMA-IA, fibers-g- MMA-UP and fibers-g- MMA-MWR had been observed to be 279.9 and 489.1 °C; 248.7 and 436.3 °C; 248.1 and 418.2 °C; 207.9 and 436.2 °C, respectively. In addition Kalia and Kaith [44] also evaluated the effect of binary monomers mixture [MMA + vinyl acetate (VA), MMA + acrylamide (AAm) and MMA + styrene (Sty)] graft copolymerization on thermal stability of resulted graft copolymers. A three stage decomposition process for graft copolymers was reported. IDTs and FDTs of flax fiber, flax fiber-g-poly(MMA + VA), flax fiber-g-poly(MMA + AAm) and flax fiber-g-poly(MMA + Sty) was determined to be 279.9 and 489.1 °C; 313.2 and 457.7 °C; 286.9 and 499.9 °C; 316.7 °C and 454.4 °C, respectively. Among all samples, flax fiber-g-poly(MMA + AAm) graft copolymer was stated to have better thermal strength. The TGA results of above samples were further also supported by differential thermal analysis data. Two stages decomposition process has been stated by Kaith et al. [45] during the thermal study of mercerized flax fibers and mercerized flax fiber-g-poly(MMA). A weight loss of 31.5 and 39.33%; and 59.5 and 36.67% has been found for mercerized and grafted flax fibers in temperature ranging from 307.2–345.4 °C and 345.4–559.3 °C; and 277–331.6 °C and 331.6–446.6 °C, respectively. They reported decrease in thermal stability after graft copolymerization of MMA onto mercerized flax fibers. The IDTs and FDT s of mercerized flax fiber and mercerized flax fibers-g-poly (MMA) were stated to be 307.2 and 559.3 °C; and 277 and 446.6 °C, respectively. So we can conclude, in contrast to primary monomer graft copolymerization, the surface changes strategies such as mercerization, benzoylation, silanation etc. have nice impact on thermal stability of flax fibers. Further binary monomer mixtures graft copolymerization strategies have excellent effect on thermal stability when compared with aforementioned techniques.

2.6 *Thermal Stability of Grewia Optiva Fibers*

TG analysis data for raw Grewia optiva (GOFs), mercerized [treated with 8, 10 and 12% solution (w/v) of NaOH], silane treated [treatment with 2, 3 and 5% aminopropyltriethoxy silane solution (w/v) in 60/40 ethanol/water] [46], benzoyl chloride treated [5% benzoyl chloride solution in 10% NaOH solution] [47], GOFs-g-poly(AN)-in air [48]/under MWR [47] and GOFs-g-poly(AAc)-in air/MWR [49] copolymers have been depicted in Table 3. Three stage decomposition process have been reported for untreated as well as for treated GOFs, first degradation occurs in between 100 and 220 °C (due to moisture), second one from 250 to 400 °C (partial degradation of cellulose, hemicelluloses and lignin) and third degradation occurs in between 400 and 700 °C (cellulose further degradation). For the raw GOFs IDT and FDT has been stated to be 262.65 °C and 381.06 °C, respectively. However, among various surface modification techniques, mercerization, silane treatment and AN graft copolymerization in air/under MWR showed positive impact on thermal stability of resulted fiber i.e. better thermal stability than raw GOFs. Also, if we make a comparison among mercerized, silane treated and AN graft copolymerized GOFs synthesised in

Table 3 TGA data of the raw, mercerized, silane treated and benzoylated, GOFs-g-poly(AN)-in air/under MWR and GOFs-g-poly(AAc)-in air/under MWR. Reused with permission from cited references

S. No	Sample designation	IDT (°C)/% wt loss	FDT (°C)/% wt loss	DT (°C) 60% Wt loss	References
1	Raw	262.65	381.06	381.06	[46]
2	8% alkali treated	263.01	396.20	381.78	
3	10% alkali treated	262.90	395.29	382.10	
4	12% alkali treated	262.65	394.26	379.06	
5	2% silane treated	262.14	388.69	409.00	
6	3% silane treated	270.01	395.19	447.68	
7	5% silane treated	269.53	395.41	408.53	
8	5% benzoylated fiber	250.22	395.39	374.56	[47]
9	GOFs -g-poly(AN)-IA	264.07	385.75	461.18	[48]
10	GOFs -g-poly(AN)-Under MWR	265.1	404.00	370.10	[47]
11	GOFs -g-poly(AAc)-IA	250.09	407.75	368.31	[49]
12	GOFs -g-poly(AAc)-Under MWR	257.54	399.70	359.83	[49]

air/under MWR, than silane treated fiber has been found to possess better IDT/FDT than alkali treated and AN graft copolymerized fibers, which account for its better thermal strength. For benzoyl chloride treated fiber, the IDT and FDT values were reported to be 250.22 and 395.39 °C, respectively. Diminish in thermal behaviour after benzoylation in comparison to raw and mercerized fiber has been assigned because of disturbance of crystalline structure after functionalization. The enhancement in thermal stability after mercerization, silane treatment and AN graft copolymerization has also been supported by others workers [50] and has been assigned due to strong covalent bonding between fibers surface and attached bulky groups.

Further for GOFs-g-poly(AAc)-IA and GOFs-g-poly(AAc)-under MWR the IDT and FDT have been found to be 250.09 and 257.54 °C; and 407.75 and 399.70, respectively. Decrease in IDTs for AAc graft copolymerized GOFs could be due to the degradation of anhydride of grafted AAc chains to CO_2 in between 150–275 °C [51]. The overall trend obtained for thermal stability for surface functionalized fibers is: 3% silane treated GOFs > 5% silane treated > 2% silane treated > 8% alkali treated > 10% alkali treated > 12% alkali treated > *GOFs*-g-poly(AN)- Under MWR > *GOFs*-g-poly(AN)- in air > raw fiber > 5% benzoylated fiber > *GOFs*-g-poly(AAc)-IA > *GOFs* -g-poly(AAc)-under MWR. Above results have also been supported by comparing the degradation temperature for 60% weight loss. In addition Singha et al. [52] also found increase in thermal behaviour of functionalized GOFs after evaluating the TG data of raw, delignified and MMA graft copolymerized fibers. The IDTs and FDTs values for raw, delignified and GOFs-g-poly(MMA) fibers were stated to be 241.18 and 356.38 °C; 250.13 °C and 375.39 °C; and 261.13 and 432.18 °C, respectively. Comparable sorts of results were likewise detailed by different analysts [52, 53].

2.7 *Thermal Stability of* Cannabis Sativa *(Hemp) and* Cannabis Indica *(Indian Hemp) Fibers*

Cannabis Sativa, which is commonly called as Hemp fibers, finds its origin in equatorial countries such as in Thailand, Mexico, Colombia, and so forth, whereas *Cannabis Indica*, which is commonly, called as Indian hump fibers, originates from cold area in Asian subcontinent such as in India, Pakistan, Bangladesh, etc. So we will discuss their stability one by one.

2.7.1 Hemp Fibers

Thermal degradation of untreated/surface modified hemp fibers was reported to occur in two phases in temperature between 110 and 200 °C (with a weight loss of approx 8%) and 250–360 °C (with 72% wt. loss). The initial weight loss has been assigned because of water contents; however weight loss after 250 °C could be because of degradation of fiber's constituents such as cellulose, hemicelluloses and lignin. Out of various constituents of hemp fibers, hemicellulose is least stable and decomposes around 300 °C; Lignin, which has better stability, degrades in between 300 and 450 °C and subsequently highly stable Cellulose decomposes in temperature range 275–550 °C [54]. The thermal stability of Hemp fibers after its functionalization through mercerization, silane and acetic anhydride treatment is located to be higher than that of virgin fiber by Lu and Oza [55] and Oza et al. [56]. The better thermal performance of Mercerized fibers (immersion in NaOH solution 5 wt%, for 24 at 50 °C) than raw fibers has been assigned because of removal of impurities such as wax, pectin and hemicelluloses, which usually decomposes at low temperature. Further, silane and acetic anhydride treated fibers also showed better thermal strength than raw hemp fibers because of formation of covalent bond with functional groups. The thermal stability trends obtained after surface treatment was found to be; mercerized fibers > acetic anhydride treated fiber > silane treated > raw fiber. Panaitescu et al. (2014) also stated enhancement in thermal behaviour of hemp fibers after its surface modification by 3-aminopropyl triethoxy silane (3%w/v) and further used these surface modified fibers as reinforcement for composite fabrications. Kalia et al. [58] evaluated the TGA/DTG data of sunn hemp fiber (SHFs), SHFs-g-polyethylacrylate(EA), SHFs -g-poly (EA + MMA) and SHFs -g-poly(EA + AA) graft copolymers, and reported increase in thermal stability behaviour after principal or binary monomer mixtures graft copolymerization. They reported higher thermal stability of SHFs -g-poly(EA + AA) graft copolymers followed by SHFs-g-poly (EA + MMA), SHFs -g- EA and raw hemp fibers.

2.7.2 *Cannabis Indica* (Indian Hemp Fibers*)*

Similar to Hemp fibers, Indian Hemp fiber also showed a preliminary weight reduction of around 8.5% before 100 °C followed by a loss of around 50% wt. in temperature ranging from 200 to 350 °C and is finally accompanied by a weight loss approx. 37.5% in between 350 and 490 °C [59]. The first stage decomposition in between 220 and 320 °C might be because of complex reactions other than hemicellulose degradation [60, 61]. The second stage decomposition has been assigned because of cellulose degradation and char.

An increase in thermal strength of raw Indian hump fibers after its surface modification by alkali and silane treatment has been mentioned [59]. For the raw fibers, 10% alkali treated and 2% silane treated fibers, the IDTs and FDTs has been found to be 287 and 490 °C; 285 and 507 °C; 330 and 540 °C, respectively. Contradictory to above effects, decrease in thermal strength has been cited after benzoyl chloride treatment onto mercerized fibers [62]. Impact of AN/AAc graft copolymerization in air and under MWR on thermal stability of resulted graft copolymers was also mentioned by Singha et al. [62–64].

For *Cannabis indica(CIFs)*-g-poly(AAc)-IA and CIFs -g-poly(AAc)-under MWR, IDTs and FDTs were reported to be 236.9 °C and 388.68 °C; 248.9 °C and 566.18 °C, respectively [63, 64]. These values without a doubt indicate a slight decrease in the IDT and a considerable increase in FDT value and overall we can say there is a poor impact of AAc graft copolymerization on thermal strength of resulted fibers. However, after AN grafting thermal strength has been noticed to be enhanced. The IDTs and FDTs values for CIFs -g-poly(AN)-IA [65] and CIFs -g-poly(AN)-under MWR [62] were stated to be: 290.1 and 395.4; 263.8 and 391.1 °C, respectively. All above consequences have been further supported through DTA/DTG studies.

2.8 Thermal Stability of Kapok Fiber

Macedo et al. [66] investigated the impact of cold plasma treatment on thermal stability of Kapok fibers and compared its stability with raw fibers. After TGA evaluation, they found that plasma treated fibers have a little bit higher weight loss in the initial stage in between 30 and 100 °C. This is because of the presence of free oxygen or vulnerable bonds onto the surface of plasma treated fibers which result in polarity change and causes improved wettability in some liquids. Above 100 °C, plasma treated and raw kapok fibers showed almost identical thermal behaviour (Fig. 5). Jamat and Asik [67] reported that raw and alkali treated kapok fibers undergo

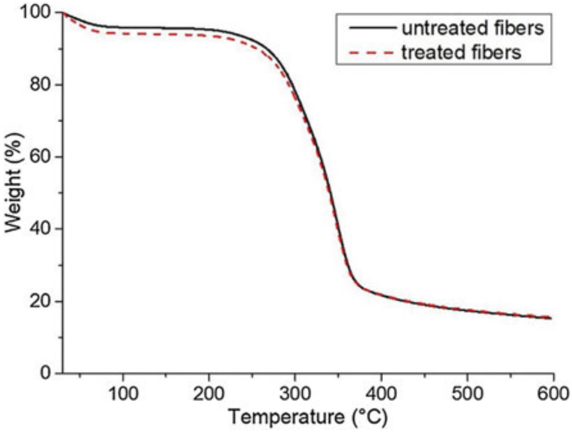

Fig. 5 TGA thermograms of raw and plasma treated Kapok fibers [66]. Reprinted from [66], Copyright (2020), with permission from Elsevier

decomposition in two major stages. The raw fiber decomposition starts at 280 °C with the deterioration of cellulose and hemicelluloses [68] and continue until it reaches the finishing touch decomposition temperature at 575 °C [69]. However, for alkali treated kapok fibers, the decomposition temperature started at 315 °C and continue till 560 °C; and during this stage, complete decomposition of cellulose present in kapok fibers was reported due to oxidative degradation and crystallite structure deterioration. In addition to alkali treatment, the impact of bleaching on thermal strength was also evaluated by Draman et al. [70] through TGA/DTG techniques. They also revealed better thermal strength of NaOH treated fibers than raw and bleached fibers.

2.9 Thermal Stability of Kenaf Fibers

Chung et al. [71] investigated the thermal behavior of raw and acetylated kenaf fibers by employing TGA technique and reported degradation in two major stages: 250–330 °C, and 340–400 °C. However in addition to two major weight losses, a preliminary weight reduction below 110 °C was also reported because of moisture evaporation. They compared the temperature for different weight losses (5, 10 and 50%) for raw and acetylated fibers and reported better stability for acetylated fibers. Further, effect of time (0.5, 1, 2, 3 h) of acetylation on thermal strength of resulted fibers was also evaluated and stated that with increase in acetylation time thermal stability of resulted fiber increases. The IDT and FDT for raw and 3 h acetylated kenaf fibers were stated to be 270 and 402 °C; and 305 and 403 °C, respectively. Azwa and Yousif [72] also reported increase in thermal strength after 6% alkali treatment of kenaf fibers.

2.10 Thermal Stability of Okra Fibers

The thermal characteristics of raw and functionalized okra fibers (OFs) were studied by De Rosa et al. [73] and they reported 220 °C onset temperature for thermal deterioration for okra fiber. The OFs was found to decompose in two phases. In the first phase, there was a weight loss of around 16.1% in temperature range 220–310 °C, which can be because of degradation of hemicelluloses, pectin and cleavage of glycosidic linkage. In second degradation step an additional weight loss of 60% was observed in temperature range 310–390 °C, which has been assigned due to decomposition of lignin and alpha cellulose.

Stawski et al. [74] have compared the thermal stability of water/dew emaciated upper, lower and middle okra bast fibers samples which were coded as BBW (Water-emaciated bottom fiber), MBW (Water- emaciated middle bast fiber), UBW (Water-emaciated upper fiber), BBD(Dew- emaciated bottom fiber), MBD (Dew- emaciated middle fiber) and UBD (Dew- emaciated upper bast fiber). The TGA curves have been depicted in Fig. 6. On comparing the data it has been obtained that Dew retted middle bast fibers is thermally more stable and is highly suitable for reinforcement purpose. Also on comparing the water retted and dew retted technique, the letter one is found to be more suitable.

Rosa et al. [75] investigated the impact of sodium carbonate (SOFs), acetylation (AOFs), bleaching followed by acetylation (ABOFs), bleached (BOFs), sulphuric acid followed by potassium permanganate (SAKPOFs) and sodium dodecyl sulphate (SSOFs) and sodium chlorite followed by mercerization (MSOFs) treatment on thermal stability of okra fibers (ROFs) by employing DTG techniques and reported decline in thermal behaviour after modification. The increasing trend obtained after comparing weight loss at T50% or by comparing temperature for maximum degradation was found to be: raw okra fibers ROFs ($T_{50\%} = 349.9$ °C; $T_{max} = 358.6$ °C) > SAKPOFs(348.9 and 353.8 °C) > SOFs(347.6 and 353.3 °C) > AOFs(343.4 and 350.5 °C) > MSOFs (339.4 and 341.1 °C) > ABOFs (336.1 and 339.8 °C) > BOFs (332.7 and 342.2 °C) > SSOFs (329.8 and 335.7 °C). The reduction in thermal strength after chemical treatments could because of the disruption in crystalline structure of cellulose. However, contradictory results were reported by Singha et al. [76] during the thermal evaluation for binary monomer mixture graft copolymerized fibers. The IDTs and FDTs for untreated raw fiber and OFs-g-poly[MMA and EA] were stated to be 228 and 466 °C; 244 and 518 °C, respectively. The better thermal characteristics of OFs could be due to formations of covalent bonds between fiber backbone and grafted polymer chain. Guleria et al. [77] also reported similar kind of result after binary monomer mixture (acrylamide-co-acrylic acid) graft copolymerization onto OFs during TGA analysis.

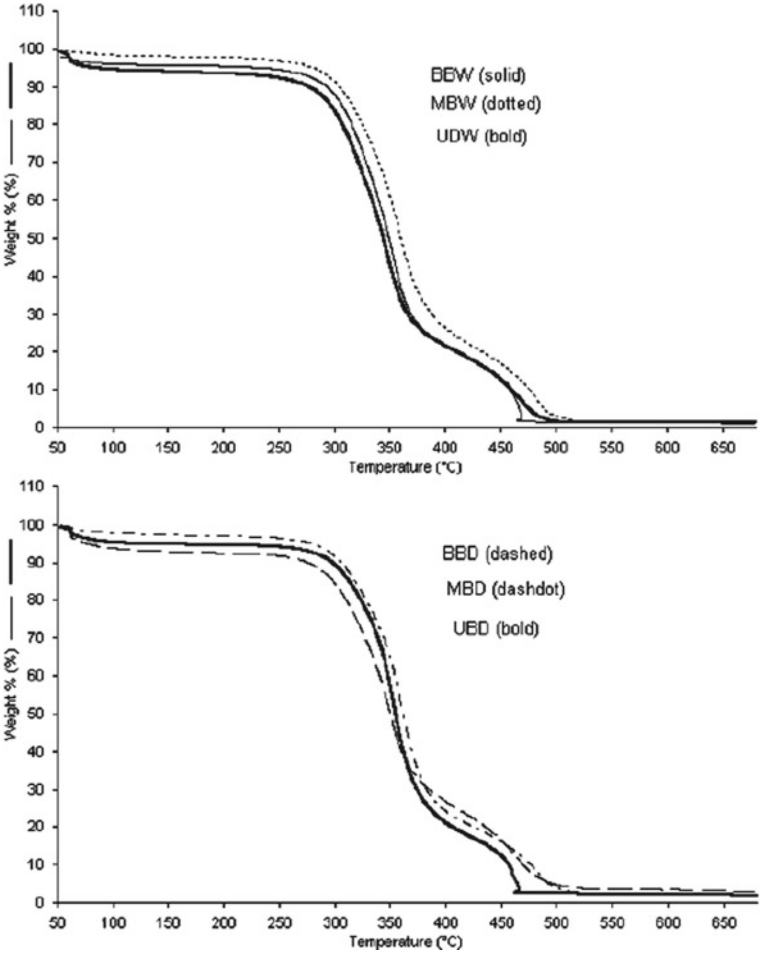

Fig. 6 TGA curves of different analyzed samples [74]. (Reprinted under Creative Commons licence 4.0 from Ref. [74]

2.10.1 Thermal Stability of Pine Apple Leaf Fibers (PALFs)

Due to high cellulosic contents in PALFs, it seems to have better fire retardant behaviour than other VFs. Raw and alkali treated PALF specimens showed three DTA peaks (Fig. 7), constituting moisture evaporation at first pinnacle, holocellulose and lignin deterioration at the second and degradation of cellulose at the preceding peak [78]. In general the second decomposition peak is the utmost decisive in analyzing the stability of fibers and after analyzing TGA/DTG curves, it can be observed that thermal stability of PALFs increased considerably after alkali treatment. Mohanty et al. [79] reported better thermal durability of AN grafted fibers than raw fibers. The reported IDTs and FDTs values for raw and graft copolymerized fibers were 220 and

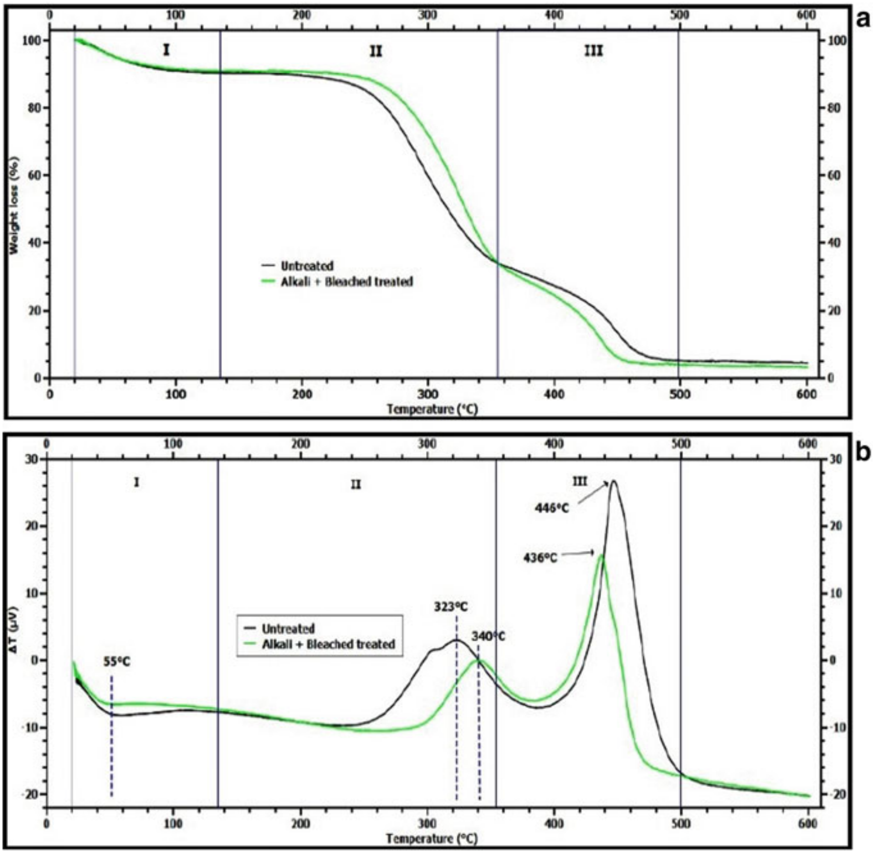

Fig. 7 TGA/DTA curves for raw and alkali + bleached pineapple leaves. Reprinted with permission from [78]

370 °C; and 260 and 390 °C respectively. Maniruzzaman et al. [80] investigated the outcome of numerous chemical techniques such as NaOH, bleaching and AN grafting on thermal stability of modified fibers. After TGA/DTA/DTG analysis, they reported better thermal stability for AN graft copolymerized fibers followed by bleached, raw and alkali functionalized fibers.

2.10.2 Thermal Stability of Pita (Agave Americana) Fiber

Similar to other VFs, thermal degradation (aside from preliminary wt. loss because of moisture evaporation) of *Agave Americana* (AAFs) has been also found to take place in two distinctive steps. In first step, a wt. loss of 50.6% weight was observed in between 240 and 346 °C accompanied by a further wt. loss of 32.3% in temperature range 346–432 °C in preceding step. [81]. In addition, on grafting thermal durability of AAFs has been reported to be boosted. Singha and Rana [81–86] evaluated the effects of principal/binary monomer combinations graft copolymerization onto thermal properties of AAFs and results had been further supported by DTA peaks, which affirm that thermal decomposition of AAFs takes place in two steps. On comparing the impact of graft copolymerization onto thermal strength then following trend was observed: AAFs-g-poly(AN) in AIR [IDT = 252 °C and FDT = 550 °C] > AAFs-g-poly[AN-co-ethylacrylate (EA)] (251 and 525 °C) > AAFs-g-poly-MMA-co-AN (250 and 500 °C) > AAFs-g-poly(MMA)-under MWR (251 and 489 °C) > AAFs-g-poly-MMA- in air (280 and 465 °C) > Raw AAFs (240 and 432 °C). The improved thermal stability after graft copolymerization was stated because of better thermal stability of grafted polymer chain than raw fiber which protects the cellulosic materials from decomposition.

2.10.3 Thermal Stability of Roselle (Hibiscus Sabdariffa) Fiber

Roselle fibers also showed three step degradation mechanisms [87]. For raw Hibiscus sabdariffa (HSFs), IDT and FDT has been located to be at 225.7 and 463 °C, respectively. However, after surface functionalization an enormous growth in thermal strength was noted. Maximum thermal strength was determined for HSFs -g-poly[Ethyl Acrylate (EA)] [88] followed by HSFs -g-poly[Methyl Acrylate (MA)] [89], HSFs -g-poly(MA + AN) [87], HSFs -g-poly (MA) + VA) [87], Silane Treated HSFs [90], HSFs -g-poly(MA + AAc[87], HSFs -g-poly(MA + AAm) [87] and Raw HSFs. A significant increase in thermal strength after graft copolymerization has been attributed due to solid covalent bond arrangement among cellulose and united polymer chain.

2.10.4 Thermal Stability of Ramie Fibers

During thermal study of Ramie Fibers (RFs) through TGA, it has been noticed that RFs undergoes preliminary decomposition in between 100 and 120 °C, accompanied by a major degradation in temperature range 285–405 °C and eventually a minor degradation beyond 405 °C [91]. However, after mercerization increase in thermal stability has been stated. Contrary to above outcomes, thermal strength of epichlorohydrin/ethylenediamine modified RFs was reported to lower than raw fibers. Kalia and Renu [92] figured out the effect of microwave facilitated MMA grafting and cellulase enzyme (Streptomyces albaduncus) facilitated burnishing on thermal durability of resulted RFs. They found that IDTs and FDTs for raw, RFs-g-poly(MMA) and Streptomyces albaduncus modified fibers are 300 and 430 °C; 300 °C and 375 °C; and 200 and 425 °C, respectively. Decline in thermal strength after MMA grafting onto RFs has been assigned because of disturbance in crystalline lattice structure after chemical remedies. In addition to above study, Kalia et al. [93] also determined the impact of *Brevibacillus parabrevis* (bacteria) modification and microwave assisted binary monomer mixtures graft copolymerization on thermal strength of resulted fibers via TGA/DTA. They found a decrease in thermal strength after chemical grafting and suggested the following trend for surface modified fibers; RFs (with IDT = 300 and FDT = 430 °C) and RFs-g-poly(MMA + AN) (300 and 430 °C) followed by RFs-g-poly(MMA + EA) (300 and 425 °C), RFs-g-poly(MMA + VA) (250 and 419 °C), RFs-g-poly(MMA + AA) (200 and 413 °C) and RFs modified with bacteria *Brevibacillus parabrevis* (IDT = 300 °C and FDT = 363 °C). So overall, we can say that besides mercerization there is negative impact of chemical or bacterial treatment on thermal stability of RFs.

2.10.5 Thermal Stability of Sisal Fibers

Thermal durability of raw, defatted sisal fiber (SFs) and its ingredients was executed via TGA and DSC techniques in air as well as in nitrogen atmospheres [94]. Degradation process has been found to rely on kind of atmosphere involved (nitrogen or air). For example, in nitrogen atmosphere SFs and its constituents exhibited distinct endothermic peaks in DSC curve, whereas in air only two exothermic peaks have been observed for all samples. Further, TGA outcomes had also been corroborated by the results obtained through DSC. Cellulose and hemicellulose have been found to degrade at lower temperatures when compared with raw SFs, it could be due to the elimination of lignin.

Increase in thermal stability of SFs has been observed after surface functionalization through bacterial cellulose or via graft copolymerization of MMA [95]. The thermal decomposition, in case of SFs, was discovered to be in two phases with weight reduction of 50.4 and 9.7% in between 250 and 363 °C and 363–451 °C, separately. However, an additional the weight loss of 6.6% in temperature range 100–200 °C was attributed due to depolymerisation and glucosan formation. Much like raw SFs, SFs-g-poly(MMA) and SFs modified by bacterial cellulase, also confirmed two step degradation with weight loss of 72.3% and 3.9%; 68.1% and 3.6% in the temperature range of 250–425 °C and 425–500 °C respectively. The IDTs and FDTs for SFs, SFs-g-poly(MMA) and bacterial cellulose managed SFs have been observed to be 250 and 363 °C; 250 and 425 °C; and 249 and 425 °C, respectively. After analysing the information it was found that surface modified fiber is thermally stronger.

Orue et al. [96] also mentioned increase in thermal stability after mercerization and silane treatment of SFs. Untreated and alkali treated fibers exhibited a weight reduction of 4% at 100 °C that is associated to water evaporation; however no such weight loss was observed after silane treatment which may be due to advancement of hydrophobic behaviour after modification. They further reported two deterioration pinnacle at 298 and 355 °C in DTA curve. However in case of alkali treated fibers no such weight reduction was observed at 298 °C, which means that hemicelluloses has been removed after alkali treatment [97]. The stability trend obtained was silane treated fiber > (alkali + silane) treated fiber > alkali treated > untreated SFs.

Chand et al. [98] during their DSC study of SFs, grafted SFs, Ag ion loaded SF and Ag nano particle loaded SFs found that all samples undergoes decomposition in two stages and their thermal stability was found to decrease after grafting however after silver particle loading, the fiber stability was observed to be increased. Increase in thermal stability was also found after benzoylation and graft copolymerization of methylacrylate onto SFs [99]. IDTs and FDTs of SFs, benzoylated SFs and SFs-g-poly(MA) were reported to be 249 and 370 °C; 220 and 373 °C; 240 and 405 °C with maximum weight loss of 78.4; 72.7; and 71%, respectively.

Naguib [100] studied the impact of the graft copolymerization on the thermal durability of SFs by using TGA technique and observed a decline in the thermal strength after graft copolymerization. This could be because of poor thermal stability of poly-itaconic acid. Similar consequences have been also reported for dimethyl itaconate grafted microcrystalline cellulose [101]. Development in thermal stability has been pronounced for SFs after binary monomer combos graft polymerization [102]. IDTs and FDTs of SFs and distinctive binary monomer mixture graft copolymers; sisal-g-poly[MA + vinyl acetate(VA)], sisal-g-poly[MA + n-butyl acrylate (BuA)] and sisal-g-poly(MA + AAc) were stated to be 249 and 370 °C; 300 and 380 °C; 300 and 400 °C; 313 and 390 °C, respectively. Increase in thermal performance after grafting might be due to the boost in crystal structure of cellulose.

3 Thermal Stability of Phenolic Matrices and Different VFs Reinforced Polymer Composites

Thermoset matrices are exceptionally cross-connected dense materials and are valuable in diverse commercial applications which require high-mechanical strength. In additions these materials also provide high mechanical modulus, physical, thermal and chemical stability [103]. Interestingly, phenolic matrix, is one of the thermoset resin and features several benefits over traditional thermoplastic or other thermoset resins, including [104].

- Marvellous rigidity, adhesive properties and mechanical strength
- Exceptional dimensional stability at elevated temperatures
- Outstanding thermal properties
- High flame resistant property
- Excellent chemical resistivity.

The future of the phenolic composites market is quite appealing and is expected to arrive at $11.7 billion by 2025 with a CAGR of approx. 4% from 2020 to 2025 [105]. The significant drivers for development in this market are expanding usage of materials, with fire retardant, wear resistant, and anti corrosive properties in end user applications.

3.1 Thermal Stability of Phenol–formaldehyde and Derived Composites

Both self made phenol formaldehyde (SMPF) and commercial made phenol formaldehyde matrices (CMPF) had been utilised by researchers for studying the mechanical and thermal attributes of resulted composites. Chen et al. [106] made a comparative examine on thermal stability, types of volatiles gaseous evolved and structure changes occur during heating of these two forms of phenol formaldehyde matrix by using TGA (nitrogen atmosphere), mass spectroscopy and solid-state ^{13}C NMR techniques, respectively. The TGA curves of SMPF as well as CMPF showed continuous weight loss for both matrix forms in three steps and their thermal stability behaviour was additionally supported through three overlapped peaks in DTG curves. A higher thermal stability was reported for SMPF in comparison to CMPF with the residual weight of 74.78% and 57.45% at 700 °C, respectively.

After the analysis of Mass spectra of major ions evolved during pyrolysis, they found that both SMPF and CMPF release same kinds of volatile gases, however their amount and temperatures of emission may be different. The pyrolysis products of CH_4, C_6H_5-OH and C_6H_5-CH_3 had been determined to be comparable for both matrixes. Also, the quantity of CH_3OH and H_2O evolved in SMPF had been stated to be much higher than that in CMPF. The series of pyrolysis products, obtained on the basis of their amount, in case of SMPF was found to be: Water > Methane > Carbon mono-oxide > Hydrogen gas > Carbon dioxide > C_6H_5-R > Methanol. However, in case of CMPF trend obtained was; Water > Methane > Hydrogen gas > Carbon monooxide > C_6H_5-R > Carbon dioxide > methanol.

On analysing ^{13}C-NMR spectra of SMPF and CMPF residues, acquired after heating to 573, 673 and 873 K they found comparable changes in spectra of residues samples. In addition, they also reported a higher number of non-substituted aromatic orth-sites and a better percentage of methylene links in cured SMPF than cured CMPF, which further supports their Mass spectroscopy results for the much higher formation of methanol and water in SMPF than CMPF. Singha and Thakur [107] also found similar results during thermal decomposition of SMPF (having percent residue of 51.47 at 1195 °C) and the results had been also supported through DTA/DTG studies. The IDT and FDT for SMPF had been reported to be 400 and 1195 °C, respectively. In addition, Singha et al. [107–110] have also used three types of VFs namely raw GOFs, SCFs and HSFs for the fabrication of VFs reinforced SMPF composites. During thermal analysis, they found that thermal degradation of VFs reinforced SMPF composites falls in between thermal degradation of SMPF matrix and the raw VFs. The IDTs and FDTs for GOFs reinforced SMPF, SCFs (Roselle fibers) -Rnf-SMPF, HS particles-Rnf-SMPF and HS Short fiber-Rnf-SMPF composites have been stated to be 337.0 and 989 °C; 250 and 900 °C; 330 and 980 °C; and 327 and 976 °C, respectively. So, we can say that presence of VFs affects the decomposition process.. Milanese et al. investigated the thermal endurance of sisal fibers fortified CMPF composites by employing DTA/TGA technique and during study they found three steps degradation process for both [111] CMPF and CMPF reinforced composites. Khan and co-workers [112] have evaluated the CMPF matrix, OBF-Rnf-PF, Alkali treated OBF-Rnf-PF composites for their thermal strength and their results have been depicted in Table 4. We can conclude from table that CMPF have poor thermal strength than SMPF matrix and further on reinforcement with raw OBFs, the thermal strength of resulted CMPF composites decreases. This is because of poor thermal stability of raw VFs than CMPF matrix. Enhancement in thermal strength had been noticed by them on reinforcement of CMPF matrix with alkali treated OBFs. Increase in thermal strength of VFs reinforced CMPF matrix, after surface functionalization of VFs had been also reported by Joseph et al. (Table 4) [31]. They have studied the effects of alkali, vinyl silane, amino silane, heat, cyanoethylated and latex on thermal stability of resulted BFs reinforced CMPF composites. Higher thermal strength was reported for Vinyl silane treated BFs-Rnf- CMPF followed by amino silane treated BFs-Rnf- CMPF, cyanoethylated BFs-Rnf- CMPF, alkali treated BFs-Rnf- CMPF, heated BFs-Rnf- CMPF, latex treated BFs-Rnf- CMPF and raw BFs-Rnf-CMPF composites. The enhancement in thermal strength for surface modified VFs reinforced CMPF composites could be because of the better compatibility between CMPF matrix and VFs after surface functionalization, as surface modification technique develops hydrophobic character on fiber surface and thus may lead to strong adhesion with hydrophobic matrix. Asim et al. [113] also expressed comparative sort of results during assessment of the outcome of silane treatment on thermal durability of resulted PALF and Kenaf fibers reinforced CMPF composites. They further reported that percent loading of VFs impacts the strength and found to diminish with increment in percent fiber loading.

3.2 Thermal Stability of Resorcinol–Formaldehyde and Derived Composites

Self made Resorcinol Formaldehyde (SMRF) matrix had been desired over CMRF by numerous researchers for the fabrication of polymer composites. During TG analysis, SMPF matrix has been found to show nonstop weight reduction in close three steps, which is very much similar to SMPF matrix and had been further supported through three overlapped DTA peaks [115–117]. The IDT and FDT for SMRF polymeric matrix had been reported to be 299 and 990 °C, respectively [109]. Singha et al. have used different forms of raw GOFs, HSFs and SCFs for fabrication of VFs-Rnf-SMRF composites. During thermal evaluation of polymer composites they found that thermal strength of fibers reinforced composites samples lies in between the strength of virgin matrix and raw fibers. The IDTs and FDTs for particle SCFs-Rnf-SMRF composites [117], short SCFs-Rnf-SMRF composite [118], particle GOFs-Rnf-SMRF composite [119] and particle HSFs-Rnf-SMRF composite samples [120] have been reported to be 248 and 943 °C; 241 and 935 °C; 250 and 950 °C; and 250 and 942 °C, respectively. The TGA data have also been supported through DTA/DTG as presented in Table 4. Further, on comparing thermal strength of aforementioned

Table 4 Thermal strength of various VFs reinforced phenolic composites

S. No	TG analysis				DTA Analysis	DTG Analysis	References
	Sample code	IDT (°C)/%wt loss	FDT (°C) %wt. loss	Residue (%)	Exothermic/Endothermic peaks °C (µV)	Exothermic peaks temperature (mg/min)	
1	Self Made Phenol Formaldehyde Matrix (SMPF)	400/15.68	1195/48.53	51.47	164 [9.0]; 421 [6.0	156 [112.8]; 215 [114.9]; 416 [126.1]; 490 [235.5]	[107]
2	GOFs reinforced SMPF composites	337/21.39	989/53.84	46.26	69 [−4]; 335 [−5]; 695 [−35]	59 [53]; 179 [67]; 325 [282]; 547 [110]	
3	*SCFs (Roselle fibers)* -Rnf-SMPF	250/19.73	900/84.12	15.05	412 [14]; 75 [0]	–	[108]
4	HS particles-Rnf-SMPF	330/25.39	980/58.11	41.89	63[−2]; 687[−27]	55[50]; 317[264]; 528[104]	[109]
5	HS Short fiber-Rnf-SMPF	327/28.2	976/64.3	35.6	52[45]; 309[257]; 478[59]; 520[97]	60[−9]; 579[−17]; 681 [−32]	[117]
6	CMPF matrix	390/0.25	490/0.00	0.00	–	–	[112]
7	OBF-Rnf-CMPF	340/6.21	490	7.95	–	–	
8	Alkali treated OBF-Rnf-CMPF composites	358/6.01	490	7.41	–	–	
9	CMPF matrix	490/13.5	820/81	19.00	–	200; 500; 700	[31]
10	BFs-Rnf-CMPF	230/23.00	595/100	0.00	–	46; 305; 402; 510	

(continued)

Table 4 (continued)

S. No	TG analysis				DTA Analysis	DTG Analysis	References
	Sample code	IDT (°C)/%wt loss	FDT (°C) %wt. loss	Residue (%)	Exothermic/Endothermic peaks °C (µV)	Exothermic peaks temperature (mg/min)	
11	Alkali treated BFs-Rnf-CMPF	250/13.7	600/50.1	49.90	–	84; 309; 392; 511	
12	Vinyl silane treated BFs-Rnf- CMPF	250/13.8	600/42.3	57.20	–	82; 311; 397; 535	
13	Amino silane treated BFs-Rnf- CMPF	255/14.6	600/56.0	46.00	–	60; 312; 394; 502	
14	Heated BFs-Rnf-CMPF	251/17.5	600/52.9	47.10	–	63; 306; 388; 482	
15	Cyanoethylated BFs-Rnf- CMPF	252/15.7	600/50.1	49.10	–	74; 314; 379; 535	
	Latex treated BFs-Rnf-CMPF	249/13.72	600/53	47.00	–	72; 315; 397; 532	
16	SMRF matrix	299/22·64	990/51.78	48·22	65 [–1·0]; 244 [8·0]; 280 [6·0]	–	[109]
17	Particle SCFs-Rnf-SMRF composites	248/14·49	943/57.37	57·48	81[–10·3]	–	[117]

(continued)

Table 4 (continued)

S. No	TG analysis				DTA Analysis	DTG Analysis	References
	Sample code	IDT (°C)/%wt loss	FDT (°C) %wt. loss	Residue (%)	Exothermic/Endothermic peaks °C (μV)	Exothermic peaks temperature (mg/min)	
18	Short SCFs-Rnf-SMRF composites	241/23.67	935/69.37	31.67	74 (−7.5); 81 (−10.3)		[118]
19	Particle GOF-Rnf-SMRF composites	250/19.50	950/57.37	43.63	77 (−8)	–	[119]
20	Particle HSFs-Rnf-SMRF composites	250/14.46	942/64.98	35.12	75(−9.8)	–	[120]

samples it has been found that particle GOFs-Rnf-SMRF composite samples have highest thermal strength, this could be due to high hydrophobic lignin contents in GOFs which may results in better adhesion with matrix. Also we can conclude from above study that fibers dimension plays a major role in matrix and VFs adhesion and mechanical/thermal strength of resulted composite materials. Between particle SCFs-Rnf-SMRF composites and short SCFs-Rnf-SMRF composite samples, the former one was found to be thermally more stable. Thus we can say smaller the size of VFs better will be adhesion with matrix or thermal strength of resulted composite materials.

3.3 Thermal Stability of Others Phenolic Matrix and Derived Composites

There are a few other phenolic matrices inclusive of o-Cresol, m-Cresol and p-cresol. Not much has been mentioned in literature on thermal strength of these matrices. However, Hamou et al. [121] have studied thermal strength of para cresol resin and suggested no degradation earlier than 400 °C and after that a steep degradation was determined by them with a weight loss of almost 60% in between 400 and 435 °C. So we can conclude that thermal strength of cresol resin is not a lot appropriate than phenol formaldehyde and resorcinol formaldehyde matrices. There is some another elegance of phenolic matrix i.e. resorcinol-furfural matrix that have been evaluated for thermal degradation by Liu et al. [122]. Resorcinol-furfural matrix showed a little bit weight loss before 200 °C which had been assigned because of the formation of volatile small molecules at the preliminary stage and is subsequently followed by degradation. The rapid pyrolysis was found in between 350 and 500 °C, because of weakening of methylene and ether bonds in backbone chains. The T_{onset}, $T_{maximum}$ and percent residue for resorcinol-furfural has been stated to be 341, 499 and 62%, respectively. Thus we can conclude that resorcinol formaldehyde and resorcinol furfural have comparable thermal characteristics.

3.4 Thermal Stability of Hybrid Phenolic Composites

The impact of binary raw/treated VFs blends on thermal strength of resulted hybrid Phenolic composites had been assessed by different researchers [123, 124]. Asim and co-workers [9, 124], during thermal evaluation, announced a significant weight reduction of 35–45% in temperature range 278–306 °C at the preliminary stage and a weight loss of 20–25% in between 394 and 411 °C at the final stage for silanated and raw PALF/kenaf fibers- strengthened CMPF hybrid composites. The weight reduction at the preliminary stage has been assigned due to degradation of holocelluloses, lignin, glycosidic linkages of glucose and pectin, whereas at the final stage weight trimming is due to thermal degradation/depolymerisation of both cellulose and phenolic matrix. Anyway they discovered expanded thermal strength for silane treated fibers fortified CMPF composites. The IDTs and FDTs for raw and silanated PALF/kenaf fibers- strengthened CMPF hybrid composites have been reported to be 278.57 and 397.66 °C; and 303.24 and 410.65 °C, respectively. The TGA results were likewise supported through DTG curve, which indicated two degradation peaks, initial one beneath the 100 °C because of OH groups in fibers and second peak corresponds to degradation of cellulose and hemicelluloses and also due to existence of voids and non adhesive fibers inside composites specimens. This zone has not been investigated up until now and accordingly required extraordinary worry of researchers around the world.

4 Conclusion

Presumably a lot of work has been done on surface functionalization of various VFs and their utility as reinforcement in phenolic composites. Anyway, there is still need to explore distinctive VFs, which yet has been not perceived at the worldwide level. Further, endeavours ought to likewise be having to further improve the market of VFs reinforced phenolic composites. Also, thermal stability of self made phenolic composites is higher than commercial made and other thermosetting matrix so one should prefer this SMPF matrix. Further, a considerable increase in thermal stability of VFs reinforced phenolic composites after surface tailoring of VFs has been noticed and these results will motivate the industrialists for fabrication of high performance automotive and aerospace products by making use of phenolic matrix based bio-composites. This chapter provides valuable literature information for further investigations on phenolic resin, surface treatments of VFs, resin chemistry and its derivatives. The future work should be focussed on development of green composite materials with bio-phenolic and innovative phenolic resins.

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Waste Management and Application of Coconut Biomass and Fibre

Ana Cristina Curia, Aline Ramalho Dias Souza, Janiel Rodrigo Zaro,
Magali Rejane Rigon Barbieri, Genyr Kappler,
and Carlos Alberto Mendes Moraes

1 Introduction

India and Brazil are, respectively, the third and fifth largest coconut producers in the world. They are the countries that stand out regarding scientific production on solutions for coconut residues, and are respectively listed as the second and fourth most mentioned countries, and the third and first having published the most in this area in recent decades.

Globally, coconut is particularly assigned to produce copra, having as principal derivatives, coconut oil (62.0%) and coconut flour (33.1%). While, in the Brazilian market, different from the major world producers, the production of coconut is chiefly to produce fresh dry coconut, grated coconut, coconut milk and coconut water [24, 25].

In the last century, the world has witnessed continuous and exponential population growth, particularly after the second decade of the twentieth century. Among other factors, this scenario has been fueled by non-renewable energies, supported by technological progress and the improvement in medicine.

The development of productive systems, in a general perspective, have stimulated changes both in population growth and in consumer behaviour leading to an increase in the demand for energy and natural resources, which are converted into manufactured products.

A. C. Curia · J. R. Zaro · C. A. M. Moraes (✉)
Graduate Program of Mechanical Engineering, University of Vale do Rio dos Sinos—UNISINOS, São Leopoldo, RS, Brazil
e-mail: cmoraes@unisinos.br

A. R. D. Souza · M. R. R. Barbieri · G. Kappler · C. A. M. Moraes
Graduate Program of Civil Engineering, University of Vale do Rio dos Sinos—UNISINOS, São Leopoldo, RS, Brazil

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_9

The production and consumption model has led to increased demand for resources and manufactured products. The consequences from this linear model—of extraction, production and disposal—became evident with the observed environmental impacts, such as the increase in solid waste generation, for example. Concerns about the environment and sustainable development started to be discussed more intensively in 1992, after the United Nations Conference on Environment and Development, also known as Eco-92, held in the city from Rio de Janeiro, Brazil. The management of solid waste is a global concern, and despite waste management in developed countries is performed satisfactorily, this is not the reality for all nations.

This chapter presents an updated survey about the coconut market. It gathers information from a global view but with an emphasis on Brazil. In this way, the authors present a bibliometric analysis, the world scenario, gathering and discussing data about coconut chain production, management of solid waste generated after consumption, studies carried out, applications and the advances in this sector in the context of the circular economy. The main objective of this chapter is to gather information and, thus, lead the reader to a current reflection on this important market that the post-consumer coconut chain encompasses.

2 Bibliometric Analysis

To subsidy and contextualize the issue discussed in this study, a bibliometric analysis was performed in the Scopus database. The research took place in October 2020, considering the following keywords: “Coconut waste management”, “Coconut industry”, “Coconut waste process”, “Coconut production” “coconut waste”. Only the results in which these keywords were present in the title, abstract and keywords field, were used.

The VosViewer software was used to manipulate the selected results by refining the outcome accurately. The filtering operations provided the number of published works and citations, both by country, of the previously mentioned strings.

Figure 1 shows the relevance of India and Brazil on the world stage when it comes to studies focused on the themes represented by the researched strings, since countries appear as the second and fourth most cited and the third and first that most published in the area, respectively.

The agreement between the scientific publications of the world’s largest coconut producers’ with the results of Vos viewer is established through a graphical comparison. Data of the coconut production by country were obtained in a survey on the FAOSTAT website in October 2020.

As shown in the graphic Fig. 2, although Malaysia ranks the 10th position between the largest coconut producers, it is the second in publications. Brazil is on the same path since it presents more scientific publishing in the surveyed areas than the Philippines and Indonesia, which are the largest coconut producers.

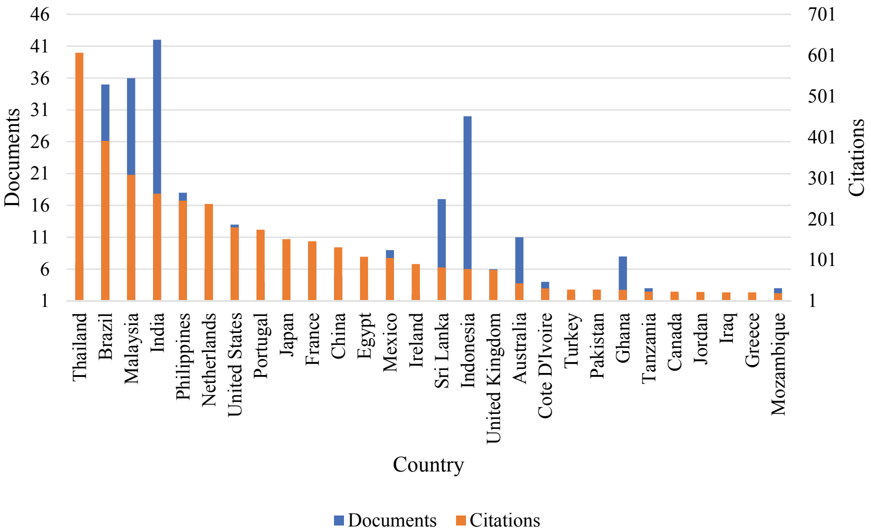

Fig. 1 Distribution of publications, by country

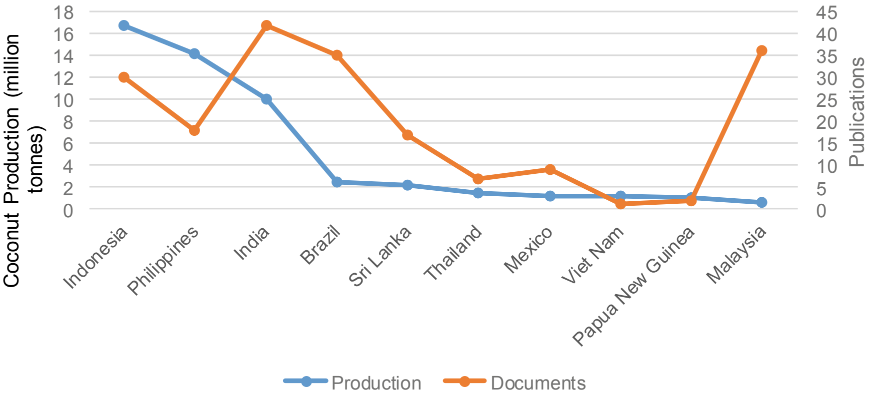

Fig. 2 World coconut production and waste generation scenario

3 World Coconut Production and Waste Generation Scenario

The green coconut is produced and consumed worldwide, and Asia is far the largest producer. Consumption is carried out both as fresh fruit and as industrialized coconut products. New applications other than food have emerged, and coconut became feedstock for many products, including the cosmetic and pharmaceutical industries. Numerous researches have already proven the nutritional value of either pulp, water or

Table 1 Quantity of coconut in millions of tons produced by the major world producers on 2016–2018

Country	2016 (million ton)	2017 (million ton)	2018 (million ton)
Indonesia	17.97	18.74	**18.55**
Philippines	13.83	14.05	14.73
India	11.34	**11.16**	11.70
Sri Lanka	3.01	**2.44**	2.62
Brazil	2.64	**2.22**	2.35
Vietnam	1.47	1.50	1.58
New Guinea	1.18	1.20	1.22
Mexico	1.16	1.16	1.16
Thailand	0.9	0.9	0.9

Source FAOSTAT [27]

coconut oil. These, added to the recent behaviour, in which consumers are improving their lifestyle healthier food such as coconut, fostered its production. The benefits resulting from the excellent nutritional values of natural coconut-based foods imply the expansion of the fruit market [48].

According to data published by ETENE [24, 25] which stands for Technical Office of Economic Studies of the Northeast, which is a Brazilian government agency responsible for preparing, promoting and disseminating studies, research and socioeconomic information, the production of coconut in the world is estimated at 63.6 million tons in 2020. Three countries concentrate more than 70% of coconut production in the world, i.e., Indonesia (30.1%), Philippines (24.7%) and India (19.0%). Brazil holds the fifth place with 4.5% after Sri Lanka. Table 1 shows the quantity of coconut produced in millions of tons by the nine largest world producers comprising the years from 2016 to 2018. After 2019, the Food and Agriculture Organization of the United Nations—FAOSTAT has not yet published new information about coconut production.

The figures in bold in Table 1 show that the production decreased in three countries in 2017 and one country in 2018, namely, India, Sri Lanka and Brazil in 2017, and Indonesia 2018. The trend for the other countries suggests from stagnation to expand. The figures in Table 1 shows that there was no significant changes on prodution of coconut during the years of 2017 to 2018.

Though some reductions or stagnations took place, in general, the world scenario is still optimistic for the coconut market. With the increase in production leveraged by the world economy, more jobs are created, increasing the income of small and large producers, providing gains for the entire chain, fostering new markets. In a contextual analysis, by consuming healthy products such as those from coconut, for instance, society can benefit in several ways, when the production chain avoids the generation of waste and adds value to all the components. Hence, healthy products are commercialized while externalities are avoided, and so repair costs. The increase in consumption is mainly due to advertisements for the benefits of coconut oil. Some countries have invested in fine chemical industries, where oils with a higher degree of purity are produced. These new products have higher added value and can be used either in the food or as an ingredient for medicinal products. As an example [6] explain that coconut is the main source of lauric acid in the world. It has a high foaming, bactericidal, and biodegradable properties. Therefore, coconut oil is used in cosmetics and soap industries, and in the production of alcohol [6].

In the year 2020 World Health Organization-WHO declared pandemic period because of COVID-19. Like many other markets, the coconut market has also been impacted. However, the figures of this impact have not yet been released by official agencies. The scenario of high demand with the scarcity of coconuts sold at a higher price went through a crisis during the pandemic period when supply did not meet demand. This peak season has been dramatically affected due to distribution and supply restrictions. Manufacturers of coconut products suffered heavy losses during the first and second quarters of 2020 as a result of plant closures. Although they can operate in some areas, insufficient labour and restrictions on vehicle mobility have drastically reduced the supply chain process. Besides, the high season for obtaining coconut water is between June and October. With the production facilities closed, the green coconuts harvested for processing have matured. Mature coconuts are not of interest for sellers, because further processing and products are different. Consequently, the market for coconut water obtained from green coconuts was affected, and the majority of farmers and sellers lost sales during the first quarter of 2020. Besides, since more than 85% of the coconuts trades in the world come from countries like Indonesia, Thailand, Philippines, Brazil, India and Malaysia, the restrictions imposed by the governments of these nations affected trading activities. These restrictions led to lowering the stocks of coconut in countries with fewer restrictions for factory operations. The irregularities in the supply of raw materials have influenced the entire production chain in some way. Sales of coconut water at the main points of trade peaked before the restrictions took effect. Along with the coconut water, an increase in the consumption of bottled water has also been observed. Consequently, coconut water witnessed a sudden rise in sales alongside with essential goods for sanitation, for instance, hand sanitizers, toilet paper and PPE's. In general, consumers were looking for essentials with high nutritional value and health care. The nutrients and electrolytes found in the beverage are considered essential for healthy ageing. Thus, suppliers shall meet the sudden increase in demand through sufficient supply and processing capacities since business activities shall be re-established by the end of 2020. The demand growth might be prominent in several distribution channels, where suppliers can position their products according to appropriate price adjustments [25].

Even before the pandemic, mainly in the Asian continent—which is the host of the largest producers in the world, the green coconut has been an object of research in the academy. They essentially focused its production, whether in the perspective of improving techniques through automated processes, for example, and the use of biotechnology by addressing the impacts from climate and soil type. Maheswaran et al. [50], Prades et al. [62], Avancini and Wulandari [9], Pathmeswarana et al. [60], Omar and Fatah [59], Kumar et al. [46]. Regarding cleaner production, almost two decades ago, [46], carried out a study on the significant impact of simple actions in the coconut industry in Sri Lanka.

The growth projections of the green coconut market, for the future scenario, points to expressive numbers. Thus, it is necessary to make plans for the disposal of the waste generated, either by the industry or by the final consumers. The management of solid waste is still a global problem, and this is no different for the waste generated by the coconut industry. In the literature review, there were not many specific studies on the management of solid coconut waste, which shows that there is a lack of information about this topic either from large to small producing countries.

The studies indicate different conditions for the management of coconut residues. In Indonesia [23], coconut residues were mostly disposed-of irregularly in the open in inappropriate locations. The scenario changed with the action of micro-companies that started to use coconut residues as a raw material in different applications (food industry, power generation, civil construction). In Ghana Obeng et al. [58], coconut shells are disposed-of or burned raw, resulting in poor sanitation and environmental pollution conditions. In Sri Lanka Kumar et al. [46], more than 90% of the shells coconuts are burned in open pits to produce charcoal for the activated carbon industry. In India, Koteswararao et al. [44] related that the use of coconut is immense. It is regularly consumed, e.g., in temples, homes, among others for drinking purpose. After the consumption of the liquid, people get rid of the tender coconut shells as waste near to street bins and roadsides. In Southeast Asia as a whole [1], coconut husks are considered agricultural waste from the crop of rural communities and are usually disposed-of close to the harvest site, where processing takes place.

In Brazil, the national law PNRS-12.305 (short for National Policy for Solid Waste) establishes waste management structures and guidelines. It focuses on urban, agricultural and industrial solid waste where the management of post-consumer coconut shell waste lays. Although the law is well structured, there are still many barriers and challenges related to the cultural and economic aspects of the coconut waste chain. In the States where the consumption of green coconut is high, the adverse effects of waste generation are already perceived. According to [52], the Brazilian states Ceará and Rio de Janeiro generate, respectively, 150 tons/day and 180 tons/weekend of post-consumption green coconut residues during the high seasons. And even in non-coconut producing regions, i.e., Southern Brazil, there is a significant generation of coconut residues of approximately 800 tons/year [16]. The figures in Southern Brazil account for a high consumption profile of green coconut water right from the fruit, consumed at the stores located in coastal regions mainly during beach season, corresponding to summer.

The management of coconut residues in Brazil is not yet following National regulation imposed by the law previously mentioned, and the reason lays on a cultural, economic and political matter. Silveira [71] verified in field research held on the beaches of the city of Salvador/Bahia (one of the states with the highest coconut crop production in Brazil) the incidence of post-consumption green coconut waste disposed of in the open on the seashore. The reasons vary from the consumer's disregard, lack of adequate and sufficient bins, and aggravated by a deficient collection by the municipality. Silveira [71] adds that when disposed of inappropriately, the coconut waste contributes to the visual pollution of the municipality. According to Jerônimo [38], in a study carried out on the seashores of Rio Grande do Norte (one of the major coconut producing states in Brazil), he observed that the higher fraction of waste found in landfills was green coconut shells. Some reasons for that are mainly the chemical and physical characteristics of coconut shell, which decomposes slowly and occupies a large volume. Additionally, there were no sorting systems for coconut waste discarded along the beach and in the ocean itself.

In some coastal regions of southern Brazil, a study led by Curia et al. [16], describes a different pattern of engagement in the management of coconut waste compared to the studies mentioned above. In this study, they state that the observed commitment may be due to several factors combined, for example, the strict level of inspection by city halls, which requires the use of exclusive bins for coconut shell waste provided by the coconut water selling points. And non-compliance with municipality regulations is punished by the application of fines.

On the other hand, despite some municipalities require the of use of bins for disposing of exclusively coconut shells, some (30%) do not provide selective-collection, and even for those that have the selective-collection (70%) the green coconut residues are mixed with regular MSW (Municipal Solid Waste) in the landfills. Hence, it is necessary to improve public policies that effectively stimulate the development of new sustainable businesses [16]. According to [70], to foster these new opportunities to become concrete enterprises at the microeconomic level, to reflect carefully on the public policies is of the essence.

Even though reverse logistics is officially in practice, the city halls have not yet assumed their role in implementing the shared responsibility in coconut waste management, either because of the lack of specific interest in this waste that requires appropriate conditions to leverage their reverse logistics or lack of knowledge. The collectors of the cooperatives and associations point out the need for joint articulation with the public authorities to promote reverse logistics, enabling the increase of their work and income [17].

However, the literature reviewed suggests that studies, mainly in the countries where the major world coconut producers lay, have been conducted to investigate novel uses for coconut waste in e.g., the generation of energy, polymers, civil construction and in agriculture as fertilizer.

4 Applications of Coconut as Biomass and Fibre

Over the past 15 years, the potential uses of green coconut biomass have been growing in terms of higher environmental, social and economic value, resulting in a variety of products for different segments including polymers, energy, civil construction, wastewater treatment, food and others. Figure 3 shows the representativeness of studies on the application of coconut by economic activity segments.

The use of green coconut waste biomass to generate renewable energy and new products has become the cornerstone for the establishment of responsible waste

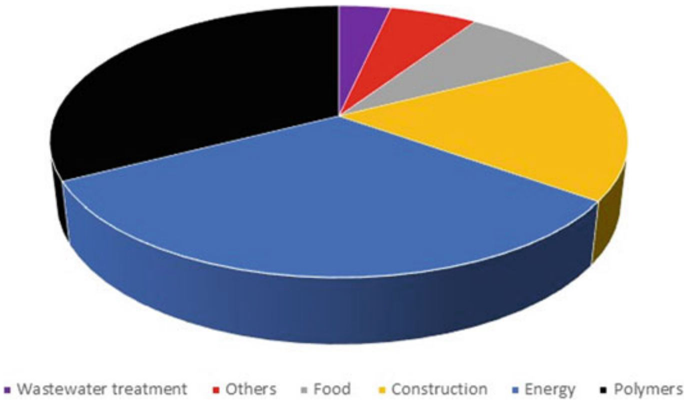

Fig. 3 Application segments of coconut biomass

management and sustainable models that can not only improve the product life cycle by reducing environmental impacts but also associate more equitable and economically viable forms of work.

Many studies have focused on the production of biochar that can replace coal by biomass of which coconut fibre attracts attention [21, 46, 44]. Another field of investigation increasing rapidly on coconut biomass is the production of bio-oil [10, 72, 77]. Table 2 presents some threats and opportunities identified by the studies related to the use of coconut biomass as biochar or in the production of bio-oil. In these studies, the main positive impacts attributed to these applications are,the

Table 2 Opportunities, threats/challenges and positive impacts of biochar and bio-oil of coconut biomass

Application	Authors	Opportunities	Threats/challenges
Bio-oil	Sulaiman et al. [73]	Good performance, low cost	–
	Mariano et al. [51]	Increased yield	–
	Sulaiman et al. [74]	Cost reduction	–
	Obeng et al. [58]	Reduction of GHG, increased calorific value	–
	Aberilla et al. [1]		Depends on the availability of biomass; by-products after operation
	Sulaiman et al. [72]	Increased yield	–
Biochar	Kumar et al. [46]	–	Lack of government funding for research
	Arena et al. [7]	–	High electricity consumption
	Rout et al. [67]	Higher calorific value	–

reduction in consumption of feedstock/product, reduction of GHG emissions and generation of labour and income.

The coconut shell versatility also allows its application in the field of renewable energies, since biomass is composed of organic matter that can be converted into mechanical, thermal or electrical power. The three well-known processes for generating energy/products by using coconut residues are: pyrolysis (production of biochar under the thermal decomposition of biomass in the absence of oxygen), biogas (biomass degradation in the presence of microorganisms) and gasification (an endothermic process that converts biomass into gas with heat capacity). Table 3 describes some works developed with coconut biomass in pyrolysis and gasification.

In general, the green coconut shell is not used directly in combustors due to its high moisture content and low energy density. Nonetheless, after a pre-treatment (drying and pressing), the specific energy content increases and gives it new characteristics and applications in products called briquette. According to Syamsuddin and Rizal [75], bio-briquette (addition of biomass in coal briquettes) has advantages such as low

Table 3 Energy generation processes using coconut biomass: pyrolysis and gasification

Processes	Authors	Field
Pyrolysis	Liu and Balasubramanian [47]	Pyrolysis of coconut fibres for energy generation, with reduction of nitrogen emissions
	Adewole et al. [3]	Kinetic co-pyrolysis of fuel mixtures indicated that the mixture of coconut shell with charcoal above 30% may increase the activation energy value
	Castilla-Caballero et al. [13]	Provides greater understanding of biochars and is a valuable tool for addressing the strategic exploration of multiple benefits
	Noor et al. [55]	The survey results indicate that the higher pyrolysis temperature reduces the mass percentage of biochar production
Gasification	Ram e Mondal [63]	The research focused on humidified air as an alternative to steam for generating hydrogen-rich fuel gas in a fixed bed gasification column. This process not only provides viability for green energy, but also reduces the pressure of environmental pollution created by unused coconut shell
	Talha and Sulaiman [77]	They have concluded that coconut residues may replace or be co-gasified with wood after making some important changes in the geometry of the gasifier
	Ram e Mondal [64]	Residual biomass has immense opportunities and many potentials to be an efficient source of renewable energy

ignition temperature, and due to the characteristics of plant biomass (high volatile organic matter), this mixture can improve the combustion of the briquette.

The use of vegetable fibres in substitution or combination with synthetic fibres has been growing due to its technical versatility, economic viability (low density and low cost), and environmental benefits (superior alternatives to synthetic fibres in composites). These new composites possess high performance due to the mechanical properties in addition to significant processing advantages [45]. These advantages are more evident according to their applications, which consequently are related to their physical properties. In the case of coconut fibre, the values of cellulose and lignin (support, weight and mechanical strength) are high compared to other vegetable fibres [71]. Recent trends of sustainable growth in the "green" fashion industry show the use of natural fibres or its combined uses (natural and synthetic fibres) with tremendous potential to add value to the final products.

The search in the database Scopus and Web of Science (WoS) with its bibliometrics allowed to evaluate with more detail the increase of studies with emphasis on the use of natural fibres associated with synthetic ones, and more specifically, concerning the efforts to investigate their properties for application in composites. Added to this is the rise of environmental concerns, increasing the interest for more sustainable products or by-products aligned with the circular economy. Figures 4 and 5 show the bibliometric data for the WoS and Scopus bases concerning the strings coconut, natural fibre, composite [18].

The bibliometrics performed in the VOSviewer® software for the WoS database generated 25 cluster networks, which collaborated to identify the frequency of occurrence of 302 keywords (Fig. 4). These keywords are closely related to research in

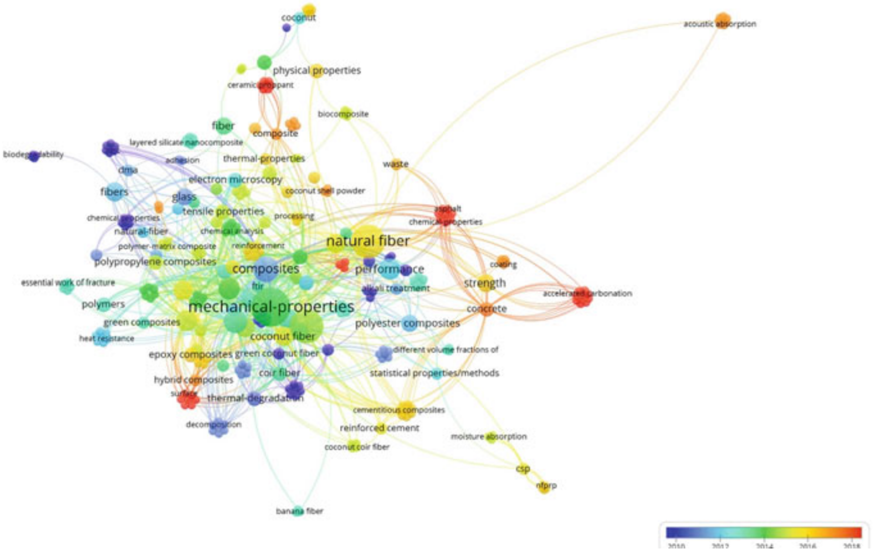

Fig. 4 Occurrence map for WoS base—coconut, natural fibre, composite. *Source* Curia et al. [18]

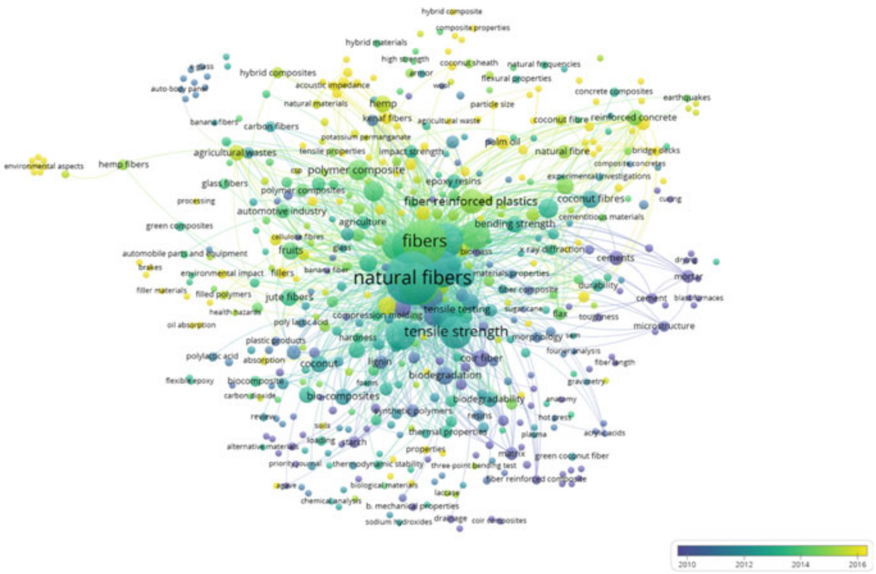

Fig. 5 Occurrence map for Scorpus base—coconut, natural fiber, composite. *Source* Curia et al. [18]

this area that addresses the influence of the use of coconut fibre on mechanical and thermal properties.

In the bibliometry performed in the VOSviewer® software for the Scopus database, it generated 14 cluster networks, which collaborated to identify the frequency of occurrence of 503 keywords Fig. 5. On this basis, research is more distributed by different applications, with emphasis on polymers/composites, related to natural fibres, of which coconut is a frequent reference, whether as coconut fruit, coconut fibre, or coconut shell.

Table 4 presents a SWOT analysis according to the literature evaluated on research developed with the use of coconut fibre composites and respective threats/weaknesses and opportunities/strengths for each type of application. All research considers scientific and technological issues related to the functionalities and attributes of the fibre application. Most studies only consider these issues, but on the other hand, some authors include dimensions related to sustainability, environmental and economic aspects in their assessments. The assessments, in general, do not take into account the social aspects and their positive impacts on society, such as employment, revenue generation and economic development in the region, nor even mention that a large part of the coconut crops in the world come from small farmers.

A widely studied application for coconut fibre is the incorporation or combination with construction materials in field of civil engineering. As can be seen in Table 5, coconut fibre can be used as a filler to produce bricks, as aggregate in cement for light non-structural buildings and other uses with some limitations and opportunities.

Table 4 Threats/weaknesses X Opportunities/strengths for the use of coconut fibre in composites

Dimensions	Threats/weaknesses	Opportunities/strengths
Environmental	High water and energy consumption in the extraction process [20]; Improvement in the process to compete with wood-based fibre boards [30]	High module, meticulous resistance, reduced carbon footprint, improved interfacial adhesion of the fibre matrix [2],reduction of the environmental impact associated with nanocrystals [20]; development of material and model structures inspired by nature, energy absorption [49]; production of bio-based and biodegradable injection moulded [14], Reduction of transport impacts by distance from the shell processing units and coconut water production, reuse of the nutrient-rich effluent generated in the shell processing units in the crop fertigation [30]
Environmental/Economic	Increased energy consumption costs Nascimento et al. [54]	Higher yield, better energy efficiency; use of reagents totally free of chlorine in the bleaching process; without using sulfuric acid [54]
Environmental/economic/social	Limitations on dimensional stability and ductility [78]	Polymer composites reinforced with renewable natural fibre, low cost, improvement of the local community [78]
Economic	Less mechanical strength than polymer with inorganic fibres [31]	Low cost, high availability [31]
Scientific-Technological	Weak interface between coconut fibre and polyester matrix [33], fibre characteristics hamper production [15]; small reduction in impact resistance [69]	Improved wettability, flammability of composites [43]; improvement in mechanical properties [42, 53, 75], improvement in thermal stability [19, 29, 35]; Improvement of the interfacial adhesion of the polymeric matrix [5, 22, 34]

Some studies indicate that coconut fibre can be used in wastewater treatment to remove pollutants in the replacement of inorganic materials [65], in the preparation of activated carbon for colour adsorption [4], metal removal [12] and other technical functionalities in physical–chemical or polishing processes.

Table 5 Applications of coconut fibre in civil construction

Authors/year	Threats/weaknesses	Opportunities/strengths
Pereira et al. [61]	High alloy content	Good fibre/matrix interface, good strength, more sustainable
Hwang et al. [36]	Density reduction, increase in superplasticizer dosage, less resistance to compression	Greater absorption, greater resistance to bending, greater resistance to impacts
Nyuin et al. [57]	–	Increase in the shear strength parameter
Jayaprithika and Sekar [37]	Low modulus of static elasticity	Satisfactory ductility rate
Kumar and Sekaran [45]	–	Increased base strength properties of the mix
Wang and Chouw [79]	–	Better performance in fragmentation resistance
Kadir et al. [39]	–	Low cost, good physical and mechanical properties
Brasileiro et al. [11]	–	Potential for thermal and acoustic insulation Potential for thermal and acoustic insulation Potential for thermal and acoustic insulation Potential for thermal and acoustic insulation

The application of biochar in the soil to improve its agricultural properties and store CO_2 is getting considerable attention recently. Adding biochar to soil may increase plant biomass and soil nutrition of slow-releasing nitrogen and phosphorus source [32], as an organic fertilizer facilitating composting [76], for soil correction as an alternative with high potential for improving soil quality while reducing CO_2 emissions [41].

Among the different ways of making use of coconut waste biomass, it is sometimes used for fewer valued applications which are termed as downcycling. These applications range from simple economic activities such as the production of handicrafts based on the use of coconut residues [23] to large enterprises in the production of gardening products due to lower production costs [56]. Though these activities guarantee the use of the whole coconut waste, these applications are viable mainly from the social point of view because it is beneficial in the development of the local community, however, in the perspective of the circular economy, they should not be a priority because in the process the biomass quality is lowered and may become a non-recyclable waste soon.

5 Use of Coconut Fiber in the Context of the Circular Economy

Most research deals with green coconut shell as a residue from the agro-industry or general food-processing industries, describing the reality of the largest coconut-producing countries, while only a few include post-consumer coconut waste (originated by the final consumer). In general, the environmental impacts associated with the inappropriate disposal of the coconut shell are related to the soil, water and air contamination. Moreover, when they are collected and mixed with traditional MSW, in the best perspective, they end up in a landfill. Hence, the service life of the landfill is compromised because the coconut shell has a low density and degrades very slowly. From this perspective, the linear model established on the coconut value chain is evident.

On the other hand, as previously mentioned, the use of green coconut shell presents opportunities for its application in many areas. Therefore, understanding the technical characteristics of all components formed in the coconut shell processing steps facilitates the development of new technologies for these materials to be transformed into by-products. These new products can, accordingly, be used in a new value chain, allowing these materials to be reinserted either in biological or technical cycles, which is a step away towards the cradle to cradle model, which is an element of the circular economy (CE).

CE stimulates the production of goods through closed-loop material flows and provides economic incentives to ensure that post-consumption products are reintroduced upstream into the manufacturing processes (Sauvé; Bernard; Sloan, 2016). It means that under the CE principles, the materials, products, and energy are kept in use as much as possible and circulating in the system, distinguishing between biological and technical materials, eliminating the concept of waste and waste generation [26]. Figure 6 shows the structure of the CE, which is based on three principles for a hypothetical design in terms of the biological and technical cycles for the green coconut chain [40].

The vast majority of studies related to this assessment, about 91%, corresponds to applications to the technical cycle and only 9% belong to applications to the biological cycle, which are essentially research carried out in the food sector, for example [59, 66], Das et al. [20] or with applications such as handicrafts, gardening and briquettes [56].

Additionally, most of the research carried out on the coconut chain, about 95%, is focused on the upcycling perspective, whether through processes or products with higher environmental value. A smaller portion, corresponding to 5% of the surveys, can be considered for downcycling applications. This scenario may have been influenced by the keywords defined for the search, which yielded works of a technical-scientific nature, and which, therefore, gives higher value to coconut fibre.

In the development of effective systems of production, a shift from a linear to a systemic way of thinking is essential, as proposed by the CE. A tool tailored for

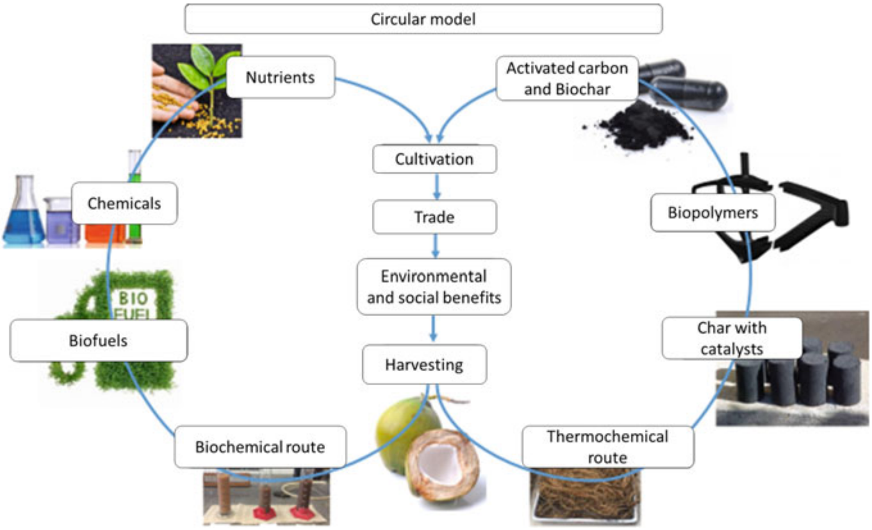

Fig. 6 Hypothetical CE model for the green coconut chain. *Source* Kappler et al. [40]

supporting this transition is the Life Cycle Assessment (LCA). LCA is a tool standardized by the International Organization for Standardization (ISO) by ISO 14.040 and holds the concept of a life cycle inserted in the purposes of its methodology. A product's life cycle is understood as the stages of a product system that covers the extraction and processing of raw materials, manufacture, transportation, distribution, use, reuse, maintenance, recycling and the disposal of the product [8].

Therefore, LCA should be applied in the design phase. It allows the planning of products and systems with lower environmental impacts associated with materials and processes, since the application of the CE model alone does not necessarily mean achieving environmentally safe benefits. Figueirêdo et al. [28], for example, showed that the production system of cellulose nanocrystals affects the environmental impact categories of climate change and human toxicity at the same level as carbon nanofibers. This observation complies with the importance of research to investigate the production chains. Thus, new products or by-products are planned to design out pollution and waste contributing to the improvement production systems towards the CE objectives.

Some research developed is aligned with the principles of CE, and through the application of LCA, they seek technical evidence of the real environmental gains using coconut shell throughout its various applications. Table 6 describes some of these works developed with coconut biomass and LCA.

On the other hand, only a few of those surveys are developed with a systemic view, accounting for the entire production chain. Though they show a series of practical opportunities for the circular economy, they lack integrated system management. When many of these initiatives are implemented within a linear production model, the lack of a value chain for the by-products, products or processes to be inserted puts

Table 6 Research developed within the scope of the LCA

Year	Journal	Reference	Title
2017	Journal of Cleaner Production	Freire et al. [30]	Environmental assessment of bioproducts in development stage: The case of fiberboards made from coconut residue
2017	The International Journal of Life Cycle Assessment	Salzer et al. [68]	Environmental performance of social housing in emerging economies: life cycle assessment of conventional and alternative construction methods in the Philippines
2016	Journal of Cleaner Production	Arena et al. [7]	Life Cycle Assessment of activated carbon production from coconut shells
2012	Journal of Cleaner Production	Figueirêdo et al. [28]	Life cycle assessment of cellulose nanowhiskers
2019	Renewable Energy	Aberilla; Gallego-Schmid; Azapagic [1]	Environmental sustainability of small-scale biomass power technologies for agricultural communities in developing countries
2016	Industrial Crops and Products	Nascimento et al. [54]	A comprehensive approach for obtaining cellulose nanocrystal fromcoconut fiber. Part II: Environmental assessment of technological pathways

at risk the new practice developed. Expanding this vision is an opportunity to shift from the linear production models towards the circular economy and consolidate it as the predominant economic model.

In Brazil, based on the LCA [30] evaluated the environmental performance of solar panels produced from coconut shell fibres. Figueiredo et al. [28] evaluated two production systems used to obtain cellulose nanocrystals. Nascimento et al. [54] studied different methods of extracting cellulose nanocrystals from coconut fibres to determine the most sustainable for the application in enzymatic immobilization, controlled release of chemotherapeutics, and reinforcement agent for films and nanocomposites, for example.

In Indonesia, Arena et al. [7] evaluated the environmental impacts of the production of activated carbon from coconut shell. Also, on the Asian continent [1] evaluated the use of biomass obtained from agro-industrial residues, including coconut shell, for small-scale energy generation.

When specific processes are assessed from the perspective of LCA, it is possible to identify critical points and develop products with lower environmental impact. However, the impact categories of any study are evaluated according to their functional units while the system limits are established for each study, therefore, they can vary significantly.

As an example for the limits of the system definition, Freire et al. [30] set the limits for the coconut chain from the cultivation of the fruit until the final product, i.e., fibreboard manufacturing. Others, like Arena et al. [28], considered the limits of the system from cradle to gate in their evaluation. These illustrate that even studies that intended to work with a systemic view on the coconut chain, under CE's thinking, were not able to address all the players involved in the process. One of the reasons to adopt such limits may be related to the lack of essential and reliable data for studies of the LCA.

Among the principal negative impacts generally associated with coconut processes is the high consumption of electricity, which is even higher in countries where the energy matrix comes from non-renewable sources, such as coal in Indonesia.

In the process of obtaining cellulose nanocrystals, the high energy consumption to operate the high-power ultrasound is highlighted [54]. Still, for the development of a laboratory-scale production chain, which uses coconut fibres and PLA to make a polymeric board, the energy consumption is also one of the most relevant environmental aspects observed by Zaro et al. [80].

The best scenario evaluated by Arena et al. [7] uses coconut shells not only as a raw material for the production of activated carbon but also to produce biofuel and generate the energy needed for the process, reducing about 80% of the impact on the Global Warming Potential category. This scenario shows the importance of having integrated steps in the production process, such as the use of gases produced during carbonization to be used as fuel gas used to supply heat to the process itself.

Most of the applications shown produce positive impacts by reducing the need of inputs of energy and raw materials with an emphasis on those from non-renewable sources. The GHG reduction is also one of the principal environmental gains, especially in energy-related applications. Therefore, it has been observed that for all studies identified as an application of LCA in the coconut chain, the Global Warming Potential category was shown to be significant. Also, eutrophication proved to be a category of high impact, resulting from the effluent generated by the processing of the bark. Freire et al. [30] put the potential of reusing the nutrient-rich effluent generated in the bark processing units in the fertigation of crops, especially in the cultivation of coconut trees.

Furthermore, the establishment of a responsible coconut shell management model is an option to manage what is now waste in developing countries that are the largest coconut producers, making it possible to associate decent and economically viable forms of work.

In some cases, the use of small rural communities to generate energy can improve the quality of life in the region, as it meets the need for power [1].

6 Final Considerations

The increasing demand for products derived from coconut demonstrates its outstanding market potential. This potential is essentially a result of its natural attributes which are strengthened by the media for being eco-friendly, healthy and beneficial to human well-being. Consequently, this perspective serves as a motivation for the largest coconut products to review their agriculture cultural model as well as their production processes to increase competitiveness and fully meet the expectations of the new consumption trends.

The expectation is the revision of the traditional production models, with the migration from intensive agriculture with several problems related to the lack of technology and training, to an agriculture model with modern techniques that involve the use of modern technologies with automated processes, use of biotechnology and other actions aimed at boosting productivity. Thus, besides obtaining diversified and higher quality products with added value, the generation of waste is reduced and converted into diversified marketable products.

The Covid-19 pandemic intensified the opportunities and barriers identified for this sector of agribusiness, in which crop residues, coconut processing, and post-consumption, and in particular coconut fibres are increasingly being studied by different experts and sectors in the economic activities (polymers, energy, civil construction, wastewater treatment, agriculture, food and others).

The use of coconut fibre can significantly evolve once the barriers obstructing its efficient and frequent application are overcome. These barriers are frequently related to economic, social or environmental aspects, i.e., high consumption of water and energy in the extraction process, technical difficulties in processing, limitations related to mechanical properties, lack of government funding on research, and public policies as well. Furthermore, the opportunities and benefits on the use of coconut fibre, such as low cost of raw material, good physical and mechanical properties, higher yield, better energy efficiency, lower carbon footprint, high availability, work and income generation for local communities, development of the local economy, among others; may spark the expansion of this market.

However, for the coconut products to be fully integrated into the circular economy, it is necessary to develop a systemic view of the entire coconut value chain. In this sense, it is essential to identify and improve aspects related to the linear model behavior established according to the linear production/consumption system to push the shift to the circular model, contemplating the value chain for co-products, products and collaborative and complementary processes.

Acknowledgements The authors thank CNPq (Brazilian Government for the financial) support given to the authors: Technological Development Research Grant—DT2/CNPq, and CAPES for the Ph.D. students scholarships, and Post-Doc grants.

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Effect of Hybridization and Chemical Modification on the Water-Absorption Behaviour of Banana Fibre–Reinforced Polyester Composites

Deeksha Jaiswal, Ishan Srivastava, Himani Agarwal, Anish Khan, and G. L. Devnani

1 Introduction

The persistent research in the field of composites has enlarged the fact that they are fit to be viewed as an alternate to the catastrophic synthetic materials [1]. The consistent experiments reveal the flamboyant nature of composites specifically when amalgamated with natural fibers [2]. The implementation of natural fibers provides an added advantage of biodegradability alongside the sturdy mechanical and thermal strength [3]. The composites so produced are highly cost effective as well. The natural fibers are classified on the basis of their generation. Figure 1 illustrates its broad classification.

In this chapter we will be laying emphasis to the vegetable fibers (or Lignocellulosic fibers), i.e. the fibers derived from plant cellulose. The properties of composites are highly influenced by its constituent materials i.e. the polymer matrix and the vegetable fiber [4]. Therefore it is often a typical choice to make for the selection of perfect combination of matrix and fiber. We have listed below the chemical constituents of few of the widely used vegetable fibers (Table 1).

Out of the all the above vegetable fibers we will be narrowing down our intention to Banana Fiber. It is considered to be the most robust fiber. Scientifically known as Musa Sepientum, it is highly efficient when incorporated into the matrix. The cellulosic content of 62.5% and 11° microfibrillar angle gives ample evident of its ordered bonding [10]. On an average 30 large leaves are produced by a Banana tree of around couple of meters in length and 0.3–0.6 m wide [11]. 100 g of Banana pulp

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D. Jaiswal · I. Srivastava · H. Agarwal · G. L. Devnani (✉)
Department of Chemical Engineering, Harcourt Butler Technical University, Kanpur, U.P., India
e-mail: gldevnani@hbtu.ac.in

A. Khan
Center of Excellence for Advanced Materials Research , King Abdulaziz University, Jeddah 21589 , Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_10

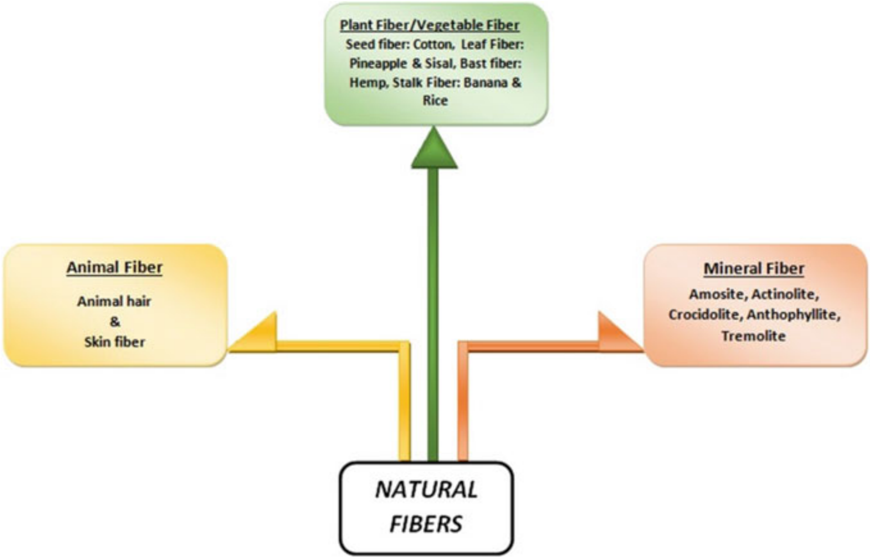


Fig. 1 Classification of natural fibers (*Source* Author)

Table 1 Chemical constituents of most commonly used vegetable fibers

Chemical constituent (Wt. %) natural fiber	Hemi cellulose	Cellulose	Lignin	Pectin	References
Ramie	14.9	72.4	0.65	1.9	[5]
Bagasse	29.5	43.5	22	–	[6]
Kenaf	21	50.5	17	2	[7]
Banana	7	62.5	7.5	4	[6, 7]
Cotton	5.7	82.7	1.15	–	[5]
Sisal	11.9	52.1	15.45	–	[8]
Sponge gourd	17.44	66.59	11.2	–	[6]
Bamboo	30	40.5	22.075	2	[9]

contains about 73.9 g of water, 18.8 g of carbohydrates, 1.15 g of proteins and 0.18 g of fats alongside vitamins C1, B1, B2, B6 & E [12]. Figure 2 shows the composition of banana fiber.

The Banana is amongst the oldest cultivated plant which accounts the dependency of approximately 400 million people as their source of food. Over the last few decades the global production of Banana has undergone steep growth of 175% [13]. The global production of Banana is estimated to be around 102 million tonnes which has grown to 130 million tonnes by 2010. By 2006, 70% of the world's total import was accounted by the Japan, United States and European Union whereas Ecuador, Colombia, Costa Rica and Philippines were the top exporting nations adding up

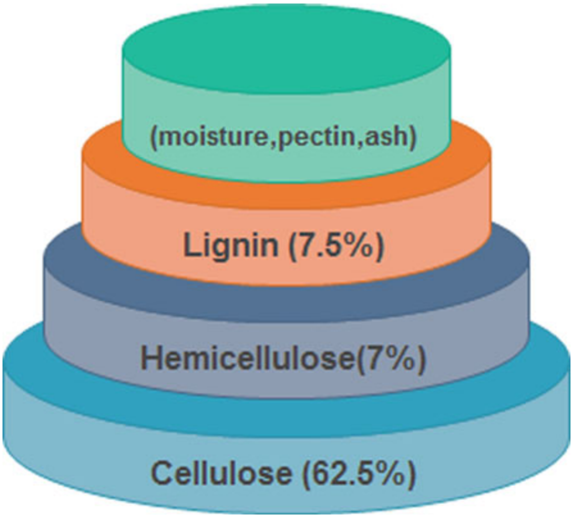
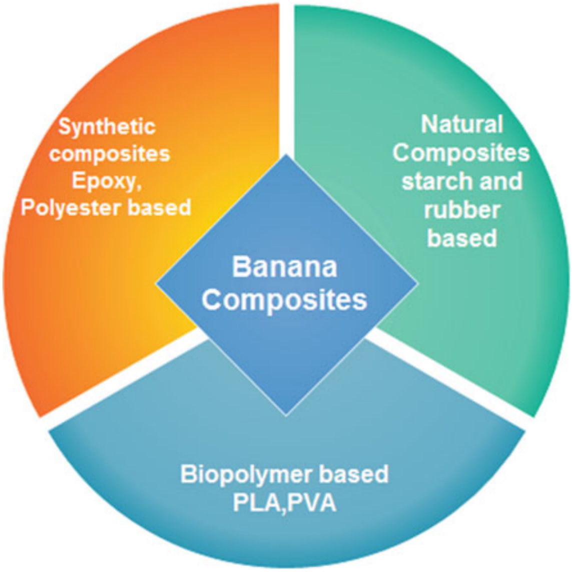


Fig. 2 Lignocellulosic composition of Banana fiber [6, 7] (*Source* Author)

to 64% of world's total export. Alongside big nations, India also holds a prominent position as of producing 31% of globally produced Banana. Precisely the entire India is rich in producing Banana, but states like Maharashtra and Tamil Nadu occupies the leading position [14]. In Canary Island, Banana crop is of prime importance which is evident from the fact that it produces 25,000 tonnes of Banana fiber per year with 9562 ha of cultivable land [15]. The production of Banana has pulled the income sources for many small-scaled people, held the international trade on its own and often enriches the food security of the nations.

The vegetable fibers are highly inefficient when used in their raw forms [16, 17]. As described above the fibers contains Hemicellulose and Lignin in ample amounts which thereby lead to poor adhesion between the vegetable fibers and the polymer matrix [18]. Thus poor adhesion affects the mechanical and thermal characteristics which makes composite of no use [19]. Besides this we observe the water absorption capacity of the composites. Higher the capacity of absorption, poorer will be the bonding. It is assumed that the presence of hemicellulose and lignin degrades the interaction of fiber and matrix. The fact that hemicellulose is highly hydrophilic and lignin contains both hydrophilic and hydrophobic groups justifies the above assumption [20, 21]. Therefore it is advisable to treat the fibers before incorporating them with the polymer matrix. Though the treatment methods broadly classifies into three categories of Chemical treatment, physical treatment and biological treatment, but here we keep our discussion limited to chemical treatment methods itself.

Fig. 3 Types of Banana composites (*Source* Author)



2 Types of Banana Composites

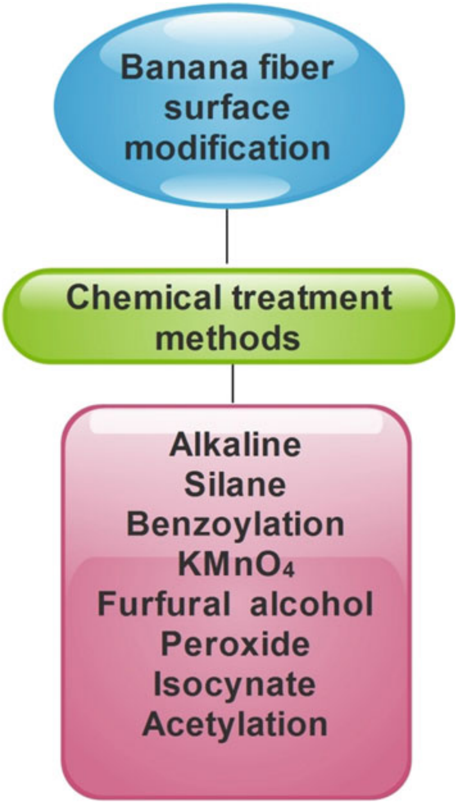
The composites usually consist of Polymer Matrix and Vegetable fiber. Now there are various classes of Polymer matrix. These are broadly classified on the basis of biodegradability. The three types are pictorially represented in Fig. 3.

The Green/Natural Banana fiber composites include Chitosan, Natural rubber, etc. as the reinforcing materials, whereas the Biopolymers include Polyvinyl Alcohol, Polylactic Acid, etc. as the reinforcing material. The Synthetic composite makes use of Epoxy, Polyester, etc. as a reinforcing material. In this chapter our discussion is limited only to Banana Fiber reinforced Polyester composites.

3 Surface Modification of Banana Fiber by Chemical Treatment

All the chemical treatment methods are generally inclined to increase the compatibility of vegetable fibers and the polymer matrix. The vegetable fibers are purely hydrophilic in nature and the polymer matrix (here unsaturated polyester resin) are entirely hydrophobic in nature. The Banana fibers contains Lignin and Hemicellulose which contains hydroxyl groups, this imparts the hydrophilic character to the fibers. Therefore when the fibers are reinforced in the polymer matrix the interfacial interaction often doesn't supports well. Hence we need few surface modification methods

Fig. 4 Types of chemical treatment methods for Banana fiber (*Source* Author)



which may improve this adhesive strength between the fibers and the matrix which could thereby reduce water absorption capacity [22] (Fig. 4).

Out of all the treatment methods available the alkaline treatment method is considered to be most superior [23]. Alkaline treatment is also known Mercerization [24]. The treatment of vegetable fiber through Alkali results into the removal of Hemicellulose and Lignin [25]. Simultaneously the microfibrillar angle also gets smaller after the treatment. The removal of outer smooth waxy layer also takes place thereby making the surface of fiber relatively rough than before. This roughness aids the polymer matrix and Banana fiber interaction [7]. The treatment also affects the cellulosic part as it gets de-polymerized exposing the crystalline region which improves the amalgamation [26]. The end results infer us the increased cellulosic content in the fibers which are more susceptible to penetrate into the matrix [27]. The treatment involves the short fiber fragments of 3–7 cm in length; these are treated with known concentration of alkaline solution, depending upon the situation in hand. The beaker is then left for an hour or so at 90 °C till the fragments turn soft [28]. This is followed by a cooling period of ½ hour to which the fibers are thoroughly washed and rinsed in distilled water and ethanol for removal of all kinds of chemical [29, 30].

These are then left to dry and later be used as a reinforcing material. The composites formed with the reinforcement of untreated and treated fibers largely differ in their mechanical and water absorption properties [31]. Both the mechanical strength as well as water absorption characteristics of the composite undergoes deep enhancements [32]. The BF/Unsaturated Polyester Resin composites when tested for water absorption reveals that at the end of 7 days period untreated fiber composite absorbed 9.74% moisture whereas treated fiber composites absorbed only 1.9% moisture [33]. This decent growth in the water resistant proves to be a significant factor at the time of implementation [34, 35]. Acetylation works dissimilar to alkaline treatment and other methods [27]. In this method our major concern shifts from the removal of non-cellulosic contents to replacement of hydroxyl groups present in the fiber, thereby reducing the extent of hydrogen bonding [36]. The treatment method proceeds with the treatment of fibers with the esters popularly known as Esterification. In order to increase the rate of reaction we use certain catalyst such as Potassium, Sodium acetate, etc. [37]. The alkali treated fibers are used in this treatment, in which the fibers are reacted with acetic anhydride at 20 °C for an hour followed by cleansing action by rinsing them in the distilled water [38]. At the end the fibers are dried in the air oven at around 60 °C for 24 h. The FTIR analysis reveals the fact that the hydroxyl group (−OH) were largely substituted by bulky ester groups thereby reducing the hydrophilicity [39]. Although it interesting to note that the treated fiber results into the declination of the cellulosic content in the fiber alongside little increments in the Hemicellulose and the lignin percentages [40]. Benzoylation treatment method requires alkali treated fibers as a prerequisite [5]. The fibers are treated with benzoyl chloride which attacks the hydroxyl group of the fibers present in the form of Lignin and Hemicellulose. It works similar to the Mercerization (i.e. alkali treatment method). The fibers after alkali treatment (so as to make their hydroxyl group more susceptible to react) are subjected to react with 10% benzoyl chloride and alkaline solution for 10–15 min [18]. The fibers are then continuously washed with ethanol for discharging the useless chemical content. This is followed by leaving them to dry in an oven at 80 °C for a day. The result of treatment reveals the better interfacial adhesion between the fiber and the resin [41]. Permanganate is another standard method of increasing the cellulosic contents. Better interlocking between the fibers and the matrix is seen after the treatment [42]. The most commonly used permanganate is Potassium Permanganate (KMnO4), which reacts furiously. Therefore it is advised to be very precise with its use as because its excess can distort the properties of the fibers. The alkaline soaked fibers are reacted with 0.05% KMnO4 for 1–1.5 h thereafter exposing them to cleansing action for the removal of excess chemical contents. Potassium permanganate is very reliable as for the removal of hemicellulose and lignin thereby increasing surface roughness [41]. Ample increase in the hydrophobic character is clearly depicted which refers to low water absorption strength [43]. Treatment with Furfuryl alcohol functions in a different way than the other treatment methods. In this method the fibers are coated with a unique layer, covering the hydroxyl groups of lignin that formed hydrogen bonding with water [44]. Therefore hydrophilic character of the composite gets minimized up to a certain extent. Along with this, the non-cellulosic content hemicellulose also dissociates and get offsets from the fiber aiding the adhesion strength of fiber and the resin. The Isocyanate is also known as coupling agent, as it works simultaneously on the removal of hydroxyl groups of cellulose and the non-cellulosic content of the fibers [45]. The moisture trapped within the fibers reacts with the foreign urea that yield the product which thereafter work for the disposal of above mentioned species. The final test after the treatment method reveals that water absorption capacity has highly decreased; also the moisture present earlier has already been removed. Thus, we find improved interfacial interaction between the Banana Fiber and the Unsaturated Polyester resin [46].

Like Acetylation, Benzoylation, peroxide treatment is another chemical treatment method that requires the alkali treatment as a prerequisite. The Benzoyl Peroxide is most commonly used peroxide. The treatment initiates with the reaction of peroxide and the alkali treated fibers in the presence if Acetone as a catalyst. It proceeds through the free radical mechanism under which the peroxide dissociates into free radicals which directly attack the polymer. More precisely, the cellulosic contents are forced to get rid of their hydroxyl groups [43]. Another dynamic method of fiber treatment that adversely affects water absorption characteristic of the composite [47]. The basic framework on which silane treatment works is the breaking of large chunks of fibers into smaller fibrils thereby increasing the aspect ratio. This method is more effective than the alkaline treatment when it comes to aspect ratio. It begins with the formation silanols from silanes through the process of condensation [27]. The Banana fibers are then soaked into the solution of alcohol-water mixture with a hint of vinyltrimethoxysilane. The hydroxyl groups of the vegetable fibers are then discharged with the assistance of so produced silanols. The fibers were then left for drying for half-hour period followed by drying them into the oven [41]. The treatment specially looks towards transforming the hydrophilic fibers to hydrophobic fibers, to increase the interfacial interaction as because the polymer matrix is also hydrophobic in nature. It is advised to be precautious while carrying out the Silane treatment as few other side functional groups of Silane may react with other parts of fibers, causing unnecessary shifts from the desired outcomes [46]. Thus one should keep a check on the factors affecting the treatment rate like time duration, concentration of the agent, etc. [48]. Apart from water absorption characteristics, this treatment method enhances the flexural and tensile modulus to a large extent. Hence fibers after treatment are mechanically stronger and absorb less water than before [49].

4 Water Absorption Behavior of Natural/Banana Fiber Composites

Study of water diffusion/absorption characteristic is an important parameter for lignocelluloses fibers are hydrophilic in nature which is an undesirable characteristic when we talk about quality and commercial application of their finished composites. Celino

[50] analyzed diffusion phenomena in natural fibers. The samples of 4 different fibers were put for the purpose of hygro-thermal aging in total water immersion and in an environmental chamber maintaining at a temperature of 23 °C and having relative humidity of 80%. Various predictive modeling approaches were used for the simulation of experimental curves. Hosseinihashemi et al. [51] Investigated long duration behavior of water absorption of thermoplastic composites made by thermally treated wood. In this analysis wood plastic composites were fabricated from thermally treated beech wood and the matrix material was polypropylene and the method of fabrication was injection molding. Water immersion procedure was used to address the long term water absorption nature of composites. The composite, developed with wood treated at temperature of 180 °C and for duration of 120 min showed the minimum water absorption. The calculation of Diffusion coefficient parameter was done by fitting the model predictions. It was also concluded that theses composites obey Fickian diffusion process [52]. Analyzed the water immersion behavior of the wood plastic composites which were developed by industrial wood residues. Modeling strategies were used for the better understanding of water absorption behavior. Two way preparation methods were used for the sample preparation that is extrusion compounding and injection molding. The changes in swelling and water absorption behavior were understood by applying fundamental Fick's law of diffusion. Both calculation and practical approaches were used in this job. Short duration diffusion parameters were also evaluated along with long duration parameters for better knowledge of complex sorption process of wood polymer composites. The water absorption testing composites use to be examined with the help of ASTM D570 standard. The dimensions of the sample are kept 76.2 mm × 25.4 mm by the thickness of composite. The following mathematical equation has been used for analysis

$$\%M = \frac{M_f - M_i}{Mi} \times 100$$

where, M_i is the dry initial weight measured in the starting and M_f is the weight after immersion in water and $\% M$ is rate of water absorption. The water absorption behavior in reinforced polymer composites obeys fundamental Fickian as well as non Fickian diffusion behavior. To analyze diffusion behavior following kinetic equation can be applied.

$$\%M = \frac{M_f - M_i}{Mi} \times 100$$

where M_t the percentage of the water which is absorbed in the material at time t, while M_m is the maximum percentage of the water absorbed, and k and n are the kinetic parameters. The diffusion coefficient (D) for the water absorption by composite can be calculated using the following equation and mathematical analysis [50]. Here **he** is the thickness of sample.

$$F_s = \frac{M_t}{M_m} = \left(\frac{4}{h}\right)\left(\frac{Dt}{\pi}\right)^{1/2}$$

Muktha and Keerthi Gowda [20] examined water diffusion and fire resistance characteristics of unmodified banana fiber reinforced polyester composites and it was concluded that between 3 and 5 mm thickness samples, 3 mm samples have less water absorption and fire resistance properties as compared to 5 mm samples (Fig. 5).

Ghosh et al. [53] observed the effect of alkali and ultrasonic treatment on mechanical and water absorption properties of banana fiber reinforced vinyl ester composites they also concluded that ultrasonic treated fiber possess superior qualities as compare to untreated banana fibers and composites prepared from ultrasonic treated fibers have potential for commercialization. They also did the diffusion modeling and estimated the kinetic parameters k and n and found that initial behavior follows Fickian diffusion.

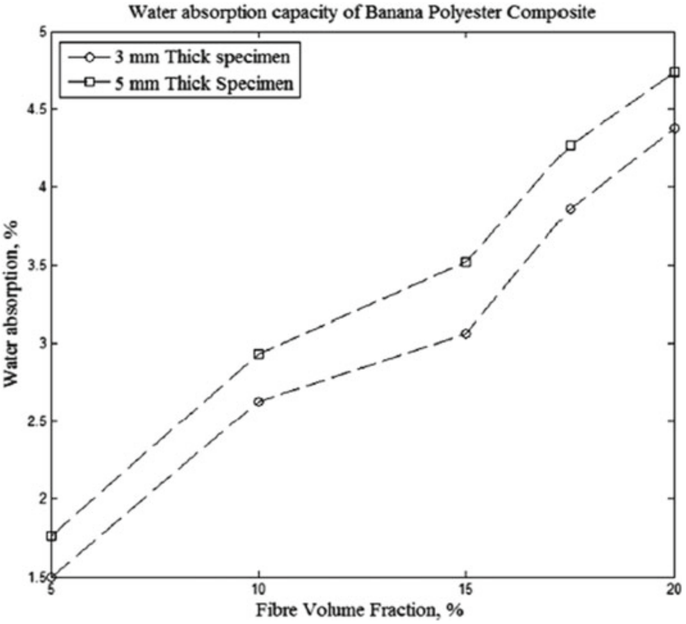


Fig. 5 Moisture absorption of banana fiber reinforced polyester composites Reprint from (Mukhta et al. 2017)

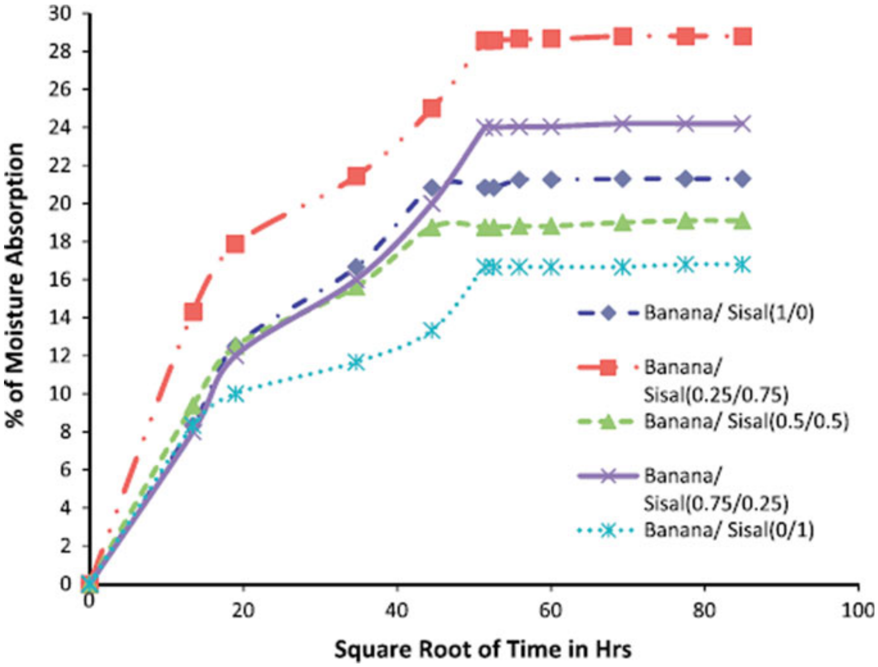


Fig. 6 Moisture absorption of Hybrid banana Composites Reprint from [54]

5 Hybrid Banana Composites

Hybrid composites can be fabricated by natural or synthetic fibers or the combination of two. Sometimes very encouraging results are obtained by the combination of these fibers in different proportions. The constituent fibers combination may be optimized to get the best properties. The static and dynamic mechanical properties of banana/sisal hybrid composites in polyester matrix were studied. The maximum value of activation energies was obtained in composites having combination of 3:1 banana and sisal and the experimental results were also compared with theoretical findings [1]. Banana fiber was hybridized with sisal fibers to improve the mechanical properties [11, 54, 55]. Figure 6 is showing the water absorption behavior of banana and sisal hybrid composites.

The tensile and flexural behavior of snake grass blended composites were compared with snake grass and banana hybrid composites and it was concluded that hybrid composites have better properties as compared to single fiber composites [58]. The chemical treatment and hybridization of sisal fiber was used to improve the properties of banana reinforced PLA composites. Table 2 shows the short summary of hybridization effect on different properties of banana reinforced polymer composites [56] (Fig. 7).

Table 2 Hybridization effect on banana reinforced polymer composites

S. No.	Matrix used	Fibers used	Methodology	Key observations	References
1	Hybrid with Isopthalic polyester	Banana and sisal fibres	Hand layup method	3:1 Banana, sisal ratio is optimum for the optimum results	[57]
2	Hybrid with epoxy composite	Banana and sisal fibers	Hand lay up	The addition of sisal fiber in epoxy composites reinforced by banana fibers is done up to 50%. Mechanical properties were improved and water absorption was decreased by this modification	[54]
3	Hybrid with epoxy resin	Banana &sisal fibers	Hand layup method	Rule of hybrid mixture was applied and validation of experimental results was done	[55]
4	Hybrid with Isopthalic polyester resin	Snake grass, banana and coir fibers	Hand layup method	Hybridisation of banana fiber with snake grass improved the properties of composites	[58]
5	Hybrid with Polylactic as its matrix	Banana and Sisal fibers	Injection moulding method	Chemical treatment with NaOH is effective for up gradation of properties of hybrid composites	[56]

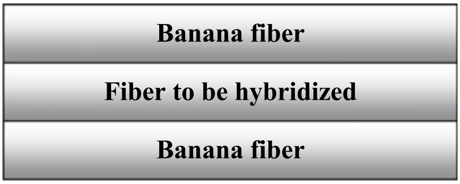


Fig. 7 Sequencing pattern (*Source* Author)

6 Effect of Hybridization and Chemical Modification on Banana Fibre–Reinforced Polyester Composites

Polyester is a thermosetting polymer which is known to be comparatively cheaper than the other thermosets [59, 60]. It is tested to possess a flexural modulus of 1.35 GPa and a Tensile modulus of 0.95 GPa [34]. It is pale yellowish in appearance and is about 600 CP viscous at 25 °C [19, 61]. Diols and dibasic acid polymerize to give the polyesters [62, 63]. Polyesters are usually reinforced with accelerator, catalyst and a coupling agent in general [34, 63]. Most commonly Methyl Ethyl Ketone peroxide, Cobalt Naphthalene and Maleic anhydride are used as accelerator, catalyst & coupling agent respectively [64, 65]. The coupling agents are seen capable of treating the Vegetable fiber and the polymer matrix simultaneously [66].

The use of raw fibers is highly prohibited as the properties largely suffer and the composite is of hardly any practical use [67]. Therefore we use any of the above described chemical modification method so as to achieve the desired characteristics of the composites [68]. Studies revealed that the mechanical properties like flexural strength; flexural modulus, tensile strength, tensile modulus, impact strength and impact modulus were largely dependent on fiber loading [3, 69–71]

Effect of hybridization: When Banana fiber was reinforced along with Glass fiber, the layering pattern of glass fiber played significant role in defining the characteristics of the so produced composites. In addition to this the mechanical properties also surged up [3]. Another study involving the hybridization of Banana-Sisal fiber infer us that the tensile and flexural strengths deviates positively relative to Banana fiber composite or Sisal fiber composites [61]. The Banana-Jute hybridized polyester composites also underwent mechanical enhancements [69].

The effect due to hybridization and chemical treatment on moisture absorption behavior was extensively studied [4]. The glass fibers were hybridized with banana fiber in polyester matrix. The glass fiber fractions were kept 0.07, 0.11, 0.15, 0.16, and 0.17. The water diffusion coefficient was lowest in case of high glass fiber content. Different chemical treatment like silane, acetic anhydride and alkali was applied on these hybrid composites and it was found that lowest water absorption is in silane treated composites.

7 Conclusion

The Banana fiber reinforced polyester resin composites were seen to absorb ample quantity of water. This distorts the internal framework of the composites, resulting into fiber pullouts which are not recommended. Therefore there was an intense need to modify the constituents of composites. The vegetable fiber (here banana fiber) were chemically treated with different agents imparting the hydrophobic nature to the fibers. We have seen that alkaline and silane treatments are the major treatment methods which gives the significant amount of alterations to the fiber surface.

The fact that lignin and hemi-cellulose are being removed by these curing agents assures that the fiber automatically leaves its hydrophilic character. Along with this ample enhancements in the dynamic mechanical properties occurs which makes the composite much more compatible to be put to industrial implementation. We also discussed the effect of hybridization of the composites mainly banana-glass, banana-jute, etc. All of them showed positive deviation from those consisting of Banana fiber only. Therefore these composites are liable to find large application in the engineering field.

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Properties of Hemp Fibre Reinforced Polymer Composites

A. V. Kiruthika and Anish Khan

List of Abbreviations

HF	Hemp fibre
TS	Tensile strength
TM	Tensile modulus
FS	Flexural strength
FM	Flexural modulus
IS	Impact strength
ILSS	Interlaminar shear strength
YM	Young’s modulus
TGA	Thermo gravimetric analysis
DSC	Differential scanning calorimetry
DMA	Dynamic mechanical analysis
SEM	Scanning electron microscopy

1 Introduction

Increasing environmental consciousness, global waste concerns and rising crude oil prices have driven policymakers worldwide to raise legislative pressure. This stimulates industrialists, researchers and materialists to enhance the environmental

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A. V. Kiruthika (✉)
Seethalakshmi Achi College for Women, Pallathur, Sivagangai Dt., Tamil Nadu, India

A. Khan
Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_11

concepts, sustainability and the reconsideration of renewable energy. Natural sources from agriculture or forestry products create a novel materials or alternate energy sources like hemp fibres [18]. Hemp, a high fibre yielding crop could have pesticide proof, requires less humidity to grow and minimal cultivation.

Hemp fibre (HF) a member of bast fibre family obtained from the hemp plant (Cannabis Sativa). An ecologically friendly fibres have been given more focus in the field of composite materials, construction and in textile, paper, automotive industries (Bhat and Rong 2005). Compared to conventional fibres, hemp has specific strength, high sustainability, stiffness and low density. Hemp is an annual plant similar to other fibre crops like flax, kenaf, jute, nettle but it was only differentiated by the cellulose content present in the fibres. Two types of fibres are obtained from the stalk of a hemp plant i.e., (i) long bast fibres (20–40 wt%) has low lignin content are same as soft wood used for the preparation of bio-composites for rope, paper, vehicles etc., (ii) short core fibres are same as hard wood fibres (60–80 wt%) used for the preparation of building materials such as particle boards, hempcrete, absorbents, etc. A typical fibre yielding plant of HF is greatly recognized as medicine, recreational drugs and food.

From the last decade, the usage of HF has been raised for various applications. The varieties of hemp were Cannabis Indica, a short, densely branched and low quality fibre have a higher Δ9-THC (Tetrahydrocannabinol), the other variety Cannabis Sativa L.Marijuana have 18 to 38% of THC conc. Christelle et al. [16]. Hemp consists of many ingredients includes amino acids, proteins, lactones, vitamins, steroids, sugars, enzymes, pigments, terpenes, fatty acids and cannabinoids [59].

1.1 Structure of Hemp Fibres

Hemp Plant is native to Central Asia grows up to a height of 1.2–5 m and the stem has the fibre content of 28–46% [44]. The length of the HF strand are 1.8 m or longer and the elementary fibre are 13–25 mm long. HF has a complex and multi-celled structure of different layers in the hemp stalk. The fibres comprised of elementary fibres (EF) which are glued together with middle lamella by pectin. The cell wall consists of primary cell and S_1(outer), S_2(central), S_3(inner) secondary walls (Fig. 1). Based on the cellulose content, the fibres have 5–10 nm in diameter and length, which is varied from 100 nm to several micrometres [37]. Placet et al. [42] explained the elementary fibres of HF as 10–40 μm in diameter and 10–20 nm in length.

1.2 Extraction of Hemp Fibres

Fibres from stalk could be extracted through a variety of retting process like dewing and water retting. Retting is nothing but, a biochemical mechanism in which microorganism generated enzymes, target pectin content which bind fibre cells together

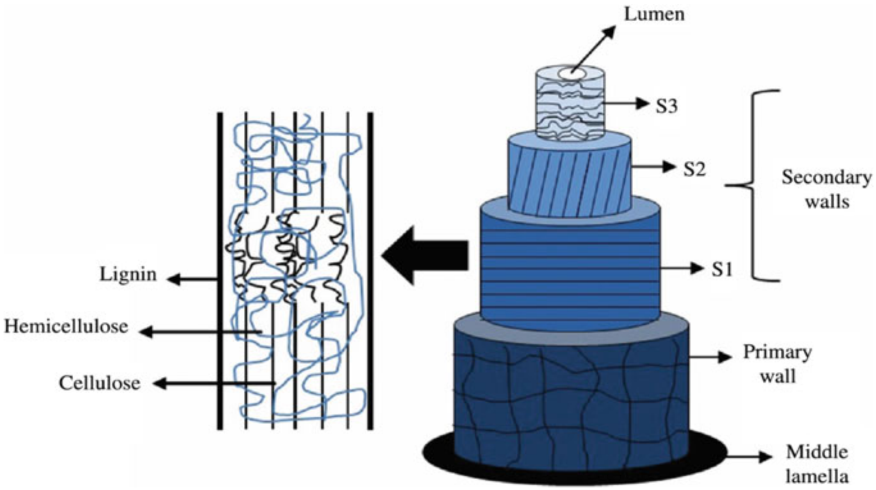


Fig. 1 Structure of hemp fibre [41]

serving to separate bundle fibre from bast fibres and shives. Hemp stalks are spread on the ground in dew or field retting and pectins are disrupted by mainly fungi [23]. Conversely, in water retting process, the stems are immersed in water basins where a pectinases enzyme is developed. Moreover, this process need huge amount of fresh water to get a high quality fibres but expensive one. So, the water retting process was dropped in the mid 1990s due to the contamination and consumption of huge quantity of both clean water and energy [4]. Dew retting process is carried out without use of water, hence it is natural process and more favourable method for the manufacture of bast hemp fibres [17].

Microwave degumming (MD), another process to separate the fibre from bundle, used for the preparation of composite materials especially for structural components. Here the microwave energy targets the middle lamella binding the fibres together. The polar molecules, pectin is mainly degraded than cellulose by the MD process [32]. Chemical retting, a type of retting process utilizes harmful chemicals like NaOH, sodium benzoate, hydrogen peroxide and yield smooth bast fibre within a short period of time(75 min to 1 h). The major disadvantage of this retting is chemical treatment, it might be diminished the mechanical characteristics and the natural colour of the fibres. Enzymatic retting separates the cellulosic fibres from non-cellulosic fibres within 12–24 h by using the enzymes like pectinases, xylanases, lacasses etc. Scutching or scraping process done by beating the stem with metal blades either by hand or mechanically [60].

1.3 Constituents of Hemp Fibre

Like other plant fibres, HF also consists of cellulose, hemicellulose, lignin, pectins, wax respectively. The proportions of the chemical composition is highly depend on the climatic conditions, harvesting time, source of the fibre, retting methods adopted, age and size of the plant. Cellulose was the primary constituent which provides strength and stiffness to the plant cell walls and also to the fibres. Hemicellulose, a highly branched, hydrophilic, low molecular weight polymer provides little stiffness and strength to individual cells. Usually, lignin are amorphous, present in the middle lamella of fibre bundles. Higher the lignin content, higher the rigidity, whereas higher pectin content denotes higher flexibility [28]. Cellulose content present in HF lies in between the flax(highly crystalline cellulose) and kenaf (semicrystalline). Jankauskiene et al. [25] determined that compared to water retted fibre (WRF), dew retted fibre (DRF) has the lesser amount of cellulose (78.4%), hemicellulose (5.85%), larger content of lignin (13.1%) and ash (2.99%). But the water retted has the greater amount of 81.7% of cellulose, 6.32% of hemicellulose, lesser amount of lignin as 10.2% and ash as 1.23% respectively. Similarly DRF has the highest strength of 19.9 KgF and flexibility of 25 mm than the WRF. As said, the results of flexibility and strength of HF are highly dependents on its chemical composition of the fibre.

1.4 Fabrication of HF Composites

Fabrication method played a prominent role and it has an impact on mechanical characteristics of composites. Various techniques were administered by many researchers. Yan et al. [66] explored the orthogonal experimental design, a most powerful and cost efficient method to examine with the influence of three parameters (mixing temperature, mixing time and rotor speed) for the noil HF/PP composites. From the range analysis and variance of analysis, the mixing temperature has substantial impact on TS, FS and IS, mixing period has less impact on TS and FS, rotor speed primarily influenced the IS.

Twin screw extrusion and injection moulding method was used to manufacture the HF/PP composites with the influence of surface modification of fibres (NaOH and MAPP). Experimental results inferred that injection moulded composites had the superior mechanical performance of all the samples tests, it is because of the addition of HF and an optimum MAPP content [10].

Composites derived from HF/sisal reinforced hybrid epoxy were manufactured by using traditional cold pressing method. In this investigation, maximum FS and CS were obtained for the hybrid composites, then these fibres could act as a superior reinforcement for the preparation of novel bio-composites which have high strength to weight ratio [3].

The interfacial bonding between the HF and epoxy were enhanced with NaOH treatment and trimethoxysilane (as a coupling agent). The surface modified fibres were utilized for the production of HF/Epoxy composites by vacuum infusion process (VIP). From this, silane treated HF had improved the TS and FS of composites, but no higher values were reached [51].

The influence of HF length on the mechanical characteristics of PP/SEBS(poly(styrene-b-(ethylene-cobutylene)-b-styrene)/HF composites were studied. During extrusion and injection molding process, average length of HF was reduced approximately 2, 2.5 or 4 times. Due to the presence of SEBS and injection moulding, the obtained reduction was greater for the prepared composites. The authors disclosed that the fibres length with more than 2.5 mm had a potential candidate for electrical vehicles such as dashboard or door panel parts [19].

The combination of single screw extruder with pultrusion method were used to fabrication green composites derived from HF/organo clay modified poly butylene succinate(PBS) matrix. Tensile modulus was increased and TS maintained the same value, when the content of organoclay increases. After 30 days of environmental exposure such as distilled water and soil, the TM and TS was higher for PBS/Hemp than the PBS/HF/organoclay hybrid composites [26].

Composites from silicone reinforced with alkalized, silanized and raw HF were manufactured by two methods (a) moulded and (b) 3D printing process. It was noted that the 3D printed specimens had greater stiffness and TS, compared to molded one. The surface modified HF were enhanced the mechanical properties than the untreated HFs. These results indicated that a hexagonal honey combed structure and simple soft gripper were designed to demonstrate the application of 3D printed specimen [40].

2 Physical Properties of Hemp Fibres and Its Composites

The physical appearance of HF varies in color. For dew retting process, the fibre appears as steel grey and dark grey in colour whereas for water retting, it is in light grey [25].

Microfibrillar Angle (MFA)

It is the main parameter of plant fibres that affects the inherent mechanical behaviour of the fibre. According to the literature, various methods were used to find MFA, they are X-ray diffraction, IR-spectroscopy, polarization techniques etc. [42]. Wide angle X-ray scattering was utilised to find the MFA of hemp fibre and the values were ranged between 8° and 112°. According to Dasong and Mizi [18] the orientation of MFA in the HF treated with copper(II)nitrate was more effective than cobalt II chloride solution. The results predicted (Fig. 2) that the average MFA in S_2 layer is 2.65° and in S_1 layer is 80.35°

Density

An investigation was conducted to determined the density of hemp fibre by using Pycnometer. The authors used the formula as $\rho_f = \frac{M_1/(M_3-M_2)-(M_4-M_2-M_1)}{\rho_l}$ and

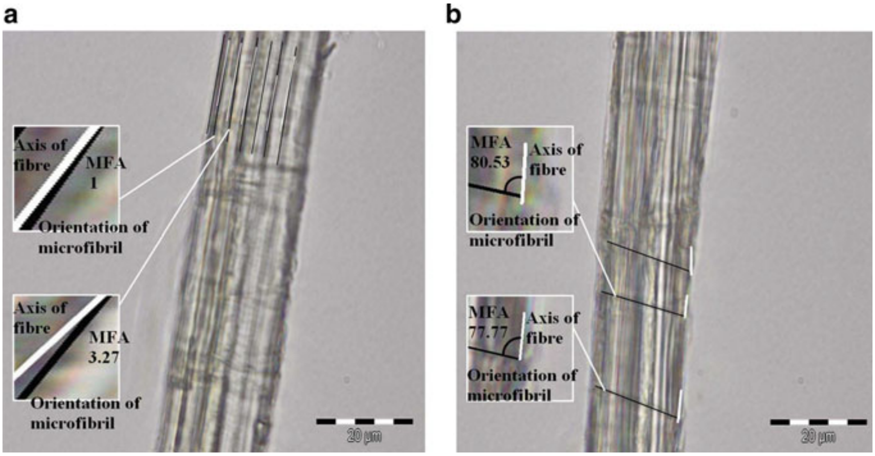


Fig. 2 Microfibril angle of hemp fibre: **a** MFA in S2 layer, **b** MFA in S1 layer [18]

found the average density of hemp fibre as 1.393 g/cm^3. On the other hand, Na Lu et al. (2011) reported in their work as 0.86 g/cm^3. The influence of surface modification with alkali (2, 4, 6%) and silane (2, 4, 6%) treatment varies the density value of HF from 1.170 to 1.203 g/cm^3 whereas the untreated HF has 1.249 g/cm^3 [53]. Amandine et al. [5] compared the densities of various natural fibres such as sisal (1.058 g/cm^3), jute (1.201 g/cm^3), flax (1.358 g/cm^3), and found that the hemp has the highest density value of 1.403 g/cm^3.

Using the equation $\rho_{theory} = \rho_f W_f + \rho_e W_e$, the theoretical density (ρ_{the}) was calculated and compared the results with experimental density (ρ_{exp}) for the hemp fibre reinforced epoxy composites. The obtained results were listed in Table 1. From the results, it was understood that, increasing the HF content, increases the density values. In addition, the theoretical values is greater than the experimental density [45]. The density of polyurethane/HF composites were increased from 36.02 to 48.09 kg/m^3 with the influence of fibre content increased from 5 to 30% [47].

Asokan et al. [8] successfully prepared the hybrid fibres (sisal and hemp) enhanced polylactic acid composites via extrusion and injection molding techniques. The material has density value of 1.14 ± 0.07 g/cm^3 and have been used as a potential candidate in interior, packaging and agricultural applications. According to the results of Vijay et al. [62] the HF/epoxy composites has the highest theoretical density (1.176 g/cm^3)

Table 1 Density of hemp fibre composites with varying fibre content

Composites	ρ_{exp} (kg/m^3)	ρ_{the} (kg/m^3)
Hemp fibre 5%	1100.0	1119.0
7.5%	1102.4	1128.5
10%	1108.4	1138.0

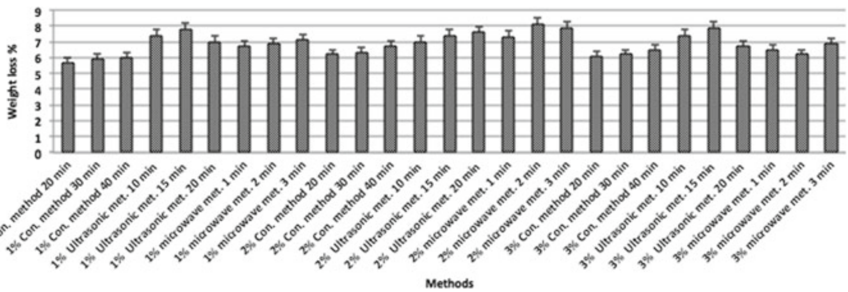


Fig. 3 Change in weight for lacasse treated hemp fibre [35]

and experimental density (1.104 g/cm^3) than the hybrid fibre(jute/HF/Flax) epoxy composites.

Weight Loss

Higher weight loss values were achieved for the alkali treatment of HF, due to the elimination of chemical ingredients like ash, pectin etc. during the treatment [53]. Contrarily, the silane treatment gained the weight of fibres from 0.6% to 2.17% respectively. In other work, hemp fibres were treated with laccase enzyme (1, 2, 3%conc.) for different durations using conventional atmosphere (20, 30, 40 min), ultrasonic energy (10, 15, 20) and microwave energy (1, 3, 5 min). Among the various treatments, more weight loss has been noted in the microwave energy method at 3 min with 2 %conc (Fig. 3). Hence the outcomes revealed that the residual size and impurities present in the fibre were diminished, during microwave energy treatments [35].

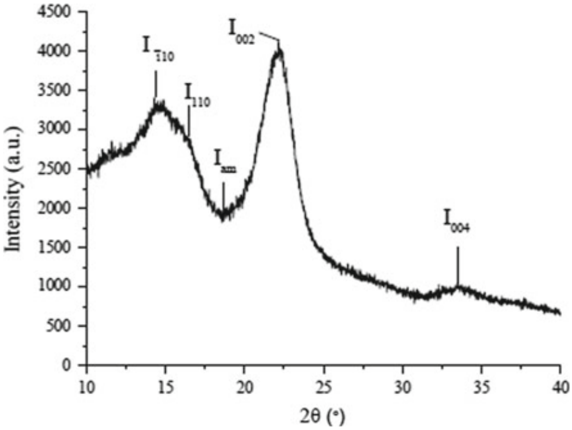
The influence of chemical solvents of three acids (CH_3COOH, HNO_3 and H_2SO_4) and three alkalis ($NaOH$, NH_3 and $C_6H_5NH_2$) on the HF/PP composites were studied. The percentage of weight loss (WL) was found by using the formula $WL = \frac{M_b - M_a}{M_b}$ where M_b is dry sample weight and M_a, after the sample immersed in chemicals. A considerable decrement in weight was observed with increasing chemical immersion time. Also, the reason for further deterioration in the composites is due to the weak interfacial adhesion between the HF and PP [11].

Using hand layup cum compression molding method, HF/epoxy composites were prepared and studied [12] the effects of eggshell nanoparticles (ESP) and alkali treated HF/epoxy composites. From TGA analysis, higher thermal stability were achieved for biodegradable ESP. At different temperature, the different weight loss temperature yield at 498.1 °C were observed as 312 °C, 428 °C and 94.5% respectively. More mass loss such as 43.51, 53.71, 54.56 and 56.11% were noticed for 0, 7, 14, 21 vol% of ESP at the same temperature(498.1 °C).

Crystallinity Index (CI)

It determines the degree or order of crystallinity of plant fibres. Using XRD, CI was calculated by using the formula $CI = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$. The CI of HF is found to be

Fig. 4 X-ray diffraction of hemp fibres [18]



56%. Similarly the maximum intensity at 2θ = 22.1° and minimum at 2θ = 18.6° for 002(Fig. 4) and 110 peaks respectively [18]. In other research work, the crystallinity and amorphousness of HF was calculated using WAXD. Crystal size of HF is 2.8 nm and crystallinity percentage as 89% [52] was noted. An increment in CI was noticed in the following order: 70.36% > 73.18% > 74.60% > 76.02% for the alkaline treated (from 0, 2.5, 5, 8 %conc.) HF, but at 10% NaOH treated it was 72.20%. This is attributed due to the higher conc. of NaOH which distracts the cellulose structure [48]. A similar result could be achieved by Tom et al. [58] CI of untreated should be 64.87% whereas the alkaline treated(1 h) as 71.16% and granulated as 80.65%.

X-ray diffractometer was used to find the crystallinity percentage (%Cr) and CI of untreated and surface treated (alkali, benzoylation and hydrogen peroxide) HF reinforced cellulose filled epoxy composites (HFRCFEC). CI(0.40) and %Cr(62.59%) was smaller for HFRCFEC, whereas it was higher for treated one. The range of %Cr lies from 71.59 to 63.18% and for CI, it is from 0.6 to 0.042% respectively. From the XRD analysis, it was observed that, the removal of amorphous substance lead a higher value in %Cr and CI, due to the surface modification of fibres, conversely poor value achieved for the untreated HFRCFEC because of the low order of cellulose crystals to the fibre axis [6].

Moisture absorption (MA)

It is nothing but the plant fibres absorbed the quantity of water when it was submerged in water for a stipulated period of time. MA is highly dependent on fibre crystallinity and chemical constituents. The major disadvantages of plant fibres is MA, because it creates a lot of problems when it was used as the reinforcement especially in the production of composites. Because of MA, the plant fibres swelled which leads a crack formation and reduces the stiffness of composites. According to D IN 53495, the MA was measured with dry and humidity exposure samples. Under normal conditions, the MA of HF is 7% and further increased with respect to time. Many scientists measured the equilibrium moisture content of various natural fibres but the HF has the MA value of 7–9%.

The influence of HF diameter 20, 40, 80 mesh size and HF volume fraction of 10, 15, 20, 30% reinforced with polybenzoxazine (BZ) composites were prepared by compression molding techniques [1]. The MA properties of all composites were much higher than the pristine BZ, because of hydrophilic nature of HFs.

In addition, larger MA was noted for composites with lower diameter and for 20 vol% fibre. The MA value was 4.459%, 5.131% and 5.398% then the corresponding confirmed diffusion coefficient values were 9.01, 9.85 and 10.86 t^{-9} m^2/s respectively for 20, 40, ad 80 mesh sieve HF composites [2].

2.1 Morphological Properties

Surface topography and structure of treated HF is clean, which was identified by SEM analysis. The separation of bundle fibre with largely unsmoothed surface has been seen. Another interesting study, exhibited that the existence of waxes, oils and impurities in the untreated fibre bundles whereas 6 %NaOH treated has a clean surface but roughened by chemical modification with a clear indication of removal of impurities [9]. However, according to Nadezda et al. [34] the changes in structure and morphology of hemp hurds was analysed by optical microscopy. The unfibrilled images with the existence of dirt and waxes on the surface were seen in raw hemp. Then the strongest defibrillation, partial detachment of fibres, calcium ions saturation to the fibre surface was noticed for the hurds treated with NaOH (Fig. 5), $C_{10}H_{16}O_8N_2$ and $Ca(OH)_2$ respectively.

From TEM analysis, aspect ratio(fibre length to diameter ratio) was found to be 88 for unbleached and 82 for bleached HF. The main criteria to determine the reinforcing capability of these nanofibres are aspect ratio. Here, the bleached fibre was thinner and very short compared to unbleached one. Surface modification of fibre might be reduced the cellulosic chain length resulting cutting the length and weakening the cellulosic nanofibres. High pressure fibrillation was evidenced by AFM images where the fibres size is in nano and the width range is from 30 to 100 nm [63].

One of the major concern that cause the impacts of physico-mechanical characteristics of both fibre and matrix are the SEM analysis. Francucci et al. [22] used the fracture surface of HF/AEHO(acrylated epoxy hemp oil resin) composites and compared the results of vinyl ester(VE) based HF composites. Due to the surface chemical compatibility, the better interfacial bonding between the HF and AEHO was noticed for this composites than the HF/VE based one. Also a considerable reduction in the gap were noted for HF/AEHO matrix.

For the determination of adhesives between the HF and cellulose acetate(CA) matrix composites, environmental scanning electron microscopy(ESEM) was taken for the fractured samples. The result revealed that a smaller amount of fibre pull-out and higher value of modulus of elasticity were observed for the composites prepared

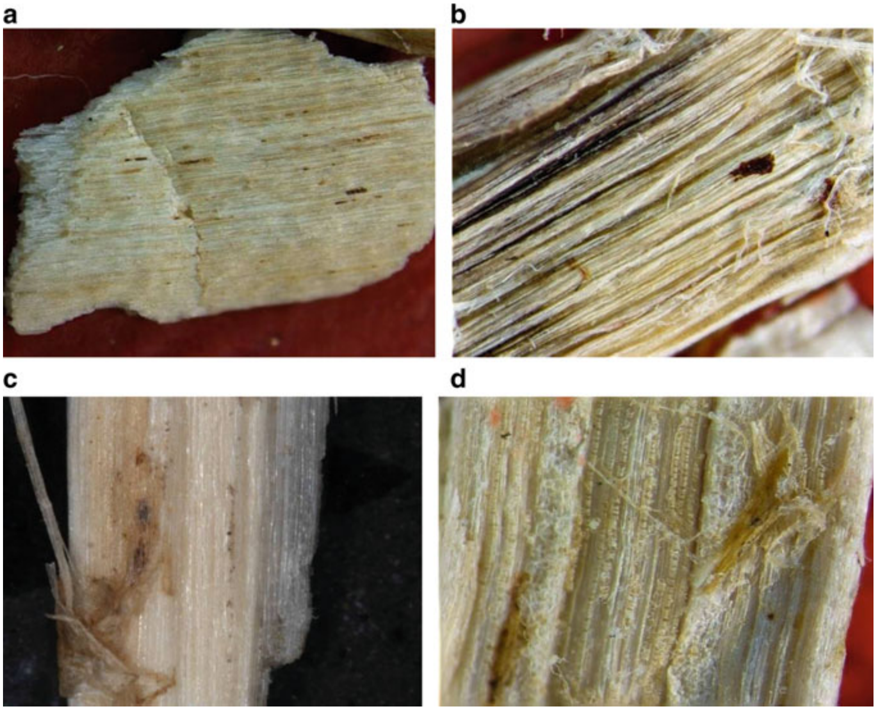


Fig. 5 Optical Micrographs of **a** hemp hurds, **b** chemically modified by NaOH, **c** EDTA and **d** $Ca(OH)_2$

with the extrusion and injection moulding process, but reverse the case in the powder impregnation process [7].

According to the researchers [13] SEM analysis showed fibre pull-out, matrix fracture, fractured edges of fibre, dislocation of fibres under tensile, flexural and impact loading respectively for the hybrid(banana-hemp-glass) fibre reinforced epoxy composites. Fibre pull-out from matrix and crack propagation from the light microscopy (Fig. 6) for the hybridized (with flax) HF/PU composites was observed by Pankaj Pandey et al. [39]. The influence of $Ca(OH)_2$ treated HF reinforced concrete (HFRC) has higher interfacial adhesion between the fibre and matrix, which improved the load transfer process. But untreated HFRC has less sufficient adhesion between the fibre and matrix [65].

2.2 *Thermal Properties*

Aziz et al. [9] studied the thermal properties of HF (treated with alkali 6% and untreated) by using DSC. From their studies, the endothermic peak could be observed

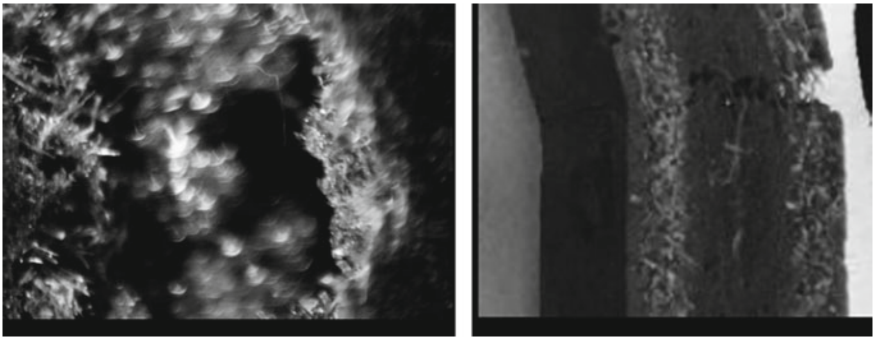


Fig. 6 Light microscopy of hemp fibres [39]

at the temperature range of 50–175 °C which denotes the existence of water molecules in the fibre. For treated four peaks and untreated three exothermic peaks were found. The indication of decomposition temperature was noticed at the temperature greater than 200 °C. Similar study was taken by Mwaikambo and Ansell [33], sharp decrease in decomposition temperature was observed for the alkali treated fibres between 0.8 and 8 %conc.

The TGA and DTA analysis showed that untreated HF was degraded at earlier stage, meant it has lower thermal stability than the alkali, acetylated and maleic anhydride treated fibres. At 100°C, a mass loss is observed due to the loss of water molecules. An enhancement in thermal stability was noticed for the treated HF, this is attributed to the removal of chemical constituents present in the fibres [24].

Composites of HF and PCL(polycaprolactone) were prepared with various aspect ratio(AR) of 00, 19, 26, 30 and 38, and studied their thermal properties [20]. The effect of HF on the TGA analysis showed a lower value of degradation temperature for the AR30(424°C) and AR38(432°C) followed by AR19(428 °C) and AR26(432 °C). Similar outputs could be reflected in the DSC samples. The degree of crystallinity $\chi(\%)$ is higher(60.6%) for AR26 followed by AR38, AR30 and AR19.

The surface modification of HF with alkali (NaOH), silane and alkali-silane based polyamide PA10101 biomass composites were taken for TGA analysis. The first and second weight loss were notified due to the dehydration of HF at 80 °C to 200 °C and decomposition of cellulose in HF at 300 °C respectively. During second heating scan of DSC, the silane treated HF/PA1010 has the highest melting temperatures (T_{m1} and T_{m2}) and heat of fusion ΔH_f(J/g) than the alkali, alkali-silane treated HF and plain matrix composites [67].

In other research work, the storage modulus(E') decreases, as the temperature increases for untreated and surface modified HFRCFEC. This is due to the increment in the molecular mobility of the polymer chain. Similarly, the loss modulus(E'') and tanδ were also decreasing with increasing temperature and matrix loadings [6].

The dynamic mechanical analysis (DMA) of sisal fibre (SF)/HF reinforced PLA hybrid composites were carried out. At 80°C, the T_g were increased for hybrid composites because of cold crystallization. But at room temperature, the increment in E′ was noted with the inclusion of fibres. Also a decrease in E′ was observed with temperature increases, in which the E″ was increased [8].

2.3 Mechanical Properties

The mechanical strength of HF could affect the performance of its fabricated output products say composites, that is HF compounded with polymeric resins. Cherouat et al. [15] used digital imaging method to study the geometry of unitary and bundle HFs. A large scattering of TS and YM were observed. After 4 weeks of exposure, there is a loss of initial modulus in HF at 88%, 86%, 73% with the effects of moisture, UV and temperature aging respectively.

The determination of TS of HF obtained from various varieties were analysed [46]. For the dry and wet fibers, Tygra(506 MPa) and Epsilon (498 MPa) varieties had considerably higher TS and YM than the other varieties like Futura 75, Woeka, Beniko, Bialobrzeskij. From this studies, the authors suggested that HFs tensile strength was similar to steel strength and could be used for foam gypsum reinforcement.

A comparative analysis of TS and elongation was given [43] for HF rope and sisal fibre ropes with 6, 8, 10 mm diameters at temperature −40 to 60°C. There was a considerable increment in TS was noted, primarily for 10 mm HF rope followed by 8 and 6 mm. An opposite influence was reached for sisal rope, i.e. 8 mm showed greater values followed by 10 and 6 mm. The extension of ropes was higher at room temperature (25°C) than the freezed one (−20°C). From the results, it was proposed that the performance of these fibres could be used as moisture and temperature sensor cables as inside grain bins.

Mechanical behaviour of single HFs(diameter 25–35 μm) and bundle fibre (75–85 μm) were analysed for chemically treated and raw fibres with different retting periods 2.5, 5.5, 7.5 weeks [38]. Due to the removal of surface impurities of fibres, the alkali treated and stretched fibres had better mechanical properties than the raw and unstretched fibres. Compared to other retting periods, the micro and macro-mechanical characteristics at 5.5 weeks retting period fibres showed highest YM, failure stress and strain. Hence the authors inferred that the diameter of the fibres played a vital role and an important parameter while considering the quality of fibres. Conversely, the tensile properties of single HF with various diameters and surface treatments such as alkali, acetyl and silane were experimented by Kabir et al. [27]. The treated single fibre exhibited lower stress (MPa), modulus (GPa) and failure strain than the untreated fibres.

Zineb et al. [68] summarized the results of mechanical features of polyvinyl alcohol (PVA) resin composites reinforced with hemp stalks which was derived from cellulose microfibers (CMF), cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF). Interfacial modification was given to extract pure CMF, CNC, CNF. Based on the experimental analysis, it was noted that, a considerable increase in mechanical performance of PVA based composites reinforced with CNC and CNF rather than

CMF. Also, compared to plain PVA, the addition of 7.5 wt% CNC_{15}, CNC_{30} or CNF showed higher TS of 26.3%, 13.4% and 48.6% respectively, where CNC_{15} and CNC_{30} referred as, CNC treated with H_2SO_4 for 15 and 30 min.

3 Various Parameters Affect the Mechanical Properties of HF Composites

The effect of three parameters like filler content as coconut shell powder (5, 10, 15%), reinforcement (25, 30, 35%) and thickness (6, 8, 10 mm) on the fracture toughness of the HF/vinyl ester composites were studied by using response surface methodology [30]. The results indicated that under optimum conditions, i.e. 25% reinforcement, 10% of filler content and 8 mm thickness specimens, the maximum toughness value was obtained.

The structural behaviour of HF blended with polymer concrete columns was affected by the various variables includes the number of confining layers and slenderness ratio. For the samples wrapped with 1, 2, 4 layers, an increase in compressive strength of about 9%, 13% and 22% respectively was noted whereas the ductility indices were 2.78, 3.95, 6.98 for 1, 2, 4 layers of unconfined layers. In addition, increase in slenderness ratio leaded decreased in ultimate strength and the ductility enhancement [29].

Physico-mechanical properties of HF/NR composites along with the effect of elastomer crosslinking was taken out using benzoyl peroxide. It was found that hardness and tearing strength exhibited an increasing value with the increasing of fibre content from 0 to 20%. Contrarily, TS was decreased due to the low interfacial bonding between the fibre and matrix, and agglomeration of filler particles. The elongation at break showed decreased value due to the highly cross-linked polymers. It could be observed that larger value of gel fraction (96.65%), crosslink density (4.0724×10^{-4} mol/cm^3), solubility (1.4689%), swelling coefficient (0.039), swelling index (3.92%) was noted with the increasing fibre loadings. From this properties, the obtained specimens could be used in manufacturing products in automobile and furniture industries [21].

Using injection moulding process, HF reinforced HDPE (50% plain + 50% recycled) composites were prepared with varying HF content as 10, 20 and 30 wt%. Compared to virgin HDPE, a considerable reduction in TS an FS by 0.53 to 2.20 MPa and 3.82 to 4.99 MPa with increasing HF (10–30 wt%) was noticed. SEM analysis imaged the failure mode, fibre fracture and weak interfacial bonding between the HF and HDPE, during the mechanical testing [54].

The reinforcement HF/Basalt and their hybrid fibres epoxy laminates manufactured by using hand lay-up and compression moulding methods [55]. The consequences of temperature (at 30 and 65 °C) and hybridization on drop weight impact and post impact residual strength of hybrid laminated were studied. From the experimental results, the following conclusions were drawn: (i) a small reduction in permanent deformation and residual strength at 65°C was noted for HF/epoxy, due to the ductile nature of epoxy, (ii) highest value of absorbed energy reflects highest damage creation for HF/epoxy followed by basalt/epoxy and hybrid/epoxy laminates, and (iii) maximum cumulative rise angle was noted in the hemp laminates which was less than 3000ms/V, and it was higher for the other laminates at 65°C.

Senthil et al. [50] comprehensively evaluated the properties of HF/sisal reinforced bioepoxy hybrid composites with the influence of various stacking sequences. Experimental results illustrated that, TS(31.997 MPa), CS(47.47 MPa), compressive modulus (1.892 GPa) and Interlaminar shear strength (4.08 MPa) respectively were higher for pure HF/epoxy, than the other hybrid and pure sisal/epoxy composites. Pure fibre(hemp or sisal) provided better mechanical properties than the hybrid ones. The results also predicted that (i) the poor compatibility between sisal and HF, (ii) poor adhesion between the hybrid sisal-epoxy-HF, and (iii) there was no significant improvements with the influence of layering sequence was observed in the hybrid composites.

The development of hybrid (sisal and hemp) fibre epoxy composites with the effect of various fibre percentage(10, 20, 30, 40, 50%) by using compression moulding method. It was found that increase in fibre loadings, increases the hardness strength. Furthermore, the mechanical properties such as TS (53.13 MPa) and FS (82.07 MPa) were higher for 40 wt% of sisal/HF/epoxy than other hybrid composites [61].

Similar trend was observed in HF/PP composites with the effects of NaOH and MAPP treatments. At 30 wt% fibre loading with treatments, possessed greater mechanical properties compared to 15 wt% loadings. A slight variation in length was observed before and after moulding the specimens. Composites containing MAPP had better adhesion between matrix and fibres, whereas raw and alkali treated one had poor adhesion, fibre pullouts, defibrillation which were evidenced by SEM analysis [57].

The TS, FS and impact energy ranged from 35.51 MPa to 38.47 MPa, 0.22–0.29 kN and 4.99 to 5.83 J were observed for HF/Glass fibre reinforced epoxy composites. The authors also reported that the natural fibre epoxy could be superior reinforcement for the synthetic fibre in the world of composites [14].

According to another research work, HF filled NR composites were characterised by using electron beam (EB) radiation. The hardness value and TS were raised whereas the elongation at break was decreased, when the EB dose increased (Fig. 7). The samples of NR + 20phr hemp at 600 kGy has the highest value of gel content (97.20%), volume fractions of 0.2128 and cross link density of 1.6544×10^{-4} mol/cm^3, due to the formation of 3D network. The WA characteristics of composites have increased with increasing fibre content and decreased with absorbed dose [31].

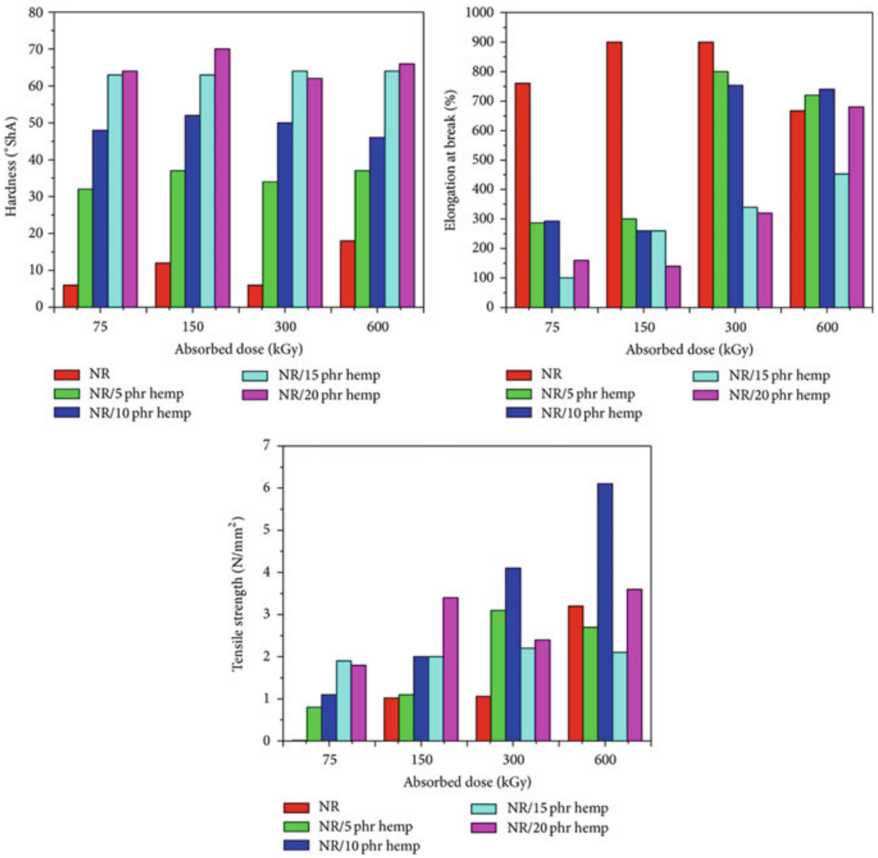


Fig. 7 Hardness, Elongation at break and tensile strength of HF/NR composites with electron beam radiation [31]

4 Applications of Hemp Fibre Composites

At present, there is a growing interest in HF composites in industrial applications and also in fundamental research. Instead of synthetic fibres, hemp could act as a strengthening materials which is less expensive and have a superior properties in the production of products [49]. One of the primary issues to be considered for HF polymer composites in external applications is durability. This issues could be resolved by treating hemp fibre with coupling agents, UV absorbers etc. Hemp is used in packaging, building construction, textile and composite industries [36]. The recent applications of HF are in sporting goods or musical instruments because of their high vibration damping capacity [56]. The uses of natural fibre composites in the automobile industry can be traced back to the 1940s, since Henry Ford prepared hemp fibre composites in a vehicle [64]. Hemp fibre reinforced thermoplastic and thermoset composites have potential candidate of the European automobile industries. Hence, bast hemp fibres plays a major role in structural and non-structural components that have no adverse effects on human and environmental health.

5 Conclusions

Hemp fibre reinforced polymer composites have major ecological benefits such as biocompatibility, non-toxic, light weight, specific mechanical properties and reduction in cost. It is more suitable to utilize these fibres in composites, which is an alternate for man-made fibres(Aramid, Carbon, glass) because of not only their environmental friendliness but also it is derived from green resources. This chapter addressed the studies related to the properties of HF reinforced polymer composites. Various extraction process of hemp fibre including microwave degumming, dew retting, water retting, chemical and enzymatic retting are discussed. Different fabrication methods were used by the researchers, to prepare HF polymer matrix composites are presented. The impact of various parameters like various fibre loadings, stacking sequence, confining layers on the properties and the applications of HF/polymer composites are reported. Therefore, it is to infer that the HF composites have a large scale applications in engineering, construction industries and it could create a new path for rural economic growth.

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Sustainable Product Packaging Using Vegetables Fibres and Its Composite

Guravtar Singh, Sumit Sharma, Kamalpreet Sandhu, Abdullah M. Asiri, and Anish Khan

1 Introduction

In current scenario research in sustainability are growing day by day, sustainable packaging one of the interesting area of work for young scholars, Product designers, Material scientists and Industrial experts. There are different materials and types of packaging are used now a days has been shown in Fig. 1. Indeed, non-biodegradable materials i.e., plastics, glass, and metals in packaging applications and produced every year with the intention of use and throw are raising concerns about environmental pollution.

The major problem is dependency of packaging industries relying heavily on the use of plastic products due to which the percentage of plastics in municipal solid waste continues to grow rapidly [1]. When plastic wastes are dumped in landfills, they interact with water and form hazardous chemicals, and the quality of drinking water may also be affected [2]. Moreover, during the manufacturing of plastic bags, the emission of carbon and many other harmful gases have serious impact on ecological

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G. Singh (✉)
School of Mechanical Engineering, Lovely Professional University, Phagwara 144411, India
e-mail: guravtar.14443@lpu.co.in

S. Sharma
Department of Mechanical Engineering, Dr. BR Ambedkar National Institute of Technology Jalandhar, Jalandhar 144011, India

K. Sandhu
School of Design-II, Department of Product and Industrial Design, Lovely Professional University, Phagwara, Punjab 144411, India

A. M. Asiri · A. Khan
Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_12

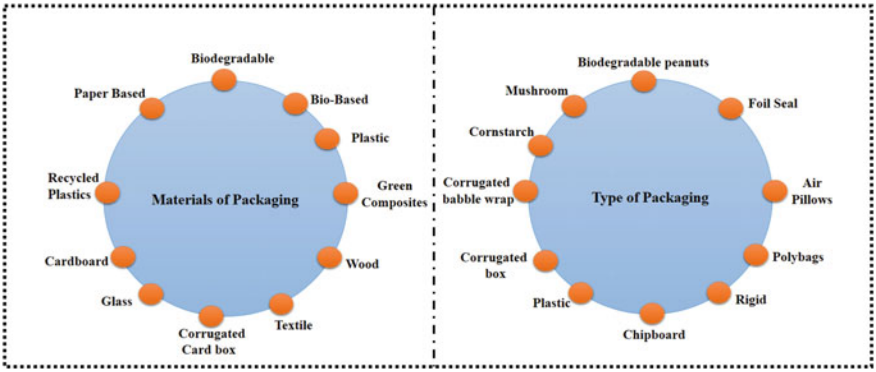
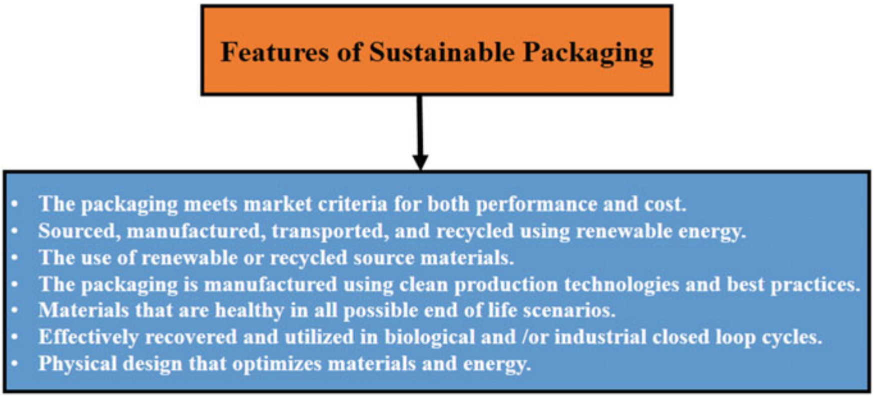


Fig. 1 Materials used for packaging and types of packaging

system. Therefore there have been substantial studies to develop alternative packaging products, with focus on re-packaging products. To improve the sustainability (Social, Economic and Environment), the sustainable packaging has been developed. By this, the increased of life cycle assessment and reduce its environment impact. The sustainable packaging to be consider by the availability of the features that is shown in the Fig. 2. From literature it was observed that for cutting the soft packaging materials, the High Speed Steel (HSS) tools has been used to make form of packaging to protect the product but the manufacturing of packaging consider to be high with using this process. Recently, studies [3, 4] was underwent to reduce the cost of polystyrene packaging by cutting novel 3D Print thermoplastic tool.

Studies have reported that the use of natural composites fabricated from plant fibre may reduce the plastic waste and thus consecutively solve the waste disposal problem to some extent owing to its biodegradability [5–7]. The biodegradability characteristics of plant based fibres create a positive impact in society as packaging



- The packaging meets market criteria for both performance and cost.
- Sourced, manufactured, transported, and recycled using renewable energy.
- The use of renewable or recycled source materials.
- The packaging is manufactured using clean production technologies and best practices.
- Materials that are healthy in all possible end of life scenarios.
- Effectively recovered and utilized in biological and /or industrial closed loop cycles.
- Physical design that optimizes materials and energy.

Fig. 2 Technical features of sustainable packaging materials from forest-based resources can provide advantages from a carbon footprint perspective when compared to alternatives such as conventional plastics or glass packages [8, 9]. For example, two recent studies have shown that paperboard is beneficial for packaging liquids over glass or plastic bottles due to its origin in renewable. Furthermore, fibre-based packaging has the benefit of lower weight, which is beneficial from a shipping viewpoint, and it is usually possible to recycle the final goods. Other research suggests that buyers choose packaging material based on fibre because it is shown to be eco sustainable [10]. Cellulose based fibres from natural resources which are derived from plants are recognized as the most abundant and renewable polymeric material as well as a key source of sustainable materials at the industrial scale [11–14]. Natural fibre reinforced composites are gaining growing interest in research because of their easy availability, recyclability, lightweight and low cost [15]. Many natural fibres have been effective strengthening for thermosets and thermoplastic matrices with organic matrices such as polylactic acid (PLA) [16, 17], but natural fibres such as bamboo, banana, wheat, sisal, sugarcanes, oil palms, cotton, flax straw, silk and coconut have been losing predilection because of low reliability as a result of the use of synthetic materials such as glass and carbon fibrillation [17, 18]. Natural fibre such as jute, hemp, kenaf, bamboo, banana, sisal, etc. has been in usage for a long time along with reinforcement [19]. With regard to the possible applications of such full-bio composites, they could be used as in place of plastics in various sectors which comprise 40% of the general market for plastic [20]. Table 1 shows the Classification of natural fibre, origin and yearly production around the world.

Table 1 Classification of natural fibre, origin and yearly production of these fibres around the world [21]

Fibre (plant)	Origin	Production (10^3 t)
Coir	Fruit	650
Banana	Leaf	200
Hemp	Stem	214
Bamboo	Stem	10,000
Cotton	Seed	19,010
Flax	Stem	830
Jute	Stem	2850
Kapok	Seed	123
Kenaf	Stem	970
Phormium	Leaf	–
Pineapple	Leaf	–
Ramie	Stem	100
Sisal	Leaf	318.8
Abaca	Leaf	91
Bagasse	Stem	102,000

2 Need and Principles of Sustainable Packaging Using Plant Fibre

Sustainable packaging through the development of packaging films which are using recyclable materials recyclable materials and it involves the use of life cycle assessments helps in reducing carbon foot prints therefore play an integral role in healthy societies and communities [22–25]. When working with sustainable packaging everything starting from manufacturing to transportation and recycled using renewable energy. Moreover concept is a dynamic concept that involves research and documentation to determine product design, material design, and documentation. Packaging waste was accounted for, according to Valdes et al. [26] 29.5% of the total municipal solid waste (MSW) in 2009 in the USA and in 2006, 25% of the overall MSW in Europe. Thus, a lot of work still needs to be done to reduce the packaging waste present in MSW considerably. Moreover, the governments around the world have introduced legislation to restrict usage of plastics and to reduce the quantity of waste from packaging [27]. Therefore focus is shifted towards the plant fibre for the use in packaging applications [28]. The major reason is due to high abundance of these fibre, low weight, high strength, rigidity and biodegradability therefore these fibres can play important role for sustainable packaging [29, 30]. Table 2 highlights the Impact of Sustainable plant based fibres in packaging applications.

3 Properties and Structure of Plant Fibre

The fibre from the plants can be in the form of hairs (in case of cotton, kapok), hard fibre (in case of coir, sisal fibres), and fibre sheaves (flax, hemp, jute) [41]. The plant fibres are basically classified depending on their utility such as primary and secondary. The fibre for primary applications include hemp, jute, kenaf, etc., while the by-products of plants such as coir, pineapple, etc., and belong to the secondary group [42–46]. Lignocellulose (cellulose, hemicellulose, and lignin) are the primary chemical composition of plant fibres. The physical properties of the fibres are partly determined by these basic components. Throughout the plant cell wall, these polymers can be distributed unevenly, making it difficult to know the structure and properties of the fibres. The largest amount of cellulose is in cotton fibre, while coir fibre has the largest amount of lignin [47–52]. One concern of natural fibres for use as reinforcements in composites is the unevenness of the chemical composition of the plant [53]. Cellulose, a linear 1, 4-β-glucan polymer composed of D-anhydroglucose (C6H11O5) repeating units containing hydroxyl groups, is the strong and stiffest part of the fibre [54–59]. Inter- and intra-molecular hydrogen binding is formed by the OH groups, rendering it hydrophilic in nature [60–64]. The phenolic compound that is believed to sustain the plant structure is lignin, and it is also resistant to microbial degradation unless disrupted by physical/chemical treatment. While most functional groups and units are known, the chemical structure of lignin is still not clear until

Table 2 Impact of renewable plant-based fibres in applications for packaging

S. No.	Principle	Sustainable packaging approaches	Main features of pant-based fibres in sustainable applications for packaging industry
1	Effective	Minimize the production of waste	Plant fibre is biodegradable, recyclable and available in abundance, so the use of this fibre in packaging can lead to the recycling and reuse of packaging materials [31]
		Maximize features	The special properties of plant fibre, such as low weight, high strength, rigidity and toughness, will strengthen the packaging's mechanical and barrier properties [32, 33]
		Cost effective	Since plant fibres are plentiful, recyclable and reusable, the application of these fibres in packaging would therefore be cost-effective [33–37]
2	Efficient	Maximize products to packaging ratio	In packaging applications, plant fibre has the high potential to optimise the ratio of goods to packaging due to the durable and versatile nature of cellulosic materials
		Maximize materials efficiency	In packaging applications, plant fibre can be continuously recycled with limited deterioration since cellulosic fibre is derived from natural resources [38]
3	Clean/safe	Reducing airborne and waterborne environmental pollutants	With the use of these fibres in packaging, the environmental impact will be minimised. These fibres can be discarded of after any use due to their biodegradable nature. The use of these products in the application of packaging would also reduce carbon dioxide emissions [39, 40]
		Minimize greenhouse gas emissions	
		Reduce toxicity and effects on litter	

today. Hemicellulose functions as a micro cellulose agent, forming a hydrophobic interface Lignin and hydrophilic cellulose, and cellulose and cellulose relations in plant fibre cells with lignin [65, 66]. Hemicelluloses and lignin usually 15–25% and 20–30% (wt. %), respectively of the total, make up chemical make-up of cellulosic fibres. Table 3 highlights the Natural fibre and their chemical composition.

Table 3 Natural fibre and their chemical composition [67]

Chemical composition (%)			
Type of fiber	Cellulose	Hemi-cellulose	Lignin
Jute	61–63	13	5–13
Banana	60–65	6–8	5–10
Coir	43	<1	45
Flax	70–72	14	4–5
Mesta	60	15	10
Pineapple leaf	80	_	12
Sisal	60–67	10–15	8–12
Wood	45–50	23	27
Sun hemp	70–80	18–19	4–5
Ramie	80–85	3–4	0.5

3.1 Hemp

Hemp (*Cannabis sativa L.*) is a multi-use, multifunctional crop that can supply a large number of useful raw materials. The key drivers for the potential expansion of the hemp crop are its goods various advantages [68]. Hemp is considered one of the oldest crops known to man. This plant is very abundant and widespread, economically important for some societies. The essence of this important crop of industrial origin is important. The high yield potential that can be achieved in a relatively short time is crucial for industry [69]. Crop cycle; dry biomass production of up to 20 t/ha has been recorded in Europe [70]. Hemp is also highly adaptable and can be grown in a wide variety of habitats, from northern latitudes to northern latitudes [71] and also in climates in the tropics. The economic value of hemp can definitely be attributed to the likelihood that it can be grown for wide range of applications for end-use use. Traditionally, hemp is grown for its three primary products: Fibre, seeds and psychoactive substances that accumulate in the female inflorescence in particular [72]. Currently, it is commonly used as well, Grown in countries with temperate climates such as Chile, North Korea, India, Japan, and many countries of the European Union (EU) [73]. The EU considers the promotion of hemp production in its member countries. Hemp is nowadays used in a range of applications, including textile fibre, paper, composite fibre, seed food, oil, wax, the use of resin, pulp, biofuel, etc., depends primarily on the grade/quality of the hemp [74]. Table 4 shows the typical physical and mechanical properties of hemp.

The flowering tops and hemp leaves create resin secretions containing the narcotic 9-tetrahydrocannabinol (THC) for which marijuana and hashish are popular to a lesser degree. It cannot be used as a narcotic because industrial hemp produces less than 0.2% THC. The Small quantities of tetrahydrocannabinol (THC) are secreted from the hemp. Renowned for the narcotic drug cannabis. Since the amount of THC in hemp is present, like other Cannabis sativa strains, it is less than 0.2% and should not be used as a drug. Various reports indicate that the oldest hemp fibre dates back

Table 4 Typical physical and mechanical properties of hemp [75]

Properties	Values
Length (ultimate) (mm)	8.3–14
Diameter (ultimate) (mm)	17–23
Aspect ratio (length/diameter)	549
Specific apparent density (gravity)	1500
Microfibril angel ()	6.2
Moisture content (%)	12
Cellulose content (%)	90
Tensile strength (MPa)	310–750
Specific tensile strength (MPa)	210–510
Young’s modulus (GPa)	30–60
Specific young’s modulus (GPa)	20–41
Failure strain (%)	2–4

to 8000 BC (The History of Columbia about the World). Between 1971 and 1993, hemp fibre production was briefly prohibited. It has expanded exponentially since the ban has been lifted. The chemical composition of the cellulose content varies from 70.2 to 74.4% in hemp [76–80]. Even though it has several applications, owing to its high strength and stiffness so it is used as reinforcement in bio composites. Hemp is the most commonly used natural fibre, after sisal, in composites, as reinforcement [65] naturally, hemp is one of the most ecologically friendly fibres and even the most environmentally friendly fibres. The Columbia History of the World notes that pieces of hemp fibre found in tombs dating back to tombs are the oldest remnants of human industry. 8000 BC, roughly [69, 81–83]. Hemp is an annual plant that originates in Central Asia and it is believed to have been cultivated for over 12,000 years. In the Iron Age, it possibly entered central Europe, and there is evidence of its creation in the United Kingdom by the Anglo-(800–1000 AD) [84]. It is mostly grown now in the EU, Central Asia, China and the Philippines. The world’s industrial production of hemp is cultivated in China, with most of the rest being grown in Chile, France, the People’s Democratic Republic of Korea and Spain. There is an exponential rise in the use of hemp for different types of goods in recent years, applications. The universe, according to the FAO, Hemp fibre production has risen from 50,000 tonnes in 2000 to nearly 90,000 tonnes in 2005 [85–87].

3.2 Jute

Jute is a natural fibre grown annually. It is biodegradable and respectful of the environment. It provides millions of people with sustenance. It has a broad usage range. It is also commonly used as floor coverings, home textiles, decorative fabrics, shopping bags, carrier bags, handicrafts, cushion covers, curtains, blankets, nursery pots, insulation material, soil savers, composites based on jute, etc., in addition to being used as packaging material worldwide. It has different applications, such as soil stabilisation, erosion control, etc., it has the ability to be used as a geotextile on a wide scale. For making pulp and paper, it may be a good source of raw material [88]. A significant agricultural product is jute fibre. In countries such as India, China, Bangladesh, etc., it is one of the most common natural fibres. In India's economy, the jute industry has unique significance and continues to be a significant conventional foreign exchange earner [89]. Although it faces tough competition from synthetic fibres. Jute fibres are used in advanced fields such as decorative and furnishing items such as lamp shades, wall coverings, curtains, upholstery, etc. [90]. It is the least costly mass consumption fibre, at just a fraction of the cost of glass fibres; in terms of volume, next to cotton, jute is now the world's second most valuable fibre. Jute fibres have been partly replaced by synthetic fibres in conventional applications in carpets, cords, bags, etc., which have some benefits compared to jute. Non-traditional markets have to be pursued for the fibre in order to ensure a fair return to farmers [91]. The higher yield per hectare of Tossa jute commands a better price. Jute is grown at temperatures of 21–38 °C with a relative humidity of 65–95% in the rainy season. During the 4 months of the growing season, it needs a precipitation of at least 1000 mm uniformly spread [92]. Table 5 highlights the important physical properties of jute fibre.

Table 5 Important physical properties of jute fibre [93]

Properties	
Jute cell ultimate width (range)	15–20 μm
Jute cell ultimate length (range)	1–6 mm
Jute cell ultimate width (average)	18 μm
Jute cell ultimate length (average)	2.5 mm
Tenacity	27–53 cN/tex
Specific gravity	1.48 g/cm^3
Moisture regain at 65% RH, 22 °C	13.80%
Fineness (g/1000 m) per single fiber	0.26–0.46 tex
Breaking elongation	0.8–1.8%
Refractive index (parallel)	1.577
Refractive index (perpendicular)	1.536
Young's modulus	
White jute	8.6–17.4 GPa
Tossa jute	9.6–19.4 GPa
Modulus of rigidity	0.442 GPa
Heat of combustion	17.46 J/g

3.3 Sisal

Sisal plays a dominant role in the manufacturing of natural fiber materials in the region of leaf fibres. Due to some interesting properties of the fibre, Sisal is well suited for scientific applications. It is a leaf fiber derived from a plant that is generally considered indigenous to Central and South America, where it has been grown, harvested, and used for several centuries in the spinning of coarse yarns, twine, and cords. During the late eighteenth to early nineteenth centuries, sisal was also cultivated on the continents of Africa and Asia due to its potential to grow under different ecological and climatic conditions, ranging from hot and humid conditions through Kenya and Tanzania to the tropical climates of Mexico, the United States and the Caribbean coasts of Florida and Hawaii [94, 95], China has become a sisal-producing country with an annual production of about 20,000 mt in 2006. A single sisal plant can produce 200–250 leaves in which you can harvest 150 kg of fibre in a year [96]. The sisal plant is normally extracted first after 2–3 years and then at intervals of 6–12 months during its lifetime of 7–10 years. Figure 1.4 shows the pictorial view of sisal plant. And each leaf comprises about 1000 bundles of fibre on average [97]. Sisal is the world's top grown leaf fiber, accounting for about 70% of all commercial production of these fibre. As per Food and Agriculture Organization Statistics published in 2006, the worldwide production of sisal is estimated at around 427,000 t. Brazil is one of the largest producer with highest production of 247,000 t, therefore produces almost 75% of world's sisal production. The other countries like Mexico, Columbia, Cuba, Haiti and Nicaragua, Tanzania and Kenya contribute about 10% to the continent of Africa and about 5% to China. It is estimated that more than 80% of the production of sisal in Brazil is exported to over 50 countries, the United States, China, Mexico, and Portugal being the main importers. They are nursed up to a height of 15 cm and then transferred by hand to the field in marked-out rows [98]. For the growth of the sisal plant the land must be free of weeds to planting the seedlings. The first harvesting normally takes place 3–5 years after the establishment of the crop. Approximately 120–125 leaves are available for harvesting at about 1.5 m of height. Sisal harvesting is a field operation in which the outer leaves are cut so that approximately 30 leaves are left on the plant so that the plant can grow up to the next harvest cycle after 15–18 months. This process of harvesting is continued until the end of the life of the plant [99]. After this, cutting of the leaf is carried, and leaves are packed together to load them into a truck and to carry them to the factory. A large-scale automatic decoration machine that can treat nearly 25,000 leaves or 10–20 t of leaves per hour is ideal for large plantations, but hand-decorticators are suitable for small-scale or pilot testing. Produce approximately 150–200 kg dry fiber bundles in a 10 h change [100]. Different fibre are divided into different categories based on the size, colour, and presence of impurities in the grading process. Most plant fibre, like sisal, are primarily composed of cellulose and lignin, but they also contain a variety of other minor constituents, such as pectin, wax, inorganic salts, nitrogen and pigments. The total sisal fiber content of cellulose and lignin is about 67% and 12% respectively and the sisal leaf comprises nearly 4% fiber, 0.75% cuticule, 8% dry matter and

87.25% water [101]. Moreover the fibre being multicellular, with small single cells connected together. On average, the single fiber is around 20 µm thick and 3 mm long and the fiber bundle can achieve a thickness of over 400 µm and a length of over 1000 mm. Such cells serve as reinforcement to matrices of hemicellulose and lignin. The cell wall is therefore a composite structure of lignocellulosic material, supported by helical microfibrillary cellulose band [102]. The sisal leaf comprises three fiber types: mechanical, rope, and xylem. The mechanical fibre, also classified as structural fibres, are mostly situated along the periphery of the leaf, while the ribbon fibre are aligned with the conductive tissues in the median line of the leaf, and the xylem fibre are aligned towards the ribbon fibres [103]. These fibres are rarely circular but mainly thick and horseshoe-shaped in cross-section therefore it is very difficult to separate in the extraction process. Moreover these fibre are finer therefore grading of these fibre is very important [104, 105].

3.4 Flax

The use of flax fibres as reinforcement in composites has gained popularity in recent years as need for sustainable materials is growing each year. Flax fibres are cost-effective and have comparable mechanical properties to those of the fibres of glass [106] it has been tested for reinforcement for various composites. *The scientific name for flax is (Linum usitatissimum L.) is translated literally as 'most useful linen'* [107]. Flax production is environmentally friendly in that few chemicals are required for the production of crops. Within a research of life cycle study, the impacts of the flax scenario in Western Europe (dew retting) and Central European The hemp scenario (warm water retting) was similar, except that the use of pesticides for flax and water was greater. For hemp, it was higher during processing [108]. It is one of the oldest fibre crops, and one of the first to be spun and woven into textiles is its fabric. Reports say that the flax fibres in Egypt and Georgia were used for many applications well before 5000 BC [58]. High grade Long fibres are commonly made into textile yarns, and low-grade fibres are used in composites as reinforcements/fillers. The average flax plant grows up to 90 cm tall and has thick fibres along the stem consisting of bark, phloem, xylem, and centre void. In order to see the fibre bundles and hierarchical organisation, microscopic studies were conducted. The chemical composition of the flax fibres differed with different authors, stressing high dependency on the flax fibres used. Flax fibre is considered for reinforcement because it has a high cellulose content and a high degree of crystallinity that makes it stronger and stiffer. The fibre's tensile values ranges from 345 to 1100 MPa. The fibre module is 27.6 GPa and the percentage Fiber elongation is between 2.7 and 3.2%. Flax fibre of decent quality has the highest tensile strength compared to other Bast Fibre, properties. The difference in tensile characteristics of flax fibres was studied on the basis of It revealed that the fibres collected from the centre of the stem had the highest strength and modulus; fibres from the Hermes variety showed better tensile strength and modulus; and that fibres from Hivernal cultivated plants showed better tensile strength and modulus.

Table 6 Chemical composition of flax fibres [114]

Fibre	Hemicellulose	Pectin	Lignin	Wax (%)	Moisture content (wt%)
64.1	16.7	1.8	2.2	1.5	10
67	11	–	2.2	–	–
73.8	13.7	–	2.9	–	7.9
65	–	–	2.5	–	–
62–72	18.6–20.6	2.3	2–5	1.5–1.7	8–12
71–75	18.6–20.6	2.2	2.2	1.7	10

On the fibre position in a stem, plant variety and place of cultivation [109]. The effect of moisture absorption and drying of flax fibres was studied and the findings were investigated. It showed that the tensile properties were affected by both moisture intake and drying. Flax is used in a grass or vegetable crop rotation system that enables pathogen reduction or the use of different types of herbicides to manage unwanted plants [110]. Seeds from high-fibre varieties are densely sown for fibre production to give a final plant density of about 2000 plants per square metre. In this way, planting and harvesting before full seed maturity produces thin-stemmed, straight and tall plants that provide thin-stemmed, straight and tall plants. Low yield fibre and outstanding properties. Fibre yields vary with cultivar, climate, and agronomic practises, as well as efficiency, but total fibre yields can be 25–30% of straw dry mass [111–113]. In comparison to the production of flax fibre, linseed varieties are sown at low densities (approximately 750 plants per square metre) in order to optimise branching for higher seed production. Linseed plants also have dense stems that are poor in fibre yield and quality when harvested at full seed maturity. The principle of dual flax usage, i.e. fibre and seed, has been discussed, and a balance is given by some varieties. Table 6 shows the chemical composition of flax fibres [114].

3.5 Abaca

The output of abaca, at approximately 80,000 t/year, is marginal compared with other natural fibres [115]. It is only produced in two countries, mostly in the Philippines and to a limited extent in Ecuador. It’s being cultivated in the mid-mountain regions up to approximately 500 m above sea level, primarily as an integrated community. The Factors that significantly affect the growth of this plant fibre are the amount of sunlight, precipitation, humidity, and temperature as well the soil condition. With the proper amount of rainfall combined with high humidity (78–88%) and mild temperature (22–26 °C), the growth of the plant is observed to be at its best [116]. Sandy loam soil with good water retention aided with aeration and drainage are essential for planting the Abaca plant. The major advantage for cultivation of this plant is that no additional inputs are needed in the form of mineral fertiliser [117]. Moreover, for fibre extraction, no water is needed. Due to the high tensile strength

Table 7 Physio-mechanical properties of abaca fibre compared to other natural fibre [20]

Fiber	Density (g/cm^3)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation (%)	Fiber length (m)	Fiberdiameter (microns)	Moisture uptake (%)
Abaca	1.5	980	41	3–10	2–4	150–260	5.81
Hemp	1.48	550–900	30–60	2–4	1–2	16–50	12
Jute	1.46	400–800	20–25	1.8	3–3.5	60–110	13.75
Sisal	1.33–1.45	600–700	17–22	4.3	1	50–300	11
Cotton	1.54–1.6	287–597	6–10	3–10	0.001–0.065	11–22	8.5
Linen	1.4	800	50–70	2.7–3.5	0.9	12–60	10–12

of this plant fibre favours it is widely used for the production of special papers such as bank notes, cigarette paper and tea bags [20]. Unlike leaf sheaths, abaca fibre stripping is the only way to remove the fibres from the leaf sheaths. The other fibres of best, such as flax and hemp, can be extracted by organic retting [118]. The isolation from the inner layer of the outer layer containing the primary fibre is Tuxying. A small and thin knife is inserted between the outside and the inside while smoking. Unlike the other best fibres such as flax and hemp, the removal of abaca fibres is the only way to remove the fibres from the sheaths of the leaves, which can be extracted by organic retting [119]. Tuxing is called the isolation of the outer layer that comprises the primary fibre from the inner layer. A tiny and thin knife is inserted between the outer and inner layers of the leaf sheath during tuxing and then pulled off the entire length to fully separate the layers [120, 121]. Table 7 highlights the physio mechanical properties of abaca fibre compared to other natural fibre [122]. Tuxies are the primary fibres in Abaca leaf sheaths that are isolated from the secondary fibres. Tuxing is the method of separating the primary fibres that can be formed by removing the outer layer of the sheaths of the leaves from the inner layer (containing the secondary fibres). The fibre bundles developed from the tuxies were subjected to stripping where different grades of fibre for industrial use are generated [123]. The stripped fibres are dried and delivered in (GBE) grading and baling facilities. In the Philippines, village dealers bought stripped and pre-dried Abaca fibres from farmers on bulk orders. The fibres will be sold by village dealers to city traders who collect and bring the fibres to GBE's [124].

3.6 Coir

Coir is a natural fibre derived from the husk covering the seed of a coconut as fibre wraps. The extraction of the oil-rich kernel for various food products such as fresh products, it is removed from the husk for Coconut kernel, copra, and desiccated [125, 126]. The husk is thus the by-product of the processing of copra or desiccated coconut [127] originally, coir mining was a domestic industry that may have developed along the East Coast centuries ago. South India and along Sri Lanka's southern and north-western coastal line [128]. Coir is a natural fibre derived from the husk covering the seed of a coconut as fibre wraps.

For the extraction of the oil-rich kernel for various food products such as fresh kernels, copra and desiccated coconut, it is removed from the husk. The husk is thus the by-product of the processing of copra or desiccated coconut. Originally, coir mining was a domestic industry that may have originated along South India's east coast and along Sri Lanka's south and north-west coastal belt centuries ago. Coir has historically been harvested from husks that have been soaked (retted) in sea water or lagoon water for 6–9 months, and then Beaten with a mallet of wood. Over time, the methods of coir extraction have greatly improved, with the extraction of quality coir fibre (bundles) either by wet processing (retting procedures) or mechanical decoration without soaking. The quality as well as the amount of fibre/fibre bundles extracted from a given number of husks can differ depending on the extraction process. In the past, coir has been known as a low-quality, low-value commodity, with coir yarn, coir nets, white coir for doormats and floor coverings, brown coir for rubberized sheets, mattress and bristle coir for brooms and brushes being its primary uses. The resistance of coconut coir to sea water is excellent, and the cordage therefore has great value for marine uses (shipping and fisheries) [129]. Gradually, the launch of synthetic polymer products took over the market for natural hard fibres in Application of cordage and twine. The use of coir has grown tremendously over the last three decades in the manufacture of rubberized coir goods for automobiles and upholstery, and subsequently as woven and knitted geotextiles for erosion control and as a basis for binding earth on sloping lands. In recent decades, developments in coir science have resulted in a better understanding of the structural, chemical and mechanical properties of coir. A single coir fibre has a mean width of 0.02 mm and a mean length of 2.5 mm, and as aggregated fibre bundles, these small fibres occur. Such a package will be referred to as a 'strand' in regular use. In contrast with other widely used agro-based fibres, coir fibre has the highest content of lignin [130]. Some of the benefits of coir are that it is non-abrasive, robust, resilient, hydroscopic, viscoelastic, biodegradable, compostable and combustible, and a chemical-change-friendly natural product. Coir has a high aspect ratio and a high strength-to-mass ratio as a fibre, is poor in energy conversion and has excellent insulation characteristics [131]. However, as compared to other fibres such as flax, hemp and wool, a major drawback of coir is the broad thickness of fibre bundles. Hence, in insulation applications, it requires large volumes. Some benefits of coir are high rigidity, strength, flexibility and elasticity of twisted coir.

Coir is a year-round commodity available, and cheaper in cost than other agro-based fibres. The key milestones enabling this industry have been simple extraction techniques, modern machinery introduced over recent decades and new and scalable coir applications as a result of technological advances from its humble beginnings, to growth [132]. In addition, these accomplishments paved the way for the coir industry to develop dramatically over the past 25 years and to retain its role in the worldwide hard fibre trade. Due to its versatility and numerous uses, the coconut palm (*Cocos nucifera L.*) holds a pride of place among the palms growing in the tropical region of the world. In over 93 countries in the tropical coastal ecosystem of the world, it is the most economically important cultivated palm, offering more than 200 items [133–137]. It covers an area of approximately million hectares worldwide, producing about 57 billion nuts per year. The Philippines is the world's leading coconut manufacturer, with Indonesia, India and Sri Lanka in second, third and fourth positions, respectively [138–141]. Total exports of unfinished coir and coir products from producing countries were 172,928 million t and 194,926 million t respectively in 2003 and 2004 (APCC 2006). In 2005 and 2006, global exports of coir and coir products were 177,527 million t and 204,863 million t respectively.

3.7 Cotton

Among all natural fibre crops, cotton is the most important. In 1960, 68% of all the fibre consumed was cotton. And, though non-cotton fibres have benefited from recent technological advances and developments in the world, Cotton has continued to erode its market share, with cotton remaining to account for no less than 38% as of 2009. Of all the fibre consumed at the stage of end-use [142]. Man-made industrial fibres can now be produced and sold at rates well below the price of man-made fibres. There are, however, a range of characteristics that are highly valued by consumers and it is exclusively found in cotton. Cotton is exceptional in characteristics such as its biodegradability, absorption of water, Convenience and thermostatic capability [143]. Each year, over 50 countries plant cotton on at least 10,000 ha. In developed countries, only about 13% of the cotton region is located, so cotton is truly a crop for developing countries. World cotton statistics on area, production, yields, trade and prices are maintained by the International Cotton Advisory Committee (ICAC), an intergovernmental organisation established in 1939. According to data on the cotton area available since 1920/21, cotton has never been cultivated on more than 37 million hectares. Since the ICAC began collecting cotton data, the cotton region has reached 36 million hectares on just two occasions. On the other hand, cotton was planted on less than 30 million hectares only once, in 1986/87, after the 1950/51 season. The world cotton region has thus remained between 30 and 36 million hectares in the years that followed, between the 1950/51 season and the present (ICAC 2008a). The global cotton industry is aware that the industry needs to continue to increase the sustainability of the production of cotton. Not only do production methods have to be safe, but the processing of cotton should also be environmentally friendly, starting from ginning through to finished goods. Efforts to enhance the commercial, environmental and social sustainability of the production and consumption of cotton are underway. Organic cotton production and no-tillage production are seen as one way of improving sustainability. Techniques of minimum-tillage and. Still a mystery is the root of the term cotton. There is, however, a consensus in specialised literature that the Arabic word al Qatar was derived from cotton. In a sacred Hindu text known as the Rig-Veda, the earliest recorded record of the use of cotton is found. Excavations at Mohenjo-Daro, in Pakistan, indicate that as far back as 3000 BC [143] human beings used cotton cloth. Other findings in Peru indicate that over 4500 years ago, people there used cotton. The push to embrace cotton seems apparent. As a fibre seed, the quest for a fibre from which to produce clothing stems from people. The cotton plant is a perennial tree, but as annuals, domesticated varieties have been bred to grow. It has a tap root system, and in search of nutrients and water, its fibrous roots can penetrate into the soil as deep as 1.5–1.8 m [144]. Cotton can continue to thrive in water-deficit conditions due to its abundant root system, and that is why it is usually considered a dry land crop. In late spring, cotton is normally planted, permitted to remain in the field throughout the harsh summer months and harvested at the start of autumn. The cotton seed has a dormancy period of about 1 month after harvesting. At a temperature of over 15 °C, the seed germinates well in the soil and ample moisture in the soil to absorb and burst the seed, allowing the root and shoot to be created. The seed germinates under normal circumstances, 5–6 days after planting and, if the germination rate is insufficient by the tenth day, the decision to replant it can be made. The first to start is radicular growth, forming the root even before the plumule breaks through.

The surface will emerge from the soil and two cotyledonary leaves will form. It needs at least 50–60 heat units the surface of the soil for a seedling to crack [145–149]. Cotyledonary leaves in cotton have a maximum lifespan of 40 days and vary in form from true leaves. Typically, on the fifth to sixth node, the first true branch appears. Monopodia branches, sometimes also called vegetative branches, are the first branches of the cotton plant. There are few monopodia branches in number, not more than 5–6, and often they can be merely rudimentary with only noticeable symposia branches on the plant. Monopodia branches do not directly bear fruit and give the plant a larger amount.

Compared to a symposia form of plant, look as soon as the first symposia branch appears on the plant, the development of monopodial branches ceases [150–154]. Mono podial plants are generally characterised by late maturity as a result of the fruiting feature of the secondary and tertiary branches. The most significant natural fibre is cotton. There are several cotton species recognised, but only four of them are cultivated on a commercial scale. Around 97% of all the cotton produced belongs to the G genus. The hirsutum, 3% to G. Barba dense, and less than 1% is G. G. and Arboreum. A variety of pests, especially insects, are naturally vulnerable to the cotton plant. Integrated pest control is reducing the number of insecticide applications in cotton after more than two decades of intensive insecticide use in cotton. Immune to Insects as a promising option for handling lepidopteron insects, biotech cotton has arisen [155]. There is a rising understanding of manufacturing and processing cotton using sustainable methods. Nearly half of the cotton that is produced. In the world, irrigation is guaranteed, while the other half comes from conditions that is rain-fed. Most cotton is still picked by hand, only if labour is not available or costly machine picking is adopted. Organic cotton accounts for less than 1% of global manufacturing and will remain as a niche market [156–158]. There is a great need to recognise alternative uses of cotton to increase the use of cotton in the world. High man-made fibre prices and recent technological advances have opened up new

Table 8 Chemical composition of the cotton plant parts [162]

Plant part	Nitrogen in %	Phosphorus in %	Potassium in %	Calcium in %	Magnesium in %	Sulphur in %
Root	0.82	0.12	1.06	0.45	0.25	0.06
Stem and branches	1.06	0.08	1.6	0.69	0.25	0.05
Leaves	2.3	0.15	2.49	3.15	0.52	0.42
Burr	1.08	0.18	3.5	1.28	0.26	0.17
Seed	3.13	0.43	2.1	0.18	0.33	0.33
Fiber	0.18	0.28	2.28	0.08	0.05	0.05

avenues for the manufacture of 'non-woven' using cotton [159, 161]. Table 8 shows the chemical composition of the cotton plant parts [162].

4 Plant Based Fibres in Packaging Applications

Plant fibres have been widely used in a variety of applications in various fields due to their uncompromising characteristics, including medical, packaging, paper and coating, electronics and membranes [160, 163, 164]. The past decade has seen significant advances in the production of biodegradable packaging, particularly from biomaterials dependent on recycled cellulose. Such advances are based on achieving improved quality and protection of food by packaging for the transition to globalisation [165]. In addition, renewable and biodegradable materials can contribute to environmental sustainability by waste disposal reduction and green-house gas balances. Researchers have been active in the promotion of the use of biodegradable and environmentally friendly packaging materials using plant based fibres These are traditional packaging materials to replace the traditional packets of plastic or glass [15, 31]. The various uses of sustainable packaging materials in various fields are discussed in the next section.

4.1 Plant Based Fibres for Packaging of Foods and Beverages

Traditionally, plant based fibres have been used in packaging for a wide variety of food types, such as frozen food products, Liquid foods, new foods and drinks [166]. The major role of food packaging is to safeguard and preserve the food to maintain its quality and protection [167]. The Cellulose-based food packaging, which is most widely used is cello-Phane, also known in the film as regenerated cellulose. The number of derivatives of cellulose, such as carboxyl methylcellulose, Methylcellulose, ethyl cellulose, propyl cellulose hydroxide, In the preparation of xyethyl cellulose and cellulose acetate, Of films based on cellulose. Cellulose acetate is also widely used as a rigid wrapping film along with cellulose triacetate than other derivatives, since they have low gas and moisture barrier properties [168]. Fibre Forms packaging consists of 100% primary fibre that provides high elasticity and strength, and its high purity is certified for direct contact with food, and can be coated with a wide range of coatings to protect food from light, moisture, bacteria and other hazards. Elopak is one of the world's leading liquid food packaging products. Suppliers, and this business produces cartons of Pure-Packs that the paper board is covered with a polyethylene (PE) sheet. Functions as a barrier to liquids. To cover milk, these cartons are used, Juices and other liquid foods and the same volume of food waste to minimise as much as practicable [169].

4.2 Medical and Pharmaceutical Products

With growing demands for personal lifestyles, chronic diseases, ageing populations and raising incomes in developing countries, the pharmaceutical products demand is increasing.

Packaging for pharmaceuticals offers reliable and quick solutions that combine product safety, quality, identification, details, convenience and security requirements [170]. Networks of plant fibres are suitable for use as raw materials in packaging for medical and pharmaceutical use. These materials are used to prepare the outer containers, such as bottles, envelopes, cartons, blisters and strips for pills, capsules and suppositories that are packed in cartons with board [171]. In pharmaceutical packaging, cartons are often used due to certain factors such as increasing the display area offers a better display of the sand item stock[172].

4.3 Industrial Packaging

Industrial packaging applications are steadily emerging compared to other packaging applications, with a few major firms, including Honeywell, Mitsubishi Gas and Chemical, Bayer, Triton Systems and Nanocor, which are presently leaders in plant based packaging applications. Unisource Company launched a reusable, bamboo shaped fibre kit in 2012, which is used to deliver laptops from around world [173, 174]. In recognition of their revolutionary products that replace up to 80% of the plastic used in conventional blister packs, LUXE PACK won the Green Award. These packages are manufactured using the technology used in the paper pulp industry, but are claimed to be cheaper than polystyrene trays with the benefit of being entirely biodegradable [175].

4.4 *Other Potential Uses*

Packaging is currently at the centre of intense research among scientists on new technologies, including the creation of environmentally friendly packaging materials that in terms of preservation interact well with foods. The packaging is designed by incorporating functional ingredients in the packaging structure with the packaged food items in order to have a positive effect on consumer health [176]. Developments in materials engineering, electronics and processing technology have been driven by new developments in packaging technology, covering several main areas, including high barrier materials, active packaging, smart packaging, nanotechnology, tagging applications and digital printing for packaging, which are critical for the growth of the packaging industry [177]. The most difficult aspect of packaging research is the production and promotion of the use of sustainable and biodegradable "bio-plastics" that can commercially substitute plastics based on petroleum and thereby help reduce the issue of waste disposal. According to Youssef et al. [178], there is a possibility to produce packages with stronger mechanical, barrier and thermal properties by adding an appropriate nanoparticle in food packaging. Beside improvement in properties of food packaging Nano materials will also prevent the invasion of bacteria and microbes into packed food products through packaging. While extensive research is being conducted, the approach to nanotechnology for packaging applications is still in the stage of progress. The key emphasis is to analyse the full packaging life cycle (selection of raw materials, manufacture, study of food contact, usage and disposal) while incorporating and managing costs, efficiency and health and environmental impacts. Liu et al. [179] also stated that the preparation of nano scale filler composites was considered to be a promising way to enhance the gas barrier and mechanical properties without affecting the transparency of packaging applications. Polymers incorporated with clay nanoparticles were among the first polymer-based nano-composites to appear on the market with advanced food packaging and are already used for industrial purposes in packaging for carbonated drinks and thermo-formed containers [30, 180–185]. Polymers with hybrid materials based on cellulosic fibre/nano clay can provide food packaging materials with high barriers, short life, fast disposal and environmentally compatible properties [26, 30, 32, 183–186].

5 Summary

The plant based fibres have been widely studied over the last decade, gaining growing interest. Numerous systems were thus created, composed of biopolymers as matrices, presenting original mechanical properties, combined to lignocellulose fibres, either targeting a reinforcing effect or new functionality, a decrease of the overall material of biomass by-products. To sum up, the following are the basic stakes that should be taken into account when designing complete bio composites that should be used in a viable way for food packaging applications. To overcome the climatic issues can be achieved by using full bio plastics as matrices, by promoting the use of agricultural waste or by-products of the food industry as raw materials in order to avoid competition with the use of foodstuffs, but also by designing packaging materials in a way that reduces the degradation reactions of packaged foodstuffs, thereby reducing food waste and loss. It should be noted today that it has not yet been demonstrated on the basis of the available resources (such as life cycle analysis) that the use of complete bio composites can minimise environmental effects, save energy and water and/or reduce food losses.

6 Future Road Maps

Packaging must ensure its fundamental function of container and food security against physical harm by displaying adequate mechanical properties, but also by regulating the properties of mass transfer, by designing it in such a way as to restrict food degradation reactions. Lignocellulose fibres have been shown to often act as defects which affect mechanical and permeability characteristics, degrading the first ones and increasing the seconds. By choosing the right formulation, increasing material permeability seems to be a valuable approach, particularly for the packaging of breathing products such as fruits and vegetables. Full-bio composite mechanical properties, by improving comprehension and modelling Approaches that are capable of understanding the full complexity of such structures. The current bottlenecks are the absence of details on the fibres and on the intrinsic mass transfer properties. Vegetal fibres and their environmental sensitivity Conditions (e.g., humidity, temperature) should be assessed.

For the use of complete bio composites on a sustainable basis, Such products must be manufactured using processes commonly used in the plastics industry (extrusion compounding, injection moulding and thermoforming), achieving output rates close to those of traditional plastics.

Given the low added value of most food items, complete bio composites should be economically embraced as a whole. Today, the willingness of customers to pay more for biodegradable and bio-sourced food packaging remains unclear. In this sense, in order to minimise the total cost of complete bio composites, effects need to be followed. It should be noted that the reduction of costs depends heavily on the industrial implementation of low cost and eco-efficient development of Bio plastics (e.g., PHAs), but also the availability of low-cost lignocellulose fibres with reproducible intrinsic properties during the year.

Furthermore, the use of lignocellulose biomass from crop waste or by-products of the food industry should be preferred.

When used as food packaging products, full-bio composites can comply with food contact materials regulations and guarantee the health of the customer. Due to the possible existence of toxicological substances capable of migrating from packaging to food, this may become very challenging when using lignocellulose fibres, especially from agricultural waste and food by-products. Therefore, particular attention should be paid to evaluating the inertness of the materials produced, but also to evaluating the inertness of the materials developed.

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Natural Composites: Vegetable Fiber Modification

Nidhi Shukla, Himani Agrawal, Ishan Srivastava, Anish Khan, and G. L. Devnani

1 Introduction

The requisition of the traditional petroleum-based fibers in every sphere of human activity is continuously debasing because for their non-degradable nature. Therefore, scholars are inclining their interest towards the fabrication of polymer with novel components which can combat with the new technologies and at the same time which is eco-friendly and sustainable [1]. The harmful impacts of the synthetic fibers had leaded the scientist towards shifting of the green technology, known as natural fibers [2, 3].

Depending on the source for extraction, natural fibers are subdivided into three categories, namely, Vegetable, Animal and the Mineral fibers [4]. Figure 1 shows the general classification of the natural fiber.

Vegetable fiber is also known as cellulosic fiber, plant fibers and Lignocellulosic fiber [5]. Plant derived fibers shows further classification on the basis of their anatomical origin, as: Bast Fibers (Ramie, Jute, and Kenaf etc.), Leaf Fibers (Sisal, Abaca, and Pineapple etc.), Seed Fibers (Kapok, Cotton etc.), Fruit Fibers (Coir, Coconut etc.) and Grass Fiber (Bamboo etc.) [6]. The continuous exploitation of these cellulosic fibers are observed in every arena of human sphere due to their physiochemical qualities like light weight, ecologically safe, cost-effective, thermally stable etc. [7]. The physical and the chemical properties of these plant fibers are given in Table 1. And chemical components are shown in Fig. 2.

N. Shukla · H. Agrawal · I. Srivastava · G. L. Devnani (✉)
Department of Chemical Engineering, Harcourt Butler Technical University, Kanpur 208002, India
e-mail: gldevnani@hbtu.ac.in

A. Khan
Centre of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_13

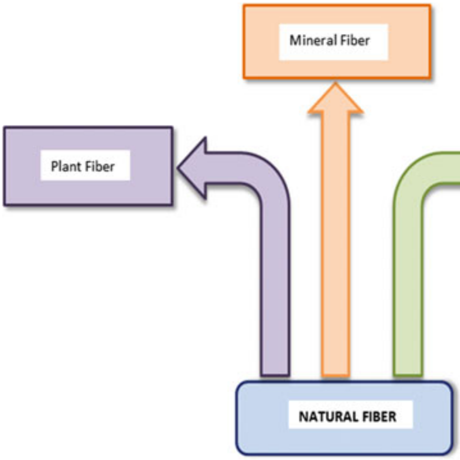

Fig. 1 General classification of natural fiber. *Source* Author

But there are few problematic issues with these fibers which are needed to be highlighted. Vegetable fibers been water absorbent and polar in nature, restrict the proper bonding of fiber with the hydrophobic matrix and whence affecting the thermal, dimensional and mechanical stability of the polymeric composites [24]. Hence, there is an at most need for the surface treatment of the vegetable fiber, for their high performance and durability. There are number of strategies for the modification of fiber characteristics, like wettability, thermal stability, interfacial bonding, these are namely Physical, Chemical and Biological treatment [2]. These treatments alter the framework the surface of the fiber and thus enable the proper adhesion between the fiber and the matrix [25]. This chapter covers the various modification techniques for the processing of the vegetable fiber surface.

Large number of researched had been done to improve the compatibility between the fiber and the matrix: Tingju et al. and Reza et al. provides an overview for the modification of the bamboo and Kenaf fiber respectively by the different chemical treatment strategies to cure the surface characteristic of these grass fiber and ensures the good bonding with the given reinforcing matrix [26, 27]. On the other side, the work reviewed by Susheel et al. and his co-workers highlights the sustainable modification treatment techniques for the natural fibres and also described the numerable applications of the treated fiber in the textile and polymer industries [28]. Thus the objective of this chapter is to present the various modification techniques required for the treatment of the plant fiber for the better adhesion between the matrixes. The detailed description is as follows.

Table 1 Chemical and mechanical properties of vegetable fiber

Fiber	Chemical composition			Mechanical properties				
	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Density (kg/m^3)	Tensile strength (MPa)	Young modulus (GPa)	Strain (%)	References
Flax	70–74	16–20	1.5	1.4	345–1500	25.6 ± 7.37	3.0	[8, 9]
Ramie	78.07	24.6	2.87	1.58	223–940	50–130	2–4	[10, 11]
Sisal	74	16	12	1.58	310–398	10–25	1–15	[12]
Hemp	73.5	17.9–22.4	3–6	1.5	500–900	76	1.67	[13, 14]
Coir	35–46	9.8	40–50	1.3	165–250	5–7	10–35	[15]
Banana	55–67	5–25	2–38	1.3–1.35	1.5–2	25–35	4–6	[16, 17]
Bamboo	20–65	30	19–30	1–1.2	150–850	10–40	1.2–8.1	[18–20]
Cotton	44	25–27	27	1.55	450–750	5.9–10.2	3–10	[21, 22]
Jute	60–74.8	12–20.8	10–15	1.3–1.45	400–803	15–30	1.2–2.0	[12, 15]
Baggase	35–45	20–30	15–20	1.2	15–300	18–28	–	[3, 23]
Pineapple	–	–	–	1.4	180–1600	55–90	1–5	[12]

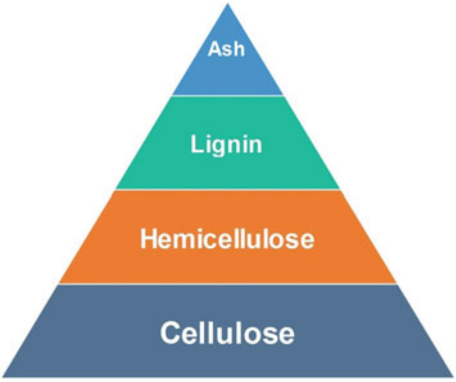

Fig. 2 Chemical composition of vegetable fiber. *Source* Author

2 Surface Modifications of Vegetable Fibers

Surface modifications are the methodologies which are carried out to optimize the interfacial characteristics. They bestowed the dimensional stability and thermo plasticity, along with the improvement in the adhesive properties between the fibers and the reinforcing matrix [6]. These modifications may be categorized as physical, chemical or biological, depending on the types of matrix to be reinforced [29]. Figure 3 is representing the various surface modification methods. The detailed treatments and the recent development in these methodologies are discussed below. Table 2 shows the compilation of work done by the multiple academicians for the treatment of the fiber.

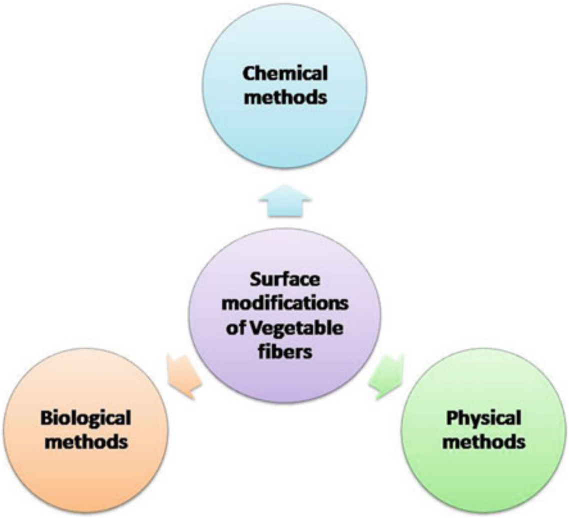

Fig. 3 Various surface modification methods for vegetable fibers. *Source* Author

Table 2 Summary of different treatment methodologies

S. No.	Year	References	Plant fiber	Reinforcing matrix	Modification	Key results
1.	2015	[96]	Hemp	LDPE	Chemical treatment—**Alkali**	Tensile strength, young modulus and percentage of elongation are enhanced Resistance to water was seen in the treated fiber along with the increment in the melt flow index
2.	2019	[97]	Palm	–	Chemical treatment—**Alkali**	Removal of amorphous substances like lignin and hemicellulose and enhancement in tensile strength
3.	2019	[98]	Wood	–	Chemical treatment—**Alkali**	Treatment with alkali activate the cellulose present on the wood surface and thus better adhesion with matrix
4.	2015	[99]	Coir	PP	Chemical treatment—**Alkali**	Morphology, physical and mechanical properties enhanced along with the increment in adhesion
5.	2018	[100]	Sisal	Starch	Chemical treatment—**Silane**	Thermal capacity is enhanced, fiber diameter becomes small and surface roughness increases and hydrophilic nature is reduced
6.	2016	[101]	Bamboo	Epoxy	Chemical treatment—**Silane**	Reforms the surface quality along with the modification in adherence with matrix

(continued)

Table 2 (continued)

S. No.	Year	References	Plant fiber	Reinforcing matrix	Modification	Key results
7.	2005	[102]	Flax	PP	Chemical treatment—**Maleic Anhydride**	Compatibility b/w the fiber and the bundle matrix increase. Enhanced tensile and shear strength of the fiber
8.	2020	[103]	Wool, cotton, silk	–	Chemical treatment—**Permanganate**	The with-scale friction is increased with the increment in fibers tensile and flexural strength
9.	2014	[104]	Kenaf	PLA	Chemical treatment—**Peroxide**	Adherence properties between the fiber and the PLA matrix are improved
10.	2020	[105]	Palm	Polyvinyl-Butyral	Chemical treatment—**Benzoylation**	Sudden improvement in the mechanical properties of the palm fiber
11.	2014	[106]	Coir, hemp and flax	–	Physical treatment—**Ultrasound**	Optimal degradation along with decrement in the hemicellulose content present in the fiber
12.	2018	[107]	Jute	Polyethylene glycol/polyester	Physical treatment—**Gamma**	Improvement in physiochemical properties of the fiber
13.	2017	[108]	Flax	Thermoplastic matrix	Physical treatment—**Corona Discharge**	Increase in fiber surface roughness and tensile properties
14.	2015	[109]	Sisal	PLA	Biological treatment—**Enzymatic**	Enhanced compatibility between the fiber and the matrix

2.1 Physical Treatment

Physical Treatments of vegetable fibers incorporates two steps: (1) Segregating the fibers bundles into the distinct filaments. (2) The framework of the plant-based natural fibers is modified in order to ameliorate its applications on composites [30]. Some examples of physical treatments are Steam Explosion, Plasma Treatment, Corona Discharge, Dielectric Barrier Treatment (DBT) etc., few of which are briefly explained as follows.

2.1.1 Steam Explosion Methodology

The pretreatment of the plant fibers with the Steam explosion technique is a high-efficacy process, which can be carried out either in the absence or in the presence of the catalyst. The latter includes the acid or base as an accelerator for the enhancement of the output so produced [31, 32]. The basic operation is to expose the sample (here, vegetable fibers) to the steam, which is at the elevated pressure and the temperature, for a given duration of time. In milliseconds, the pressurized steam hit the cells and the tissues within the plants fibers, which resulted in an explosive expansion. The consequence of this is the removal of the moisture content present within the sample [33]. The treatment resulted in the splitting of the lignocellulose into cellulose, hemicellulose and lignin [34]. The base catalyzed- Steam explosion technique proves to be more efficient in terms of the overall performance in accordance with the study of the surface morphology and the Crystallinity of the treated vegetable fiber [35]. Lignocellulosic and high-protein components, exploit the Steam explosion techniques, patent by Mason, as it serves potential advantages such as cost-effectiveness, no harmful environmental impact and energy efficient nature [36]. Steam Explosion is the notable method among researchers and academician, its efficiency for removing the non-cellulosic content from fiber was reviewed by Santosh and Suresh et al. they calibrated the mechanical properties of the Pineapple Leaf Fiber (PALF) by numbers of surface treatment analogy and found the SE method to be most reliable for removing the lignocellulose and breaking it into cellulosic components [37]. Pak Sui Lam et al. and his co-workers employed the principle of steam explosion to improve the mechanical strength and the dimensional stability of the palm fibers. They draw the conclusion that the adhesive forces between the palm fiber and the reinforcing matrix upshots along with enhancement in the chemical and mechanical properties of the given vegetable fibers [38]. On the other hand Vignon et al. investigated the morphology of the Bast and the hemp fibers modified with the Steam. He reported the improvement in the characteristics of the fibers treated with steam [39].

2.1.2 Plasma Treatment Methodology

The basic principle of the Plasma Treatment is to modify the sample surface by eradicating the feebly attached surface layer and forming new functional groups [12]. Plasma Treatment is an ecological process which inflates the wettability, adhesivity and reactivity between the fiber and the reinforcing matrix [40]. The reactive intermediates formed in the plasma environment depend upon the types of plasma gas used. These reactive species becomes highly energetic due to the imposition of the frequency of the electric fields. As an outcome, they collide with the sample surface placed in the reactors which resulted in the modification of the physical and chemical properties of the plant fibers. Hydrophilic characteristics of the fiber are altered by the implication of Oxygen-Plasma Treatment along with the increment in the mechanical properties of the vegetable fiber [41]. Processing of plant fibers with plasma had caught the consideration of many scholars' due to its exemplary results [30]. Murilo et al. along with his associates, reveals the superlative effects of cold plasma modification on the surface of Kapok Fiber. The repercussion so obtained from his studies states that Plasma Treatment leads to the activation of the fiber surface along with the augmentation of the mechanical characteristics of fiber reinforced composites [42–44]. Plasma treatments are sub-classified into two, on the basis of the operating pressure required during its implications, these are, (a) Low-Pressure Plasma Treatment and (b) Atmospheric Pressure Plasma Treatment. The low-pressure Plasma treatments were employed by various researchers for the alteration of the fiber's surface. Enciso et al. and Sanja et al. along with their co-workers exploits the low pressure methodology for the modulation of the flax/coconut and cotton/hemp fibers respectively, which resulted in the increment in the adhesive properties between the fibers and the matrix [45, 46] whereas Ying Li et al. along with his mates carried out the plasma technique under the atmospheric pressure conditions and investigated the impact of the same on the adherent property of the Ramie fibers with the corresponding PP matrix, and the findings were positive [47]. Figure 4 shows the general scheme for plasma surface modification.

2.1.3 Corona Treatment Methodology

Another treatment approach towards the modification of fiber surface is the Corona Discharge Methodology. It is an ecologically clean, solvent free analogy for the revitalization of the lignocellulose present on the fibers' surface without altering the bulk properties [48]. A substantial magnitude of electric field is applied to the plant fiber with the help of enormous sharp electrode. This leads to an increment in the polarity within the fiber and the matrix and thus enhances the adhesive property [49]. Large amount of researches had been performed by the scientist for exploiting the Corona Discharge Technique (CDT) in the field of polymer composites and matrix. Some of the examples are as follows: Molina et al. and Moshibudi et al. compares the multiple modification techniques applied over the vegetable fibers by large numbers of scholars and end up by concluding the immense application and utilization of

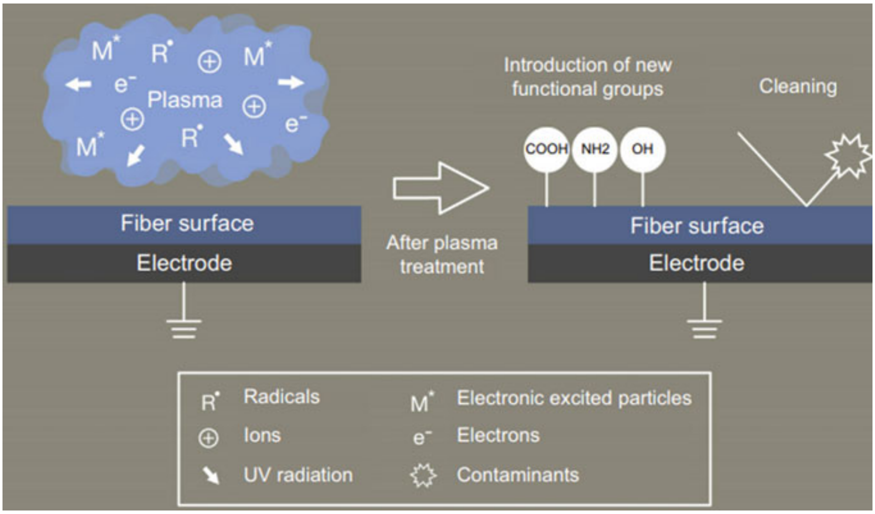

Fig. 4 General layout for plasma surface modification. Reprint from [30]

this fiber treatment in the polymer industries along with multiplication in the fibers' physical characteristics [50, 51]. In another surface treatment study by Vitor et al. and Oudrhiri et al. and their colleagues, they found the corona treatment to be the most suitable and efficient physical technique in modifying the surface characteristics of the fiber [52, 53]. Due to its low power consumption nature and the requirement of favorable conditions, like atmospheric pressure and low temperature, CDT is the point of attentions of large of scholars worldwide.

2.1.4 Ultraviolet and Ultrasound Modification

In Electromagnetic spectrum, Ultraviolet radiation (UV) falls before the Visible Light in terms of wavelength, extending from 100 to 400 nm. Lignin present in the fibers' wall is sensitive to these radiations and upon their application they disintegrate. Thus UV radiation modifies the plant fibers chemically and physically [50]. This radiation based surface treatment is immaculate and economically viable process, whence attracted numerous scholars for modification in fibers surficial characteristics [30, 54]. Some of the works presented by the scientist are listed as follows; Sharan Gupta et al. reform the physical configuration of the banana fibre by the implication of the UV radiation. He reviewed that the tensile along with the fractural strength of the treated fibers are intensified due to the formation of the network between the cellulose of the adjustment molecules [55] whereas Andres and Joes et al. amplifies the surface energy and adherence of the Wood–Plastic Composites (WPC) with the help of UV/Ozone Treatment. The morphology and the surface characteristics were calculated and were found in favour [56]. In the field of utilization of plant fiber, Kocic et al. treated the cotton and hemp fibers with that of UV radiations and came to the conclusion that UPF cotton and hemp finds a large scope in the fabrics and textile industries [57].

Another physiochemical technology in the surface modification is the usage of Ultrasound. In therapeutically and industrial sector, Ultrasound constitutes wide applications. The intervention of the fiber with this sound wave alters its morphology and mechanical properties, with enrichment of the accessibility and the reactivity of cellulose towards oxidation, due to the ultrasonic cavitation in the fluid medium [58]. Thus degradation of saccharides and improvement in the fiber-matrix reinforcing bond are the output of Ultrasound treatment [50, 55]. Alam et al. and his co-workers equate the thermal and morphological properties of the untreated, alkali treated, ultrasound treated and alkali-ultrasound treated Palm fibers. Among all the composites fabricated from Alkali-Ultrasound treatment shows better results [59] whereas Ghosh et al. combined the alkali and air bubbling (produced by Ultrasound) to amend the surface characteristics of the banana fiber [60].

2.1.5 Modification by γ-Treatment

Gamma Radiation are high-frequency, thus high energy, radiation engendered due to the nuclear decay, fission and fusion. Baring of fibers with γ-rays modifies their physical and chemical properties. Formation of reactive species, amplification of substrate to bound with cellulose, dehydration and decomposition of saccharides are the major outcome of γ-irradiation [61]. Swarnalata et al. along with her colleagues exploits the gamma technology to modify the Luffa fiber surface. Gamma irradiation proves beneficial as they improve the surface roughness and stiffness of the Luffa Fiber. The thermal, SEM and other morphological analysis reveals the increment in the physiochemical properties of the vegetable fiber [62]. Similarly Parid et al. calculated the effect of gamma treatment of Luffa on the moisture absorption capacity and studied the FTIR analysis [63]. Modification of Sisal fiber by gamma rays was studied by Bruno et al. and his co-workers. The result so obtained were presented and reveals that the bonding problem due to the absorption behaviour of fiber was cured and thus interfacial strength between the sisal fiber and the combining matrix enlarges [64]. On the other side, Rahman et al. and Rahman et al. with their fellow members investigated the impact of gamma radiation on Pineapple Leaf Fiber (PALF) and Jute/Okra fibers respectively. Observation divulged the increment in the properties of fibers by treatment with these shorter wavelength EM waves [65, 66]. Figure 5 shows the FTIR analysis of jute/okra PP composites.

2.2 Chemical Treatment

Poor interface adhesion between the Fiber-Matrix is to be reticulated along with the elimination of the waxy and pectin substances, present in the plant derived

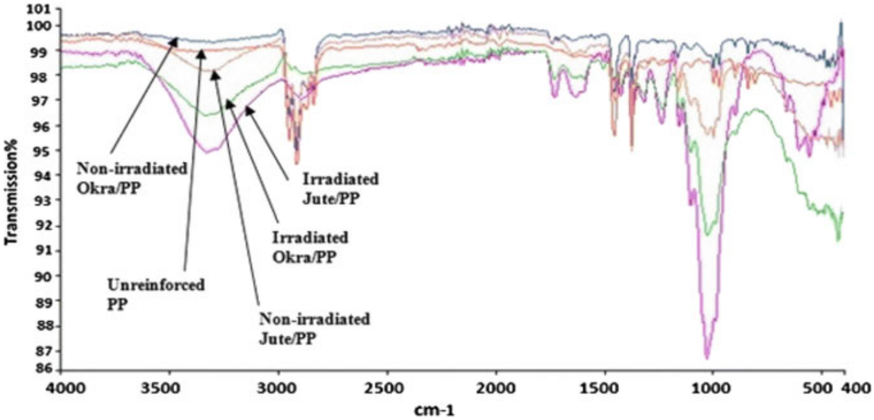

Fig. 5 FTIR spectra of jute/okra PP composites. Reprints from [65]

natural fibers, in view of the fact that these components lock the reactive functional groups and therefore thwart the fiber to reinforce with matrix. Consequently, fiber's surface is chemically treated to ameliorate the interfacial bonding. These treatments include acetylation, isocyanate, alkali treatment etc. [9]. The detailed description is as follows.

2.2.1 Treatment with Alkali Solution

Fibers are processed in alkaline medium before they are reinforced with matrix because mercerization serves two purposes: (1) Unstructured components like pectin, lignin and hemicellulose are discarded from the vegetable fibers resulting in the enhancement of their flexural strength. (2) Reactivity of the fiber with the matrix increases due to the availability of cellulose on the fibers surface [67]. The basic procedure is to treat the plant based bio-fiber with suitable amount of NaOH for a certain period of time at a particular favorable temperature. The fibers are then washed and dried. The alkali treated vegetable fibers are ready to be fabricated with the suitable matrix [68, 69]. NaOH treatment lead to the breakage of –OH group and addition of –O–Na group with the reactive molecular species b/w the cellulose, as a consequence the hindrance to the moisture absorbing characteristics of the fiber increases and thus its hydrophilicity decreases [70]. The consensus presented by the multiple scholars on alkali modification is listed as follows: Taimur et al. and Niharika et al. chemically treated the Luffa fiber with various treatment techniques and compares the resultant fibers so obtained by them. They concluded mercerization process to be superior to others. Alkali treated fibers display effective chemical and physical characteristics, along with the fibrillation on the fiber surface [71, 72]. On the other hand Pani et al. analyze the morphology of alkali pretreated Luffa, Bagase and Coir plant fiber and concluded the alkaline treatment to be the most competent

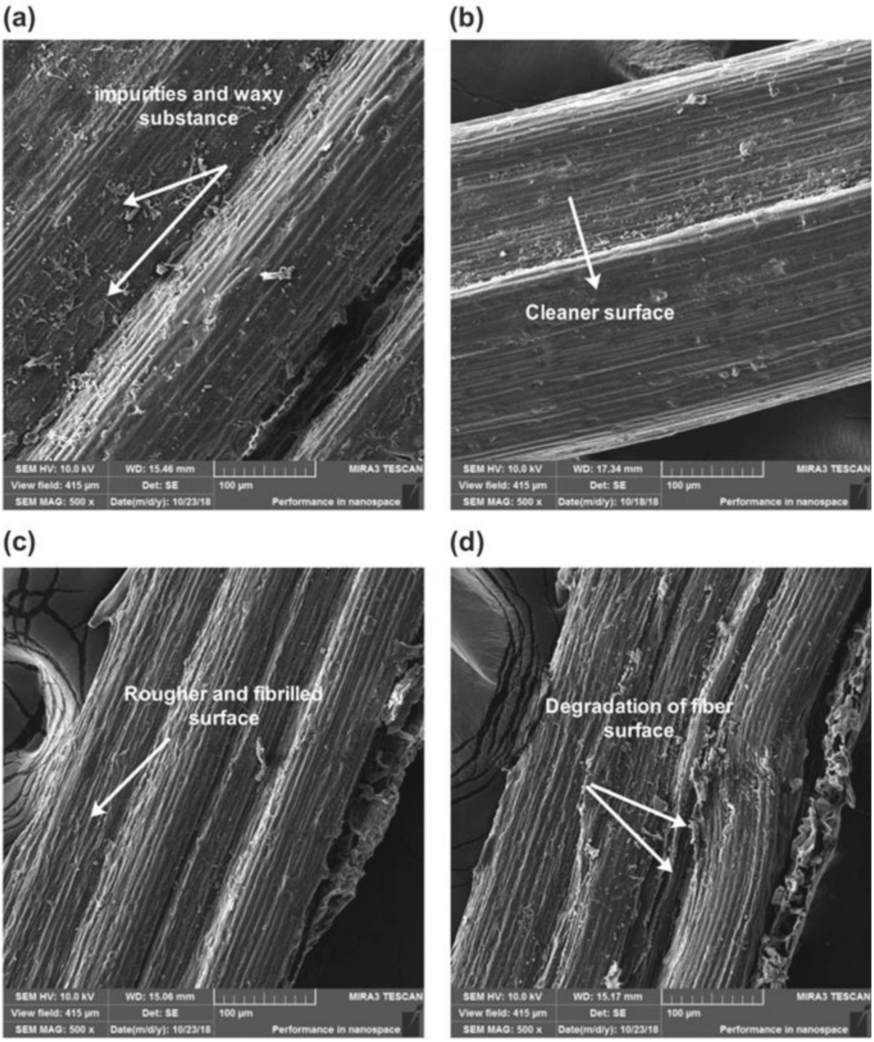

Fig. 6 SEM analysis of effect of alkali treatment on Kans grass fiber **a** untreated fiber **b** 3% alkali treated **c** 5% alkali treated **d** 7% alkali treated. Reprints from [74]

method for activating the capped cellulose on fiber walls [73]. Figure 6 shows the SEM analysis of effect of alkali treatment on the Kans grass fiber.

2.2.2 Silane Treatment Method

Hydrophilic and hydrophobic silanes are blended together to form the primer known as phenyltrimethoxysilane, which is used as the primary chemical reagent in the surface modification of the plant fiber [75]. Function of silane is to forge a chemically-stable covalently bounded compound with the free –OH groups present over the surface of the fiber, the mechanism is shown below [76]. Treatment of silane is favour in acidic medium as it increases the rate of hydrolysis and decreases the rate of condensation. The fiber-matrix adhesion is enhanced to greater extent when fibers are pre-treated first with NaOH followed by silane, along with the thermal and dimensional stability [51].

$$\text{Fiber}-\text{OH} + \text{CH}_2\text{CHSi(OH)}_3 \rightarrow \text{CH}_2\text{CHSi(OH)}_2\text{O}-\text{Fiber} + \text{H}_2\text{O}$$

The work report presented by the number of scholars for the modification of the fibers surface by treating with silane includes, Kermin et al. and his co-workers researched on the impact of the thermo-mechanical and tensile properties of the wood fiber modified by silane. They founded that silane treated fiber displays high flexural strength, good melt flow index, strong adhesion with polymer matrix and increment in hardness and young modulus [77]. Molecular continuity is of great extent in silanes than that in alkali treatment.

2.2.3 Grafting by Maleic Anhydride Treatment

Maleic Anhydride (MAN) is used as an adhesion promoter for refining the bonding strength between the fiber and the matrix by reacting with the –OH groups located in the amorphous part of the fibre's cellulose, which in turn reduce the availability of hydroxyl group on the superficial region and whence hydrophilicity of the fiber mitigates. This treatment is commonly referred as grafting [78]. Grafting is process of bonding the functional groups presented on the fibers surface covalently with that of the polymer or monomer to rectify with their wetting hindrance [79]. The mechanism scheme of treatment of fiber with MAN is shown below [78]

$$\text{OH}-\text{Fiber}-\text{OH} + \text{MAN} \rightarrow \text{C}-\text{CH}-\text{C}(=\text{O})-\text{O}-\text{Fiber}-\text{O}-\text{C}(=\text{O})-\text{CH}_2$$

Ramadevi et al. surveyed the effectiveness of using Maleic Anhydride as the coupling reagent for curing the interfacial characteristics of the Abaca fiber. The MAN treated plant fiber is fabricated with polypropylene matrix and mechanical tests on the resulting specimen are carried out, which is segregated into various fractions by weight. The result display the high tensile, flexural and impact strength of the sample along with enhancement in the adherence stability [80]. On the other hand, Kushwaha et al. studies the impact on morphology of bamboo fiber by treating the fiber with the blend of alkali and MAN in the ratio of 1:10 (wt./vol.) followed by drying and heating for 4–5 h. The outcome was the enrichment in the physical properties of the fiber with good dimensional and chemical stability [81]. The effects of maleic anhydride grafting and coconut fiber on thermal resistance of reinforced polypropylene composites are shown Fig. 7.

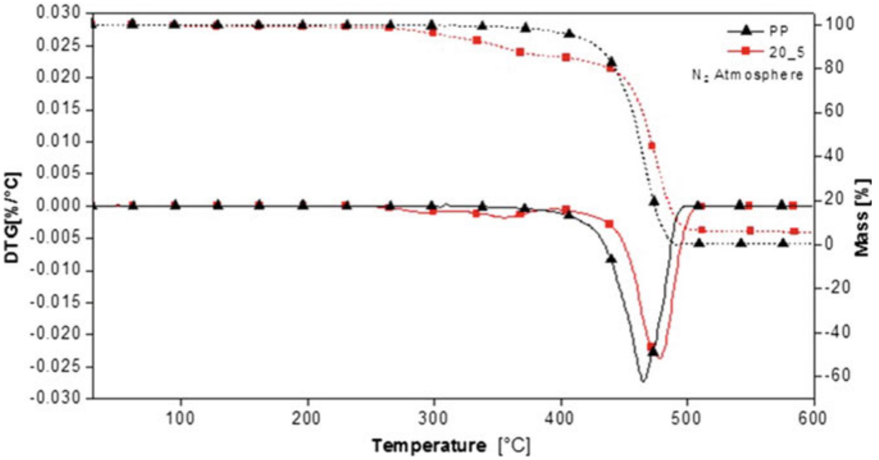

Fig. 7 TGA curves of pure polypropylene(PP) and coconut fiber maleic anhydride grafted pp. Reprints from (Techawinyutham et al. 2019)

2.2.4 Acetylation Treatment

Fibers are chemically modified by CH_3COO– reactive species in the Acetylation methodology. The plastic groups present in plants cellulose, like lignin and pectin, are locked with the help of acetyl group, thus, hydrophilicity of the fiber is affected to the greater extent [82]. The reaction for Acetylation is [9]

$$\text{Fiber}-\text{OH} + \text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{CH}_3 \rightarrow \text{Fiber}-\text{OCOCH}_3 + \text{CH}_3\text{COOH}$$

Several works outlaid by the researchers proved the effectiveness of treating the fiber by Acetylation. Buson et al. carried the principle steps which involve blending the mercerized bamboo fiber in the glacial solution for 2–4 h, followed by soaking of fiber in acidic acetic anhydride for the given duration of time. The fiber so obtained is washed, dried and ready to reinforce with the polymer matrix. The morphological study of BF shows the increment in its dimensional stability [83].

2.2.5 Treatment by Permanganate Solution

Potassium Permanganate is the core reagent of these surface modification process. This treatment is another example of graft-copolymerization reaction [84]. The ionic radical generated during the permanganate treatment is MnO_3^-. These ions react with the cellulose present over the fiber surface and thus effecting the wetting characteristics of the plant fiber [30]. In the study for the treatment of fiber with $KMnO_4$, Suhas et al. investigated the impact on physiochemical properties of fiber by treating the Flax fiber with potassium permanganate in presence of stearic acid. The results obtained were positive and favors the bonding stability between the Flax Fiber and the matrix [85]. Moisture absorption and fiber swelling is reduced to the great extent with the help of permanganate treatment [86].

2.2.6 Different Peroxide Treatment

The resilience strength of vegetable fiber can be ameliorated by treating them with peroxide. The common detecting agent used for this purpose is Benzoyl Peroxide and Dicumyl Peroxide. Premalatha et al. employed Benzoyl Peroxide for the purpose of modifying the surficial characteristics of the Luffa fiber (LCF_s). Treatment of LCF_s with 6% conc. Benzoyl peroxide solution in acetone is carried out at atmospheric conditions for the duration of 5 h. The specimen is then recovered, washed and kept for drying. The multiple test are formed on the peroxide treated LCF_S. The modified fiber is more permeable to the excellent adherence between the fiber and the matrix, high thermal and crystalline stability is also achieved [87]. On the other hand, the efficiency of using peroxide as the reaction initiator in case of using stabilizer for the natural fiber was put into consideration by the scholar Burrola et al.; he explained the function of exploiting Dicumyl Peroxide for the surface modification of the jute fiber. The grafting of peroxide with PP matrix leads to the better inter-bonding between the two [29]. The mechanism for treatment of fiber with peroxide is shown below [88].

$$\text{Peroxide} + \text{Cellulose}{-}\text{H} \rightarrow \text{Peroxide}{-}\text{H} + \text{Cellulose}$$

2.2.7 Treatment with Benzoyl Chloride

Benzoylation is the process of improving the effectiveness of the vegetable fiber by treating them with benzoyl chloride (C_6H_5COCl). The basic procedure is to treat the pre-mercerized treated fiber with 10% benzoyl chloride. The substrate is then passed in alcoholic medium to remove the traces. The resultant is then recovered, washed and dried. Benzoyl forms bond with the free –OH groups present in the plasticized region of fiber and thus the hydrophilicity of the vegetable fiber diminished and resulting in the strong bonding between the fiber and the polymer matrix [89]. Subhakanta et al. treated the areca sheath fiber with multiple treatments like alkaline, permanganate, sodium chlorite and Benzoylation, and studied the thermal, mechanical and water absorption characteristics. Areca Fibers treated with benzoyl chloride give better performance in comparison with other treatments [90]. Benzoylation is carried out as [20]:

$$\text{Fiber}{-}\text{OH}{+}\text{NaOH} \rightarrow \text{Fiber}{-}\text{ONa}^{+}{+}\text{H}_2\text{O}$$
$$\text{Fiber}{-}\text{ONa}^{+}{+}\text{C}_6\text{H}_5\text{COCl} \rightarrow \text{Fiber}{-}\text{C}_6\text{H}_5\text{CO}{+}\text{NaCl}$$

2.3 Biological Treatment

Surface treatment of fibers with physical and chemical methodology serve some disadvantages due to the desire of the solvent required for carrying out these processes. Due to the sumptuous cost of some chemicals, their hazardous nature and high energy consumption, are shifting the interest of the scholars and reviewers towards the biological treatment of fibers which involves microorganism like bacteria, fungi etc. Hence, inclining towards green surface treatment is the demand of nature. The processes involved in biological treatment are: Enzymatic Treatment, Fungal Treatment and bacterial treatment [30].

2.3.1 Treatment by Different Enzymes

Use of chemical reagents required in treating the fiber chemically harassed the environment in the negative aspects, whence which is not ecologically appealing. To overcome this issue, enzyme treatment is used as a substitute for fiber modification. Enzyme due to its reasonable cost found multiple applications in textile and polymer industry. Enzymes which are commonly used for altering the fiber surface are Amylases, Hydrates, Oxidoreductases, Laccase, etc. [91]. Enzymes are discerning in nature, and when used for treatment of fiber surface, they discard the emollient material present on the fibers' wall like water-absorbing pectin, hemicellulose and lignin [92].

The study on the Ramie fiber by Kamini et al. explains the effectiveness of the enzymatic treatment for the interfacial modification of fiber. The plant fiber is treated with Bacterial Cellulase enzyme by enzymatic hydrolysis. The treatment leads to the removal of gums and polysaccharides covering from the ramie fiber and thus enhances the adhesion between the fiber and the polymer matrix (here, PBS) [93]. Figure 8 shows the AFM analysis for enzymatically treated hemp fiber [92].

2.3.2 Cost Effective Fungal Treatment

The new biological method used for the surface modification of plant fiber is the Fungal Treatment. Due to its cost-effective and ecologically balanced nature, this modification had shifted the interest of numbers of scholars worldwide [70, 94]. Pickering et al. and his colleagues encourage the sustainable and green method for the improvement in the Hemp fiber characteristics, by the usage of fungal biological treatment (here, white rot fungi). An increment in the tensile strength of treated fiber was about 35% when compared with untreated hemp fiber [95].

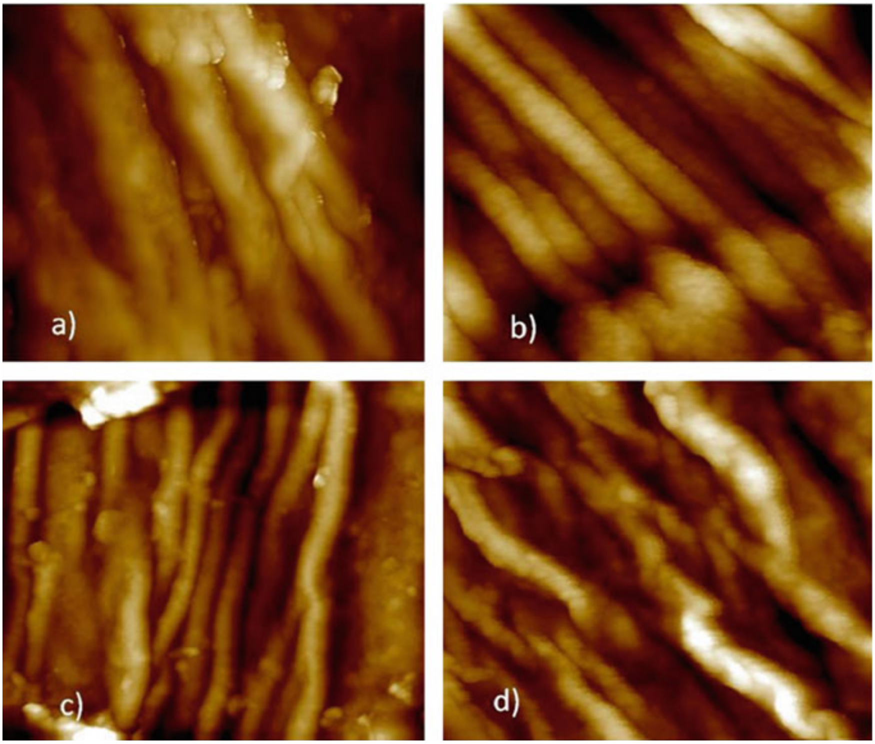

Fig. 8 AFM height images (5 × 5 μm) of hemp fibers after different chemical and enzymatic treatments. Images for **a** raw, **b** 10% NaOH, **c** xylanase and **d** NaOH xylanase treated hemp fibers. Reprints from (George et al. 2014)

3 Conclusion and Future Scope

The worldwide usability of vegetable fiber is because of their biodegradability and cost-effective nature. Vegetable fibers composites have been reusable, ecological and safe, which leads to their large applications in industrial sectors. There high specific durability—to—weight ratio, make them suitable to be used as the raw material in the manufacturing of automotive parts. Regardless of this, major problem encountered for the fabrication of plant fiber with polymeric composites is their low adhesion bonding between the hydrophilic fibers and hydrophobic matrix. Consequently, this chapter covers the surface modification techniques for improving the interfacial properties of the vegetable fibers. All the methods describe above, reveals that the alteration in the surficial characteristics of the fiber is important to reduce its hydrophilic nature, increase the roughness and to discard the plasticized components for ameliorated adhesion b/w the fiber and the corresponding polymer matrix.

In the conclusion, vegetable fiber proves to be suitable substrate to reinforce with polymer matrix after the proper surface treatment of these fibers. Chemical

Treatment, basically mercerization, is the most used method followed by the physical treatment. The future aspect involves more researches over the biological treatment due to their sustainable and environmental friendly nature.

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Bionanocomposite of Ag Nanoparticles/Jute Fibers as an Efficient Fungi-Free Material for the Automobile Industry

Raúl A. Morales-Luckie, Sergio L. Palacios-Lozano,
Víctor Sánchez-Mendieta, Oscar F. Olea-Mejia,
and María G. González-Pedroza

1 Introduction

Natural fibers can be of animal (wool, silk) or vegetable (cotton, linen, hemp) origin, artificial fibers are used from the modification of a natural polymer (usually cellulose), chemically modified (rayon-viscose, cellulose acetate) or synthetic, from the synthesis of polymers from petroleum derivatives (nylon, polyester, acrylic fibers) [1]. In recent years, natural fibers like coconut, kenaf, jute and cotton have been used in combination with synthetic polymers to make composite materials that work as substrates or structural reinforcements for some automotive components. These composite panels offer lightweight materials with good mechanical properties; however, they exhibit fungi development when exposed to extreme weather conditions like high temperature and humidity. Fungi growth causes a sticky texture and an unpleasant odor in those boards, a situation that the quality standards of the automotive industry does not allow. Based on such a problem, this research looks for a feasible solution to help produce this type of materials without fungi growing. Nanotechnology as the platform and Ag-NP's as the tool, are the guidelines to seek

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R. A. Morales-Luckie (✉) · V. Sánchez-Mendieta · O. F. Olea-Mejia
Centro Conjunto de Investigación en Química Sustentable, UAEM-UNAM, Carretera
Toluca-Atlacomulco Km 14.5, San Cayetano, 50200 Toluca, Estado de México, México
e-mail: rmoralesl@uaemex.mx

V. Sánchez-Mendieta
e-mail: vsanchezm@uaemex.com

O. F. Olea-Mejia
e-mail: ofoleam@uaemex.mx

S. L. Palacios-Lozano · M. G. González-Pedroza
Posgrado en Ciencia de Materiales. Facultad de Química, Universidad Autónoma del Estado de
México, Paseo Colón Esquina Paseo Tollocan S/N, C.P. 50000 Toluca, Estado de México, México

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_14

a feasible solution for this problem. It is well known that silver nanoparticles have excellent optical, electronic and catalytic properties but they also offer an effective alternative to stop the growth of pathogen fungi [2] like *Aspergillus fumigatus*, that has been identified in the composite material formed by jute and synthetic fibers. The effect of AgNPs and their nanocomposites as antifungal agents is well known; nonetheless, there are no works related to jute fibers and AgNPs as fungi-growth precluding bionanocomposites.

Nanoparticles have been used to coat polypropylene fibers, to improve bi-active properties in the textile sector [3]. Also, cellulose fibers modified with silver nanoparticles were prepared using N -methylmorpholine-N-oxide as a direct solvent [4], in addition to generating biocomposites of cellulose microfibrils, coming from bagasse/bast of fique, and zinc oxide nanoparticles [5]. Likewise, different synthesis of hybrid nanoparticles such as Ag/CNT have been carried out to manufacture nylon-6 polymer nanocomposite fibers for antimicrobial applications [6]. At present, cellulose-supported nanoparticle coatings have also been made, such as electrospinning [7] and electrostatic assemblies [8], assisted by microwaves [9], etc.

One typical method of AgNPs synthesis is the chemical reduction process (which is part of the "pad-dry-cure method" [10]), that involves the reduction of a silver salt by a reducing agent. $AgNO_3$ is the most frequently source of silver ions [11, 12].

In our research, the synthesis of AgNPs has been based on biological methods, which provides several advantages over chemical and physical methods, like the use of natural and renewable reducing agents [13], including bacteria, plant extracts, or fungi. Green chemistry methods to obtain nanoparticles does not require toxic chemicals, high pressure nor high energy. In addition, this biological method is fast and usually has a low cost [14]. One of the main contributions of this research is the use of *Heterotheca inuloides* named "Mexican arnica" [15] as the green reducing agent. This plant is commonly used in Mexico due to its antimicrobial, anti-inflammatory and analgesics properties [15]. The plant composition provides the phenolic and antioxidant biomolecules [16], which are excellent reducing agents of silver ions and capping agents of AgNPs.

Jute fiber is a plant (natural polymeric fiber) mainly developed in wet and warm zones around the globe are basically composed of cellulose, hemicellulose, and lignin. Jute is large, soft, and bright fiber between 1 and 4 m of length and 17–20 μm of diameter. People in countries like Mexico, the Philippines, and Thailand have developed the recollection and handcrafting of jute fibers as a way of life.

Rajeshkumar et al. [2] reported the use of silver nanoparticles as an effective antifungal agent against Aspergillus fumigatus. According to the authors, the mean, to reach AgNPs synthesis is the green route using silver nitrate ($AgNO_3$) as the silver ions provider and algae extract solution as the green reducing agent.

The base mechanism of AgNPs against fungi has to be with silver ions release that penetrates the fungi cell, attacking the respiratory function until fungi cell death [17, 18]. The effectiveness of this process strongly depends on AgNPs size and shape [19, 20]; the small size of these metallic nanoparticles guarantees that a large quantity of nanoparticles is in contact with the surface of the fungi [2, 13].

Herein, our work provides evidence that the use of this AgNPs/jute fibers bionanocomposite really inhibits the fungi activity on the natural jute fibers. Moreover, the biogenic AgNPs solution is as effective as some commercial antifungal compounds, like fluconazole, itraconazole and ketoconazole. This bionanocomposite may be used by different suppliers of the automotive industry.

2 Materials and Methods

Jute fibers were provided by a local farmer in Mexico. All other materials and chemical reagents were purchased commercially: $AgNO_3$ (Sigma-Aldrich); *Hetherotheca inuloides,* as tea bags (Therbal); Sabouraud dextrose agar (Dibico Laboratories); Muller Hinton Agar (Bomereaux de México); commercial antifungals, like itraconazole, ketoconazole and fluconazole (Wermar pharmaceuticals). All reagents were used without further purifications. All aqueous solutions were prepared using deionized water.

2.1 Preparation of Hetherotheca Inuloides *Infusion*

1 g of *Hetherotheca Inuloides* tea was boiled in 100 ml of deionized for 5 min.

2.2 AgNPs Synthesis

10 ml of *Heterotheca inuloides* aqueous extract was added into 25 ml of 10 mM $AgNO_3$ solution for 6 h at atmospheric pressure and room temperature (23 °C).

2.3 Jute Fibers Pretreatment

5 g of jute fibers were washed with 100 ml of deionized, and then with boiling water (95 °C) for 3 min, to remove the dust or any other impurity, after that, the fibers were air dried for 24 h.

2.4 Preparation of Bionanocomposite

5 g of jute fibers were immersed in a AgNPs solution for 5 min. Once the silver nanoparticles were attached to the surface of the fibers, they changed their color from light brown to dark brown.

2.5 Characterization Techniques

H*eterotheca inuloides* infusion was analyzed by FTIR using a Thermo Scientific Nicolet iS10 FTIR spectrometer. SEM analysis was carried on a JEOL JSM-6510LV instrument. Micrographs were taken at 15 and 20 kV of acceleration voltage. The biocomposite fibers were gold-coated before scanning. Elemental analysis of bio nanocomposite was done using energy-dispersive X-ray spectroscopy (EDX) with an Oxford probe attached to the microscope at 15 kV. An UV–Vis Perkin Elmer Lambda 25 Spectrometer USA instrument, with deuterium and tungsten-halogen lamps, was used to obtain the absorption spectrum of the Ag NPs in solution. The size and morphology of the Ag NPs were determined by transmission electron microscopy (TEM) on a JEOL JEM-2100 microscope. TEM samples were prepared by dropping 1 drop of silver nanoparticle solution on a grid copper of 200 mesh and left to evaporate at room temperature. The XPS spectra of the bionanocomposite was collected using a K-alpha Thermo Scientific system with an Al Kα (1486 eV) X-ray source. The jute panels with grown fungi were observed with a Hitachi 300XL optical microscope.

2.6 Obtaining Fungus

A jute-fibers panel sample (1 inch^2) was exposed to 36 °C and 95% of humidity in a controlled environment for 14 days. After this time, the color of the panel changes from light green to dark green. Once the fungi have grown over the surface of the panel, a small fungal inoculum was extracted from the panel and spread on the surface of Sabouraud Dextrose Agar. The agar plate was put in an oven at 32 °C for 72 h.

2.7 Antifungal Activity

Antifungal activity of jute fibers loaded with biogenic AgNPs were tested by the inhibition zone method [21]. Test condition is using a Muller Hinton agar plate fully inoculated with 0.5 Mc Farland concentrations (approximately 1–5 106 CFU/ml) of fungi solution [22]. After 24 h in incubator at 36 °C a jute fiber, which had been cover by colloidal solution of nanoparticles is free of fungi, meanwhile, the fibers with no AgNPs solution were fully covered by fungi activity. In addition to using commercial antifungal agents as a control.

3 Results and Discussion

3.1 Fungi Identification

Aspergillus fumigatus fungi were successfully grown on a jute fiber panel. Figure 1a shows a panel free of fungi. Figure 1b shows the same area of the panel with fungi development after humidity ant high temperature test. Figure 1c exhibit an *Aspergillus fumigatus* fungi micrograph. This evidence corresponds to the typical development of this type of fungi with white rough colony growing in radial way, the aspergillar heads and branch into dichotomy in acute angle [23].

3.1.1 UV–Vis Analysis

The typical SPR signal of AgNPs was observed at 437 nm (Fig. 2), particularly when the nanoparticles solution changes from light yellow to dark brown color [15, 23]. Sobczack-Kupiec et al. [11] mentions that the characteristic color change is due to the vibrations in the conduction electrons of the AgNPs while absorbing energy because of the incident light.

3.1.2 FTIR Analysis

Heterotheca inuloides FTIR spectra (Fig. 3) shows the presence of –OH at 3282 cm^{-1} that belongs to functional groups like alcohol and phenol [24], which are directly involved in the metallic ions (Ag^+) reduction. The second peak that may be responsible for the silver nanoparticles synthesis is located at 2918 cm^{-1}. This peak belongs

Fig. 1 Image of a panel sample before entering humidity and high temperature test (**a**). Image of a panel sample with fungi growth after 14 days exposure to humidity and temperature (**b**). Microscopy image of Aspergillus fumigatus (**c**)

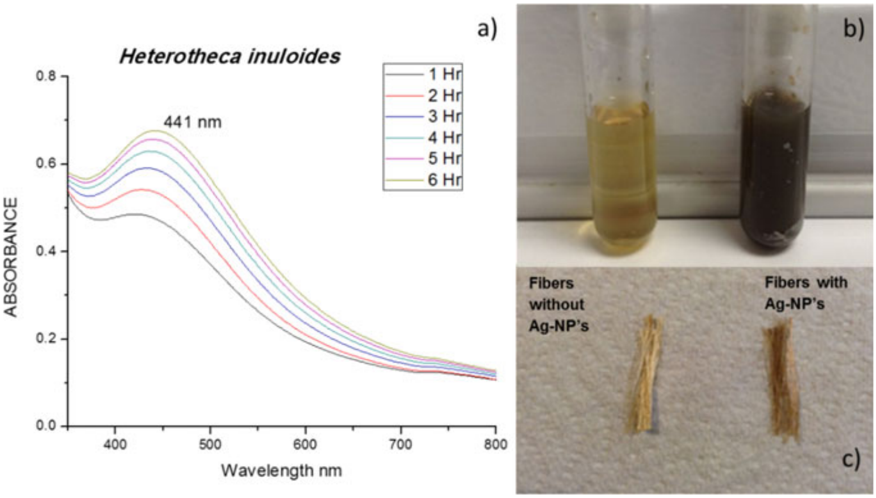
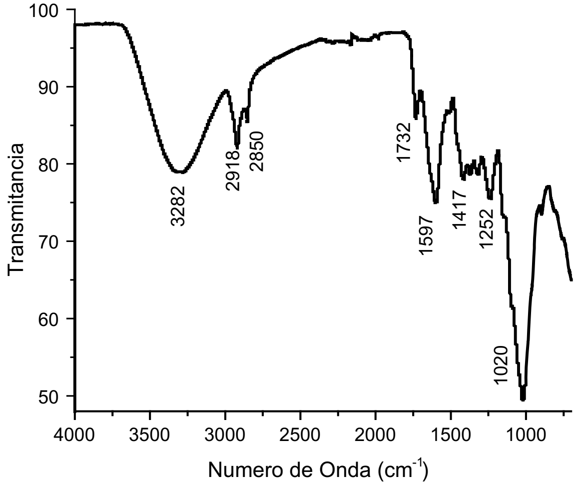


Fig. 2 UV–Vis spectra of silver nanoparticles solution (**a**). AgNPs solution during 6 h (**b**). Jute fibers with and without AgNPs (**c**)

Fig. 3 FTIR spectrum of *heterotheca inuloides*



to the stretching vibrations of aliphatic acids [25]. The absorption band at 1732 cm^{-1} indicates the presence of aldehydes and ketones (C=O) which also participates in the process of Ag^{+} ions reduction. The absorption peak at 1100 cm^{-1} indicates the presence carboxylic acid functional group [24]. The stretch and intense band of 1020 cm^{-1} indicates the presence of carboxyl acids (C–OH), which also participates in the formation of AgNPs.

Functional groups like –OH, –C=O, C–OH, support the process of reduction and stabilization of silver nanoparticles. Components like cellulose and lignin [26], which

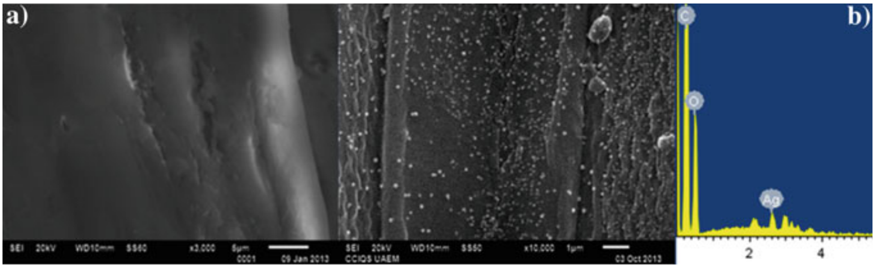


Fig. 4 Micrographs obtained from SEM; **a** jute fiber without and with AgNPs; **b** EDS analysis of jute fiber fully covered by AgNPs

are present in the jute structure, and flavonoids that are contained in *heterotheca inuloides* [15] include the presence of functional groups like aldehydes and ketones, which directly participate in the reduction process of Ag^+ ions to AgNPs [25].

3.1.3 SEM/EDX Analysis

Figure 4a shows the surface of the jute fiber without nanoparticles as a reference. Figure 4b shows the surface of the fiber with AgNPs on it. The particles are well dispersed and evenly cover most of the surface. This can increase the effectiveness of the particles against the fungi due to a larger contact area available [2, 19, 20]. To confirm the presence of silver on the surface of fibers, EDX analysis was performed. Peaks of O and C, which are the main elements present in jute fibers, can be observed, as well as a small peak at 3 keV that corresponds to Ag [27]. The EDX spectrum is showed in the inset of Fig. 4b. The particles are well attached to the surface since it required several hours in an ultrasonic bath to detach particles from it. This is due to jute fiber composition, which includes cellulose and mainly lignin. These organic and negatively charged elements of jute create an electrostatically attraction with the inorganic and negatively charged silver nanoparticles. The result of this interaction is a bionanocomposite material, which effectively works against fungi growth.

3.1.4 TEM Analysis

Although SEM analysis allowed us to observe particles of around 70–90 nm in size, many of the particles are below these dimensions and can only be seen by TEM. Figure 5 shows a TEM micrograph of the biogenic AgNPs. As can be seen, they are mostly spherical and with an average size of 9 nm and, in many cases, they are crystalline as evidenced in the inset of Fig. 5, where the [111] planes can be clearly seen. It is worth mentioning that the size and shape of the AgNPs are the most critical physical property for antifungal applications; smaller particles show an increased effectiveness against fungi [2, 20].

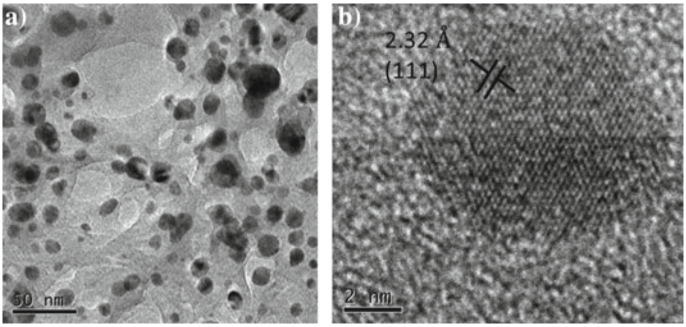


Fig. 5 **a** TEM image and **b** HRTEM image of AgNPs

3.1.5 XPS Analysis

Although the high resolution TEM image in Fig. 5 shows that the particles can be made of pure crystalline silver, we performed an XPS analysis to confirm this in a vast number of nanoparticles on the surface, since the analysis area of this technique was of about 1 mm^2. We found the presence of O and C from the fibers, in accordance with the EDX results. However, we will focus on the Ag signal to determine its oxidation state. Figure 6 shows the specific high resolution XPS spectra for silver. A doublet peak can be seen at 367.97 (Agd3/2) and 373.88 (Agd5/2) eV. By deconvoluting this signal we found that it corresponds to metallic Ag. Therefore, our green reduction method yields particles composed of pure metallic silver [28–30].

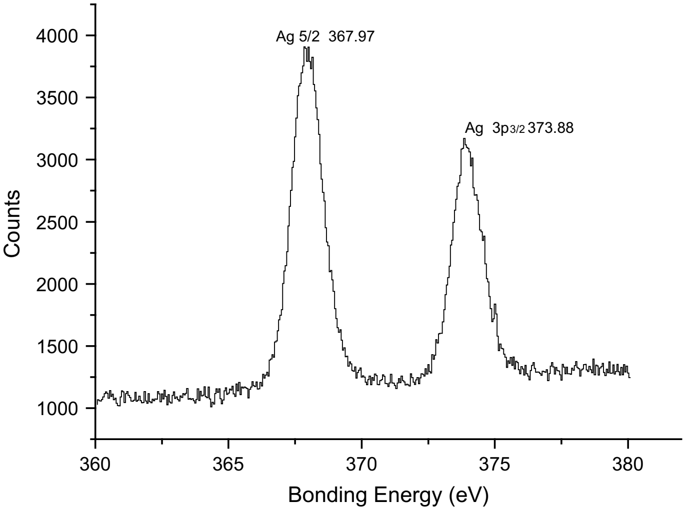


Fig. 6 High resolution XPS spectrum for Ag with deconvolution peaks showing only the presence of metallic Ag

3.2 Mechanism of Action of AgNPs Against Aspergillus Fumigatus

This research has shown that, the nanoparticles have antifungal activity when the activity of the positively charged Ag^+ ions present in AgNPs are directly attached to the negatively charged cell membranes of the pathogens microorganisms by electrostatic links [2]. Some authors like Monge [31] suggests that the smaller the size of the nanoparticles, they are more capable to penetrate into the membrane walls, inhibiting the respiratory activity or attacking the functional groups, like ADN, until cell death.

3.2.1 Biogenic AgNPs Antifungal Effectiveness

Figure 7 shows well-defined and bigger inhibitory zone (10 mm of diameter) around the jute sample.

AgNPs *versus* some of the most common commercial antifungals was a good parameter for us to measure the effectiveness of our AgNPs versus these antifungal agents. Figure 7a shows an agar plate with 0.5 Mc Farland concentrations (approximately 1–5 106 CFU/ml) with 5 discs, one of them contains 10.9 μg/ml of AgNPs, and the others contain 6.5 μg/mL of fluconazole, itraconazole and ketoconazole. An inhibition zone is formed around the discs except in the fluconazole disc, which means that *Aspergillus fumigatus* is resistant to this antifungal. Inhibition zone around AgNPs discs are noticeably clear and defined. However, AgNPs manage to have a

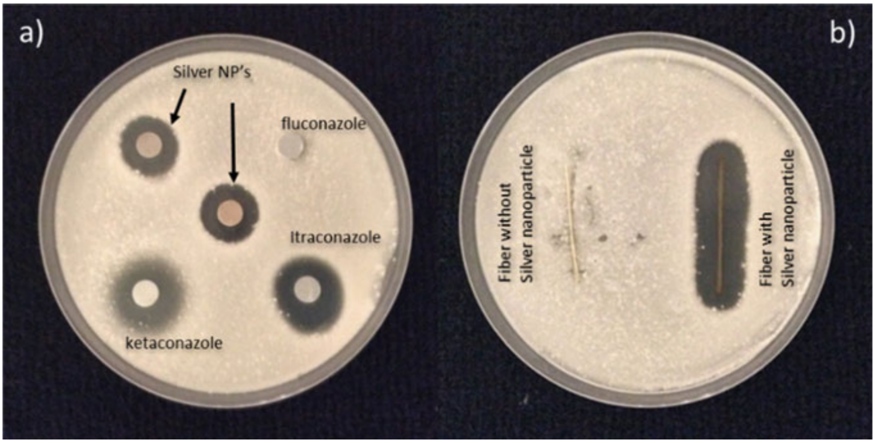


Fig. 7 Antifungal activity. **a** Inhibitory zone around AgNPs discs, in comparison with common commercial antifungals: fluconazole, itraconazole and ketoconazole. **b** Show a sample of a fiber impregnated with AgNPs free of fungi, and the other samples without AgNPs fully cover by fungi activity

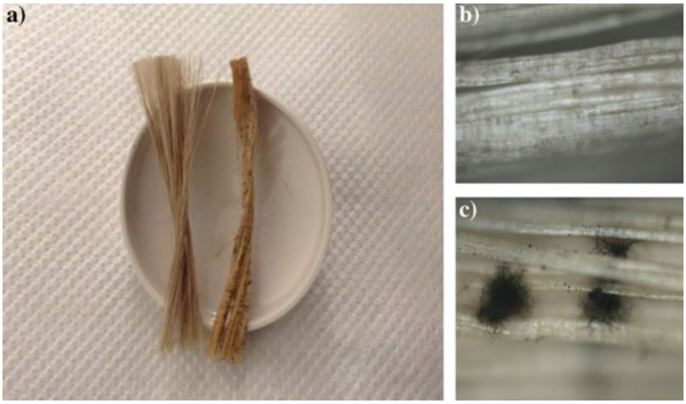


Fig. 8 **a** Picture of two samples of jute fiber with and free of AgNPs after 3 months in an oven at 36 °C and 95% of humidity. **b** Optical microscopy image of a fiber sample free of fungi. **c** Fungi growth on the fiber

great antifungal effect, compared to ketoconazole and itraconazole controls (Fig. 7a), since the inhibition halos are almost the same dimensions, which corroborates the antifungal effectiveness of our material, also in Fig. 7b shows the effect of the AgNPs covered fiber, which makes it a highly potential material for the desired purpose.

Figure 8a shows two samples of jute fibers covered by AgNPs (left) and virgin fibers (right). After being in an oven at 36 °C and 90% of humidity for 3 months, the formation of fungi is noticeable in the right-hand sample in comparison with samples of fibers treated with AgNPs that are free of fungi. Figures 8b, c show the optical microscopy of both conditions, with AgNPs (8b) and without AgNPs (8c).

4 Conclusions

Different methods of synthesis have been developed to produce silver nanoparticles. Most of them include metallic salt reduction using agents like $AgNO_3$. In our research, we also used $AgNO_3$ as ions source and an aqueous extract of *Hetheroteca inuloides* (Mexican arnica) as reducing agent, to obtain AgNPs with an excellent control over size and shape. Once these nanoparticles are attached to jute fibers, a bionanocomposite is formed and it successfully inhibits the *Aspergillus fumigatus* fungi growth as it was confirmed trough the inhibitory zone around jute fibers, which originally experienced fungi attack. On the other hand, we determined the effectiveness of AgNPs *versus* different commercial antifungals like itraconazole, ketoconazole and fluconazole. The differences were noticeable between protective zones around AgNPs discs, which is clear and well defined, in comparison to commercial antifungal discs, which were not so clear. Thus, an ecofriendly, simply and feasible solution for automotive suppliers, or any other industry that use polymer renewable natural fibers, is proposed with the formation of this free-fungi jute fibers nanocomposite.

Acknowledgements We thank Dr. Gustavo López-Téllez (CCIQS, Universidad Autónoma del Estado de México) for assistance in XPS studies.

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Tribological Behaviour of Glass Fiber Reinforced Polyamide Gears

Sandeep C. Dhaduti, S. G. Sarganachari, Arun Y. Patil, and Anish Khan

1 Introduction to Gears

Gears are wheels with tooth used for motion, power transmission and in most industrial rotating machine systems Gears are likewise utilized for changing speed of rotation of a machine shaft, alter the direction of the axis of revolution and change rotating to linear movement and the other way around. These are preferred to transmit power over a short center distance positively with constant velocity ratio. Because of a portion of the constraint of metallic gears like lubrication, noise, weight, cost, productivity and so forth, center has now been quickly changing upon polymer gears since most recent past years. Consequently, the assessment of gear failure is significant for upkeep wanting to fundamentally decrease downtime and cost [1]. Polymer gears pose many advantages upon metallic gears and are preferred because of no or less lubrication requirement, low noiseless operation, light weight, economic in production, good vibration absorbing property, impervious to erosion. But on the other hand these polymer gear drivers have low load carrying capacity, limited operating temperatures and less dimensionally stable.

The suitable element for plastic gears ought to have posed enhanced mechanical properties like modulus of rupture, resistance for deformation and compressive loads, low coefficient of friction, wear and fracture resistance of gear tooth. Thermoplastics

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S. C. Dhaduti
Mechanical Engineering Department, KLE Institute of Technology, Hubballi, India

S. G. Sarganachari
Mechanical Engineering Department, Basaveshwar Engineering College, Bagalkot, India

A. Y. Patil (✉)
School of Mechanical Engineering, KLE Technological University, Hubballi, India

A. Khan
Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah
21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_15

are widely used gear material because of their high impact strength, ease to process than thermosets.

Essentially, thermoplastic polymers have higher impact toughness, are easier to mold, and show an unrivalled adaptability in designing these power transmitting elements compared thermosets [2]. In recent with advancement in the field of materials newer polymer materials and their composites are being used as gear materials. Because monolithic materials and their alloys cannot always meet the demands of today's advanced technologies. Over past few years, newer polymer materials as well as their composites are used as gear materials like PA, PBT, PET, PEEK, TPU etc. For remolding characteristics of polymers diverse strengthening materials such fiber made from glass, carbon aramid are added. Unfilled and glass filled polyamides are generally utilised for designing gears because of their high mechanical strength, stiffness, wear resistance, fatigue strength, good dimensional stability and resistant for water absorption [3]. The mechanical properties of polymers are depicted in Table 1 [2].

The material perquisites for plastic gears are based on three concepts as indicated in Fig. 1 shows the effect of gear tooth surface stress and frequency of gear engagement [4]. The gears with superior and high performance materials are used in automotive components such as advanced steering where heat developed during operations are normally higher and thus needs external lubrication.

Table 1 Mechanical properties of polymer

Material Characteristics	Nylon	Glass filled Nylon	Acetal	Polybuthylene terephtalate	Polycarbonate
Mechanical strength	G	P	G	G	G
Stiffness	S	P	G	G	G
Wear resistance	P	G	P	G	U
Creep resistance	G	P	P	G	G
Fatigue strength	G	P	P	G	S
Heat-resistance	G	P	G	P	G
Resistance to oil and chemicals	P	P	P	P	U
Dimensional stability	S	G	G	G	P
Resistance to water absorption	U	U	P	P	P
Formability	G	G	G	G	S
Quality at subzero temperature	G	P	G	G	P
Atmospheric resistance	S	G	U	G	P

G—Good, P—Perfect, S—Satisfacory, U—Unsatisfacory

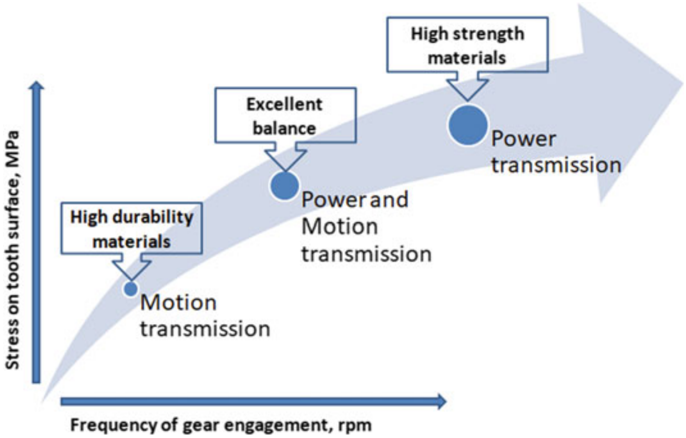


Fig. 1 Mechanical perquisites for gear material

For motion transmission, gears manufactured using high durability materials can be used in small capacity motors and office automation devices, where running temperatures are lower. Gear manufactured using materials having optimum strength and motion transmission can be used in mechanism like automotive window glass lifting and lowering, seat adjusting and door lock actuator [5]

As an outcome, enhancements in the mechanical properties of plastic materials are required. Including fortification strands, for example, glass filaments (GF), carbon filaments (CF), or aramid strands (AF), is a typical way to improve the tribological properties of polyamide. Glass fiber is most widely used strengthening agent for Polyamide.

It is very much evident that polyamide and glass reinforced polyamide materials have significant best properties compared to other materials listed in the Table 1. High resistance to wear make these materials as first choice for designing sliding parts in automobiles and industrial machines such as gear components [6].

The glass reinforcement significantly influences mechanical and tribological behaviour, with increase in weight percentage of glass fiber, friction co-efficient decreases, while improves wear rate. The increase in wear rate is more pronounce at higher loads with higher weight percentage of glass fiber [7]. Glass fibers orientation on the surface of a component influences the wear resistance and also component performance. With all these mentioned factors will significantly make polyamides with glass reinforcement as promising gear material.

Acetal and nylon are most commonly used materials for gear manufacturing. There are many trades names for acetal and nylon materials. The most commonly among acetal are Delrin, Duracon, and Celcon. The polyamides 6/6, 6/12 are generally employed for manufacturing gears. The classification of polyamide type is decided through quantity of methyl ethylene (CH2) atoms on every aspect of the nitrogen atom inside the polymer chain. So, Polyamide 12 has 12 methyl ethylene atoms on either side, which additionally shows a higher degree of crystallization.

Crystallization is basic boundary to note as it hinders the ingestion of water, so Polyamide 12 more water resistant compared to Polyamide 6. However, Polyamide is much less dimensionally stable because it does vary in shape in reaction to both heat and water. The specific method to improve the strength of Polyamide gears is to mold the material in rod shape and add reinforcements to the combination, thereby enhancing the compressive strength.

2 Techniques for Manufacturing Polymer Gears

Polymer gears are manufactured by gear hobbing, for large-volume production by injection molding techniques. However, extrusion and other traditional procedures can likewise be utilized. Stereo Lithography technique can also be used for manufacturing of polymer gears. The failure modes in polymer gears remain same independent of methods of manufacturing whether the gears are machine cut or injection molded. The major area of concern in case of injection molded polymer gears is attainment of dimensional accuracy after molding process.

3 Failure Modes in Polymer Gears

In the event that polymer gears when used for transmitting power, it becomes important to decrease the heat concentration in the friction unit. In case polymer–polymer and metal-polymer matches, impact of frictional specifications on the wear conduct are highly articulated than for metal–metal gear pairs.

The failure modes of metal gear pair and polymer gear is illustrated in Table 2 [1]

4 Wear Failure in Polymer Gears

The gear drives subjected to wear experience dimensional changes in tooth profile including erosion of material at the contact region due to mechanical, chemical or any other external parameters. The wear in gears when worked in drives of machines and systems causes a decrease in their geometrical dimensional accuracy and advances dynamic load effects and decreased strength results in tooth failure. The most common type of failure modes in polymer gear are indicated in Fig. 2.

Polymer gears ordinarily fail because of breaking at root, at pitch circle, and pitting. The temperature increase at the pitch point of meshing gears results softening of material and apparently reduces the strength of material and results in failure of gears at pitch point. The failure of the gears at pitch points are mainly caused due to unlubricated operating conditions [8]. The tooth breaks habitually happen close to the pitch point that is resulted from uneven wear [9]. The underlying investigations

Table 2 Failure modes of metal gear pair and polymer gear

Metal-Polymer gear	Polymer gear
Deformation: the involute gear profile at contact region of metal-polymer gear pair is deformed permanently	Thermal Failure: The hysteresis effect of heat and friction deteriorate mechanical properties of polymer material and thus softens the gear tooth
Tooth rupture: The contact stress doesn"t harm the surface, however stress is moved in the tooth root because of the gear contact position and tooth shape	Thermal Failure at the surface: due to accumulation of heat at the gear contact regions results in softening of tooth profile and gear failure
Stresses at root: Accumulation of root stress initiates growth and propagation of microcrackes formed at root region of gears	
Stress accumulation near the contact region of gears causes the failure of gear material locally	
Wear: The combined effect of applied torque and running speed of gear pair tends to erode the material at gear tooth surface	

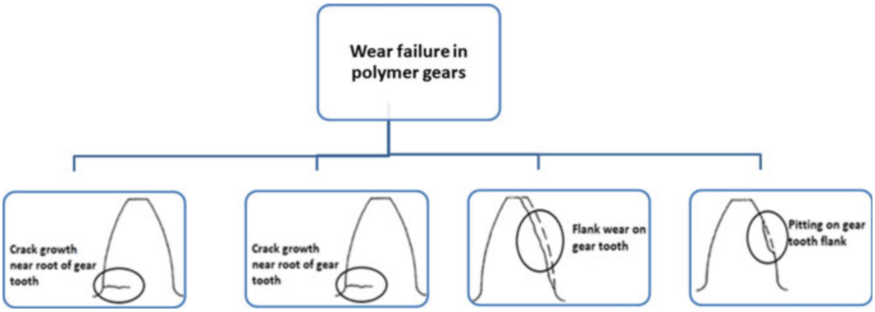


Fig. 2 Failure modes in polymer gears

of polymer gears shows that surface wear, local melting and pitting occurs when these are operated in unlubricated condition, while bending fatigue at root of gear tooth occurs in case of lubricated conditions. The damping characteristics can be also be reduced by reinforcing the polymer composites. The amount of internal heat generated inside the matrix of polymer reduced due to presence of fiber reinforcement when subjected to cyclic loading condition. Lower heat generation in gears is seen when gears were reinforced with high modulus fibers [10]. The fiber reinforced polymer composite enhances the transmission efficiency of polymer gears because of improved stiffness of gear tooth [11]. The enhancement in thermal characteristics of gear material, improves load resisting capacity of polymer gears with addition of fibers reinforcement [12].

5 Wear Failure in PA-GF Gears

Earlier studies on polymer gears, huge studies are highlighted on performance parameters of these gears. The different variables which affect the performance of polymer gears include type of mating gear, reinforcement and loading condition. The present study is more focus on type of reinforcement. The life of polymer composite gears when operated under unlubricated condition is influenced fatigue strength and wear resistance of gear material [11]. The failure framework is influenced by many criteria such as fiber volume fraction, aspect ratio and strength of fiber matrix interphase.

The inclusion of glass fiber to the polyamides enhances the strength and modulus at room temperature and even at higher operating temperatures and leads to the improved wear resistance [13]. Nylon gears with glass fiber reinforcement exhibits wear on tooth flank of gear when operated at higher level of stress because glass fibers are less heat resistant. As these gears drive the metal gear, the tip of the metal gears digs in the flank region of reinforced gear during the engagement of gear pair [14].

6 With Lubrication

The primary points of lubricating gear are to reduce friction, increase transmission efficiency, reduce wear and contact fatigue of the meshing gear tooth surfaces and hence enhance durability. In order to enhance the durability of glass fiber reinforced polyamide gears, there is atmost need for the decreasing heat developed at interface of gear tooth of meshing gear pair. The coefficient of friction of polyamide is high, which makes this material a good choice for gear material and addition of glass fiber will retain the mechanical properties even at elevated operating temperatures. In order to enhance the tribological performance of these gears, lubrication can be used to reduced the wear and operate the gears at lower temperatures. The heat generated due to friction can be reduced by external lubrication and thus dissipates the heat when compared to operation gears under dry conditions. The use of lubricants like PTFE (Polytetrafluoroethylene, commercial trade name as Teflon) can be used to reduced coefficient of friction and make gears to operate at lower operating temperatures. This will increase the life of gears and also transmit higher torque. Over 60% decrease of the coefficient of friction and 41% lower working temperature can be accomplished utilizing a PTFE self-greasing up gear pair. Life of glass reinforced polyamide gears increased significantly at higher loads [15].

The method of failure of test gear under lubricated conditions is significantly different than unlubricated operation. Gear lubricated with SAE 75W85 as standard gear oil indicated only 3 K rise in lubricant temperature and effectively dissipated heat between the gear pair. This contributed to 200% enhancement in gear life. The failure modes such as pitting, crack below the gear surface, sever plastic deformation and non uniform wear at gear root regions were seen when gear pair operated under dry conditions. Similarly, scuffing at the flank region, no to mild sliding marks on the lower flank of gear and absence of subsurface cracks in gear pair operating under lubricated conditions [16].

The wear property of glass filled polyamide gears can also be enhanced by addition of additives in nanoform. The wear of glass filled polyamide gears with addition of 0.03% weight of graphene oxide decreases the specific wear rate. The addition of graphene oxide as additive supports of dissipation of heat, thereby controlling the temperature at the interface of meshing gears. This brings down the wear loss as indicated in Fig. 3.

The specific wear rate and gear tooth surface temperature of homogenous and functional graded material PA66 with varying glass fiber reinforcement was found to dependent on magnitude to applied torque and speed. Unfilled PA66, homogenous and functional graded PA66 indicates low specific wear rate with increase in torque and constant speed. The wear phenomena can also analytically studied by applying Taguchi design of experimentation and ANOVA technique [18]. Figure 4 shows gears manufactured with varies compositions.

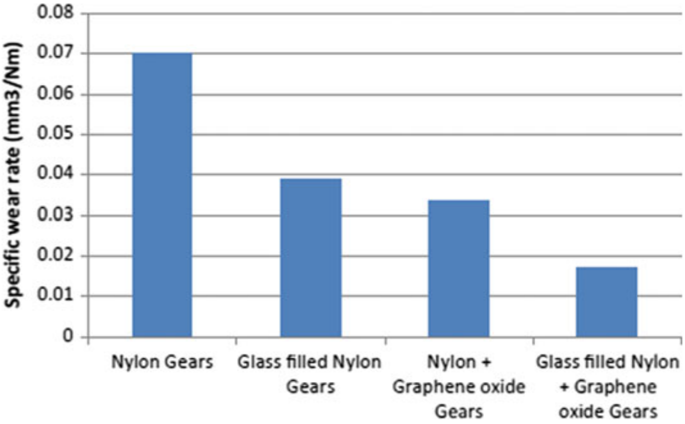


Fig. 3 Specific wear rate for Nylon gears with glass fiber reinforcement and graphene oxide [17]

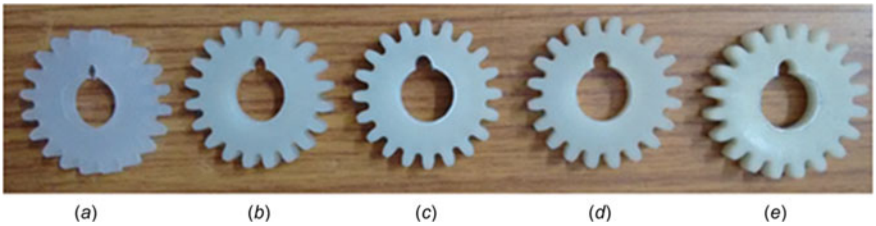


Fig. 4 Manufactured gear samples **a** unfilled PA66, **b** Functionally graded PA66 with 15wt % glass fiber, **c** Functionally graded PA66 with 30 wt % glass fiber **d** homogenous PA66 with 15 wt % glass fiber, **e** homogenous PA66 with 30 wt % glass fiber [18]

The wear and thermal properties of glass filled polyamide 66 can be improved by increasing interfacial bonding between glass fiber and polyamide 66. 1,4-Phenylene-bis-oxazoline (PBO) used as coupling material with varying weight percentage. It was found that 2 wt% PBO showed good improvement in adhesion of glass fiber- polyamide 66 interfaces and wear, thermal properties. Figure 5 indicated good bonding between PA66 with glass fiber with addition of 2 wt% PBO when compared without addition of PBO. Hence by using additives like PBO which will in turn improves the durability of gears when used as gear material [19]. The effect of addition of PBO is shown in Fig. 5.

Furthermore, fatigue wear and adhesive wear can be reduced with the addition of graphite fluoride (GrF) and fluorographene (FG) with PA66 matrix material. The mechanical properties are also enhanced with the addition of these additives [20].

Dry film lubricant like graphite and Polytetrafluroethylene (PTFE) can be coated on gears to improve wear behaviour, power transmission ratio and hence life of gear. Gear coated with PTFE shows greater improvement in reducing the operating temperature of 30 °C and wear of about 90% during running against uncoated polyamide gears [21]. Ultra-high molecular weight polyethylene (UHMWPE) can also are taken as additive for manufacturing the glass fiber reinforced PA6 composites which will help to reduce the wear and friction. The effect of additives like PTFE and UHMWPE used along with PA66 is indicated in Fig. 6 [22].

The operating performance of the PA gear can be improved by bringing some modification in gear tooth profile which delays causing damage to gear tooth due temperature rise during operation and thus enhance the durability of gear. The gear tooth profile modified and unmodified spur gear is illustrated in Fig. 7.

The depth of wear along the tooth modified gear is relatively lesser than unmodified gear as Hertz surface pressure distribution is uniform along very point the tooth profile of modified gear [23]. This led the improvement in wear behaviour of modified gear.

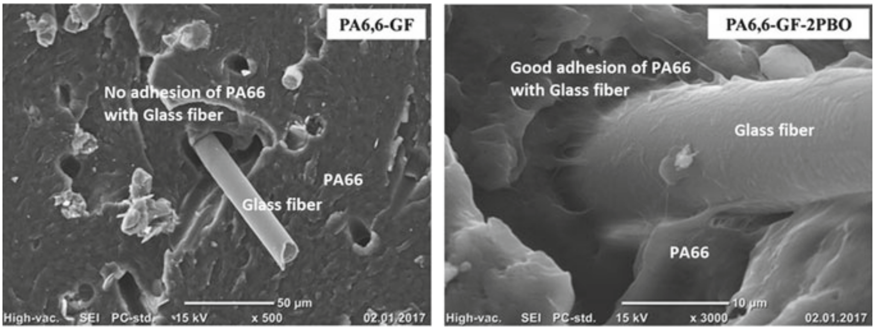


Fig. 5 SEM images of failure section of glass filled PA66 composite [19]

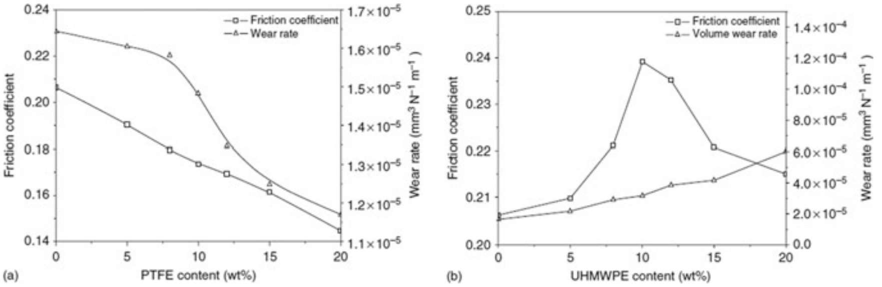
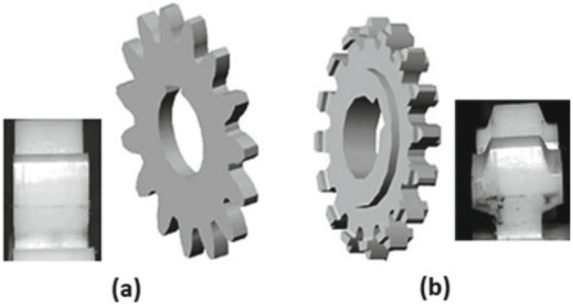


Fig. 6 Variation of friction coefficient and wear rate of glass reinforced PA6 by varying **a** PTFE and **b** UHMWPE [22]

Fig. 7 Spur gear tooth profile **a** without modification, **b** with modification [23]



7 Effect of Fiber Orientation on Wear

Usually fiber reinforced polymer gears indicate lower wear resistance but enhancement in thermal resistance. The injection molding process governors the orientation of fibers in molded components [24]. With increase in percentage of reinforcement in PA matrix and changing the direction of fiber orientation from 0° to 90° results in decline of coefficient of friction and is indicated in Fig. 8 [7].

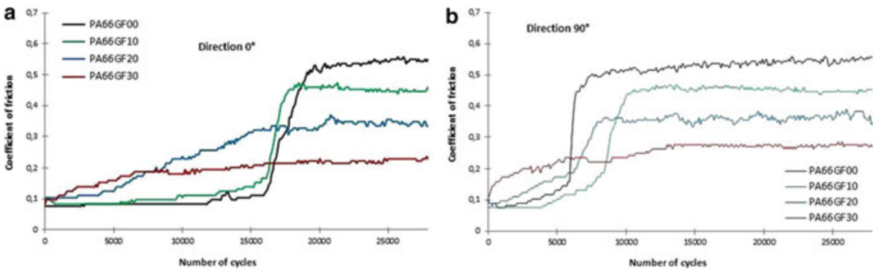


Fig. 8 Variation of coefficient of friction against glass fiber orientation when sliding **a** Perpendicular to fiber direction and **b** Parallel to fiber direction [7]

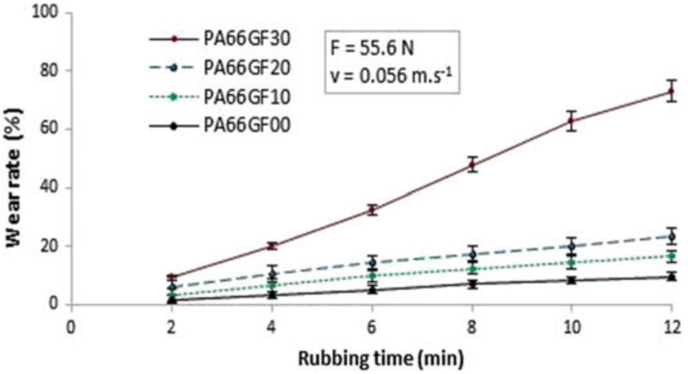


Fig. 9 Variation of wear rate with rubbing time and glass fiber content in PA matrix [7]

Figure 9 indicates increasing trend of wear rate with glass fiber reinforcement in PA matrix with respect to rubbing duration. The wear rate is tending to rise with glass fiber reinforcement. However, wear conduct is a result of the changing nature and properties of the meshing surfaces with increasing the glass fiber reinforcement in PA matrix.

8 Conclusion

The extensive study on wear behaviour of glass filled polyamide gears is carried out. It is obvious from overview that much work has been done on glass filled polyamide gears in order to analyse the failure reasons and modes of failure. Researches done on plastic gears are to a great extent dependent on experimental methods, and not more of works on computational methods. The temperature at interface of gear mesh pair decides the failure modes due to increase in coefficient of friction, tribological properties, higher operating torques and well as rotational speeds. The wear rate can be minimised when these gears are lubricated during running. The tooth surface wear can also be reduced with the aid for lubrication. The direction of orientation of glass fiber and weight percentage will also improve the tribological behaviour of these gears. Glass filled polyamide gears reinforced with additives will also tend to minimise the wear. Functionally graded materials used for manufacturing of gears and gear tooth profile modification have greater potential to delivery excellent performance and durability. Thin dry film lubricant can be applied at the interface of mating gears which will reduce the operating temperature, friction between the surfaces, increase power transmission and enhance improve durability of polyamide gears.

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Identification of Vegetable Fiber Origin

Sumit Sharma, Guravtar Singh, Abdullah M. Asiri, and Anish Khan

1 Introduction

In the early twentieth century, the discovery of polymers laid the foundation for fundamentals of a material revolution. Polymeric composites have a number of advantages, but the lack of adequate degradation is important. In addition, a large number of oil-based, mostly non-renewable, resources are needed to produce artificial polymers (such as polypropylene, polyethylene, etc.) [1–3]. Polymeric composites have a number of advantages, but the lack of adequate degradation is important. The annual worldwide disposal of millions of tons of plastics were raised, particularly from packaging. The criteria for finding new ways of handling this waste is non-biodegradable [4]. Therefore these environmental issues Problems have resulted in a substantial interest in the production of new materials based on biodegradable materials. Therefore, scientists are researching sustainable and environmentally friendly alternatives in order to minimise use of non-renewable and diminishing oil reserves. EIA (Energy Information Administration) has announced that oil production is expected to decrease by 4% per year after 2010 and, as a result, attempts to fix this issue are made to find environmentally friendly solutions [5–7]. Which created a

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S. Sharma (✉)
Department of Mechanical Engineering, Dr. BR Ambedkar National Institute of Technology Jalandhar, Jalandhar 144011, India
e-mail: sharmas@nitj.ac.in

G. Singh
School of Mechanical Engineering, Lovely Professional University, Phagwara 144411, India

A. M. Asiri · A. Khan
Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589 , Saudi Arabia

Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_16

renewed interest in natural materials that could be used as reinforcements or fillers in the composites and are also referred to as "reinforced natural fibre" Composites[8]. Therefore, several researchers have come up with ideas for strengthening polymers with various natural fibres such as hemp, sisal, and flax are used as filler materials [9–11]. Moreover these natural fibers are gaining popularity due to increase in environmental awareness among people [12]. The annual production of these composites is shown in Table 1. Not just the environmental issues but biocomposites can also sort out the problem of packaging industry to some extent once they are reinforced with different PLA grades to enhance their various properties and can also be exploited for sustainable constructions in automobile industry [13]. As far as other properties are concerned the biocomposites can help to a great extent in reducing the weight of electrical vehicle thus compensating for the weight of electrical batteries [14]. In other areas like medical science these composites are also playing a prominence role in the form of the biodegradable materials like PLLA (Poly-L-lactic Acid), PDLLA (Poly (DL-lactide) and chitosan results in generating composite with desirable material. Various factors such as type a material to be needed to be processed, component size, costing, complication in designs; and quality of the part is kept in mind while selecting technologies [15–17]. New biodegradable matrixes based on natural and renewable resources such as Polyactic acid, soy oil, and lignophenolic resins are used these days. These composites are used for various such as construction, panels for car doors, packaging, etc. [18]. Therefore the use of natural fibres as composite reinforcements has been increasing as in several applications, most synthetic fibre reinforced composites have been substituted [19]. Renewable resources, their usage

Table 1 Classification of natural fibers, origin and yearly production around the world [16]

Fiber type (plant)	Botanical name	Origin	Production (10^3 tons)
Coir	*Cocos nucifera* L	Fruit	650
Banana	Musa uluguruensis Warb	Leaf	200
Hemp	*Cannabis sativa* L	Stem	214
Bamboo	Gigantochloa scortechinii Dendrocalamus apus	Stem	10,000
Cotton	Gossypium spp.	Seed	19,010
Flax	*Linum usitatissimum*	Stem	830
Jute	*Corchorus capsularis, Corchorus olitorius*	Stem	2850
Kapok	*Ceiba pentandra*	Seed	123
Kenaf	*Hibiscus cannabinus*	Stem	970
Phormium	*Phormium tenax*	Leaf	–
Pineapple	Ananas comosus Merr	Leaf	–
Ramie	Boehmeria nivea Gaud	Stem	100
Sisal	*Agave sisalana*	Leaf	318.8
Abaca	*Musa textilis*	Leaf	91
Bagasse	*Saccharum officinarum* L	Stem	102,000

and alteration are involved in a multitude of major processes with a multitude of essential processes significant impact on our daily lives [20, 21]. In view of that, the idea of "green composites," which have emerged as new environmentally sustainable products, with engineering and industrial applications, and technologically advantageous benefits, has been introduced [22]. Natural fibre reinforced composites are gaining growing interest in research because of their easy availability, recyclability, lightweight and low cost [23]. Many natural fibres have been effective strengthening for thermosets and thermoplastic matrices with organic matrices such as polylactic acid, but natural fibres such as bamboo, banana, wheat, sisal, sugarcanes, oil palms, cotton, flax straw, silk and coconut have been losing predilection because of low reliability as a result of the use of synthetic materials such as glass and carbon fibrillation [25].

2 Constituents and Reinforcement of Green Composite Bio-Fibers

In green composites, natural/bio-fiber is used as a reinforcement material that is embedded in a matrix in the composite to form a dispersed point. This increases the stiffness, strength to the composites of certain physical properties as it holds the stress and load that is imposed on the composite. The biodegradable polymers present in green composites act as a matrix or continuous step and help protect the composite from the environment as its holding and binding property helps to pass load and stress to strengthening [16]. Table 2 presents comparison between properties of some natural fibers with glass fiber (E-glass). Green fibres such as coconut, hemp, sisel, jute, and coir etc. are now used in some applications as material reinforcement due to simple accessibility, biodegradability, recyclability, low cost and lightweight substitution of some traditional fibres such as carbon, glass etc. [26, 27]. Chemical composition of various natural fibres is shown in Table 3.

Hu et al. [42] which is obtained from renewable resources through biotechnology and has good mechanical properties and biocompatibility. The biodegradation of some materials is in moist/wet open-air atmospheres by microbial/bacterial attack. Bio-based polymer matrices have more life cycle contour than petrochemical-based traditional thermosets and thermoplastics. Biodegradation of natural polymers can be easily done by micro-organisms in sewage treatment plants [43]. As a polymer matrix, the biobased matrix plays a parallel role, which helps to pass applied shear load to fibres to protect them against physical damage. The key family of biodegradable polymers are polysaccharides and proteins obtained by separation from biomass, which is also known as fractionation. The petrochemical process synthesises polyesters such as poly-hydroxyal-kanoates (PHA) from the other family of polyesters such as polyester amide (PEA), poly-capro-lactone (PCL) etc. In addition, the other polyesters in the family that are entirely developed by the petrochemical process,

Table 2 Comparison between some mechanical properties of natural and synthetic fiber [16, 22–40]

Fibre	Density (g/cm^3)	Length (mm)	Failure strain (%)	Tensile strength (MPa)	Stiffness/Young's modulus (GPa)	Specific tensile strength (MPa/g cm^3)	Specific Young's modulus (GPa/g cm^3)
Ramie	1.4	900–1200	2.0–3.8	400–938	44–128	270–620	29–85
Flax	1.4	5–900	1.2–3.2	345–1830	27–80	230–1220	18–53
Hemp	1.4	5–55	1.6	550–1110	58–70	370–740	39–47
Jute	1.4–1.5	1.5–120	1.5–1.8	393–800	10–55	300–610	7.1–39
Harakeke	1.3	4–5	4.2–5.8	440–990	14–33	338–761	11–25
Sisal	1.3–1.5	900	2.0–2.5	507–855	9.4–28	362–610	6.7–20
Alfa	1.4	350	1.5–2.5	188–308	18–25	134–220	13–18
Cotton	1.5–1.6	10–60	3.0–10	287–800	5.5–13	190–530	3.7–8.4
Coir	1.2	20–150	15–30	131–220	4–6	110–180	3.3–5
Silk	1.3	Continuous	15–60	100–1500	5–25	100–1500	4–20
Feather	0.9	10–30	6.9	100–203	3–10	112–226	3.3–11
Wool	1.3	38–152	13.2–35	50–315	2.3–5	38–242	1.8–3.8
E-glass	2.5	Continuous	2.5	2000–3000	70	800–1400	29

Table 3 Natural fibers and their chemical composition [41]

Chemical composition (%)			
Type of fiber	Cellulose	Hemi-cellulose	Lignin
Jute	61–63	13	5–13
Banana	60–65	6–8	5–10
Coir	43	<1	45
Flax	70–72	14	4–5
Mesta	60	15	10
Pineapple leaf	80	–	12
Sisal	60–67	10–15	8–12
Wood	45–50	23	27
Sun hemp	70–80	18–19	4–5
Ramie	80–85	3–4	0.5

such as polyester amide (PEA), PCL, etc., are commercially available. Biodegradable polymers are also obtained by chemical synthesis, such as PEA and PCL, which are widely used. PLA is the most known and flexible thermoplastic material in bio-polymeric materials.

3 Plant Fibers

Plant fibres may be in the form of hair (cotton, kapok), hard fibres (coir, kapok), hard fibres (coir, Sisal), and sheaves (flax, hemp, jute) of fibre. The plant fibres are graded depending on like main and secondary, their usefulness. Plants for use as primary utility fibres include hemp, jute, kenaf, etc., whereas the by-products of plants such as coir, pineapple, etc., the secondary party belongs to six types of plant fibres are available, namely flax, hemp, jute, kenaf, and ramie. Fibers of leaves (abaca, pineapple, and sisal), fibres of seeds (coir, cotton, and kapok), fibres of straw (corn, rice, and wheat), fibres of grass (bagasse and bamboo), and fibres of wood (softwood and wood) [15]. Lignocellulose is the main chemical composition of plant fibres (cellulose, hemicellulose and lignin), and the sum of these ingredients varies from plant to plant. It is due to age, organisms, and can differ in various sections of the same plant as well. These basic basics are the physical properties of the fibres are partly determined by the materials [44]. Those polymers are capable of throughout the plant cell wall; they are distributed unevenly, making it difficult to know the fibres' structure and properties [45]. Cotton fibre has the highest amount of cellulose of any plant fibres [14, 46–49] while coir has the highest amount of cellulose the largest volume of lignin is in the fibre. One question of natural concern is the unevenness of the chemical composition of the plant [40, 50–54]. Fibers for use in composites as reinforcements. The best and stiffest cellulose is the fibre part is a linear 1,4-β-glucan polymer composed of D-anhydroglucose ($C_6H_{11}O_5$) repeating hydroxyl group containing units [55]. The classes of OH type. The bonding of inter- and intra-molecular hydrogen in nature makes it hydrophilic. For all natural fibres, the cellulose chemical structure remains the same, while the degree of polymerization is stated in the mechanical properties of some natural fibres and manufactured fibres [56]. The variance in the properties of natural fibres is the product of many variations. Factors such as the plant's geographic location, ripeness, scale, chemical composition, section of the plant from which fibres are extracted, etc. Also, the difference can be related to various stages: development, harvesting, extraction and storage of fibre, and each stage has several stages: Influencing considerations. The intensity of the fibre is also shown to be related to fibrillary, fiber angle and physical characteristics as small fibrillary angle, small diameter of the fibre, and High aspect ratio offers high mechanical characteristics [57]. Due to low density and relatively low density, Strong strength and natural fibre module, these fibres are preferred reinforcements in different applications. The elevated strength of kenaf and ramie fibres and the low coir strength the high and low cellulose content may be linked to fibre [58]. Fiber pores, relative humidity, chemical composition, and crystallinity are correlated with Fibers [59]. In general, high cellulose content, high relative humidity, high volume of pores affects the fibers' mechanical properties [60]. The bast fibres have been found to have the highest polymerization degree compared to most fibers [61]. The phenolic compound that is known to protect the other plant fibres is lignin [62]. The plant 's structure and is therefore resistant to microbial degradation before it is disrupted by Physical/chemical recovery. Even today, the chemical structure of lignin is not clear. Although most functional classes and units are known [63]. It is assumed that lignin is considered to be to maintain the structure of the plant, a binder that binds the celluloses [64]. The interfacial fiber-matrix adhesion is impaired by the implementation of a matrix. In comparison to synthetic fibres such as synthetic fibres, the cost of natural fibres is considerably low [65].

3.1 Hemp

Hemp (*Cannabis sativa* L.) is a multi-use, multifunctional crop that can supply a large number of useful raw materials. The key drivers for the potential expansion of the hemp crop are its goods various advantages [66]. Hemp is considered one of the oldest crops known to man. This plant is very abundant and widespread, economically important for some societies. The essence of this important crop of industrial origin is important. The high yield potential that can be achieved in a relatively short time is crucial for industry [66]. Crop cycle; dry biomass production of up to 20 t/ha has been recorded in Europe [67]. Hemp is also highly adaptable and can be grown in a wide variety of habitats, from northern latitudes to northern latitudes [68] and also in climates in the tropics. The economic value of hemp can definitely be attributed to the likelihood that it can be grown for wide range of applications for end-use use. Traditionally, hemp is grown for its three primary products: Fibers, seeds and psychoactive substances that accumulate in the female inflorescence in

Table 4 Typical physical and mechanical properties of hemp [61]

Properties	Values
Length (ultimate) (mm)	8.3–14
Diameter (ultimate) (mm)	17–23
Aspect ratio (length/diameter)	549
Specific apparent density (gravity)	1500
Microfibril angel (%)	6.2
Moisture content (%)	12
Cellulose content (%)	90
Tensile strength (MPa)	310–750
Specific tensile strength (MPa)	210–510
Young's modulus (GPa)	30–60
Specific Young's modulus (GPa)	20–41
Failure strain (%)	2–4

particular [69]. Currently, it is commonly used as well, Grown in countries with temperate climates such as Chile, North Korea, India, Japan, and many countries of the European Union (EU) [70]. The EU considers the promotion of hemp production in its member countries. Hemp is nowadays used in a range of applications, including textile fibre, paper, composite fibre, seed food, oil, wax. The use of resin, pulp, biofuel, etc., depends primarily on the grade/quality of the hemp [71–75]. Table 4 shows the typical physical and mechanical properties of hemp.

The flowering tops and hemp leaves create resin secretions containing the narcotic 9-tetrahydrocannabinol (THC) for which marijuana and hashish are popular to a lesser degree. It can not be used as a narcotic because industrial hemp produces less than 0.2% THC. The Small quantities of tetrahydrocannabinol (THC) are secreted from the hemp. Renowned for the narcotic drug cannabis. Since the amount of THC in hemp is present, like other *Cannabis sativa* strains, it is less than 0.2% and should not be used as a drug. Various reports indicate that the oldest hemp fibre dates back to 8000 BC (The History of Columbia About the World). Between 1971 and 1993, hemp fibre production was briefly prohibited. It has expanded exponentially since the ban has been lifted. The chemical composition of the cellulose content varies from 70.2 to 74.4% in hemp [76]. Even though it has several applications, owing to its high strength and stiffness so it is used as reinforcement in bio composites. Hemp is the most commonly used natural fibre, after sisal. In composites, as reinforcement [77]. Naturally, hemp is one of the most ecologically friendly fibres and even the most environmentally friendly fibres. The Columbia History of the World notes that pieces of hemp fibre found in tombs dating back to tombs are the oldest remnants of human industry. 8000 BC, roughly [65]. Hemp is an annual plant that originates in Central Asia and it is believed to have been cultivated for over 12,000 years. In the Iron Age, it possibly entered central Europe, and there is evidence of its creation in the United Kingdom by the Anglo- (800–1000 AD) [78]. It is mostly grown now in the EU, Central Asia, China and the Philippines. The world's industrial production

Table 5 Chemical composition of hemp fibers as reported by different authors

Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)	Other (%)	References
67	16.1	0.8	3.3	2.8	[62]
74.4	17.9	0.9	3.7	0.8	[82]
74	18	1	4		[83]
55	16	18	4	7	[84]
76	11.5	1.3	3.2		[85]
57–77			9–13		[76]
75.1	<2		8		[65]
70–74	17.9–22.4	0.9	3.7–5.7	0.8	[86]
75.6	10.7				[87]
78.3			2.9		[88]
76.1	12.3	1.6	5.7	3.3	[46]

of hemp is cultivated in China, with most of the rest being grown in Chile, France, the People's Democratic Republic of Korea and Spain. There is an exponential rise in the use of hemp for different types of goods in recent years, applications. The universe, according to the FAO, Hemp fibre production has risen from 50,000 tonnes in 2000 to nearly 90,000 tonnes in 2005 [79, 80]. The Hem core the first large-scale hemp business in the United Kingdom, has seen rapid development in the last couple of years. The only one it currently owns is Hemp processing plant in the UK and contracts at present 40 farmers will cultivate 3500 acres of cannabis a year [81]. Table 5 highlights the chemical composition of hemp fibers as reported by different authors.

3.2 Jute

Jute is a natural fibre grown annually. It is biodegradable and respectful of the environment. It provides millions of people with sustenance. It has a broad usage range. It is also commonly used as floor coverings, home textiles, decorative fabrics, shopping bags, carrier bags, handicrafts, cushion covers, curtains, blankets, nursery pots, insulation material, soil savers, composites based on jute, etc., in addition to being used as packaging material worldwide. It in different applications, such as soil stabilisation, erosion control, etc., it has the ability to be used as a geotextile on a wide scale. For making pulp and paper, it may be a good source of raw material [89]. A significant agricultural product is jute fibre. In countries such as India, China, Bangladesh, etc., it is one of the most common natural fibres. In India's economy, the jute industry has unique significance and continues to be a significant conventional foreign exchange earner [90]. Although it faces tough competition from synthetic fibres. Jute fibres are used in advanced fields such as decorative and furnishing items such as lamp shades, wall coverings, curtains, upholstery, etc. [91]. It is the least costly mass consumption fibre, at just a fraction of the cost of glass fibres; in terms of volume, next to cotton, jute is now the world's second most valuable fibre. Jute fibres have been partly replaced by synthetic fibres in conventional applications in carpets, cords, bags, etc., which have some benefits compared to jute. Non-traditional markets have to be pursued for the fibre in order to ensure a fair return to farmers [92]. The higher yield per hectare of Tossa jute commands a better price. Jute is grown at temperatures of 21–38 °C with a relative humidity of 65–95% in the rainy season. During the 4 months of the growing season, it needs a precipitation of at least 1000 mm uniformly spread [93]. Jute (*Corchorus capsularis*/*Corchorus olitorius*) is cultivated primarily for after cotton, its fibre is one of the most essential natural fibers. It belongs to bast fiber is one of the cheapest fibres cultivated in the tropics. The origin of jute dates back to the in Dunhuang, Gansu Province, China. Jute paper was found to be 206 BC–221 AD; during the reign of the Western Han Dynasty (Jute Paper), it was assumed that it was created Western Han Dynasty). Historical records suggest that the fibres of jute were during the period of the Mughal Emperor Akbar (1542–1605) were primarily used in India [94]. Jute from India was traded by the British East India Company. In Dundee, Scotland, the fibre industry grew big during the 1800s 108, 109. The worldwide production jute fibres are about 2300–103 tonnes and India contributes a large portion of them, Bangladesh, and China [95]. The height range of the jute plant is from 2 to 4 m [96]. The range of cellulose content between 61 and 71.5%. The availability of jute fibre in large amounts makes it famous for strengthening [97–99] (Table 6).

Table 6 Important physical properties of jute fibre [89]

Properties	
Jute cell ultimate width (range)	15–20 μm
Jute cell ultimate length (range)	1–6 mm
Jute cell ultimate width (average)	18 μm
Jute cell ultimate length (average)	2.5 mm
Tenacity	27–53 cN/tex
Specific gravity	1.48 g/cm^3
Moisture regain at 65% RH, 22 °C	13.80%
Fineness (g/1000 m) per single Fiber	0.26–0.46 tex
Breaking elongation	0.8–1.8%
Refractive index (parallel)	1.577
Refractive index (perpendicular)	1.536
Young's modulus	
White jute	8.6–17.4 GPa
Tossa jute	9.6–19.4 GPa
Modulus of rigidity	0.442 GPa
Heat of combustion	17.46 J/g

3.3 Flax

The use of flax fibres as reinforcement in composites has gained popularity in recent years as need for sustainable materials is growing each year. Flax fibres are cost-effective and have comparable mechanical properties to those of the fibres of glass [100]. It has been tested for reinforcement for various composites. The scientific name for flax is (*Linum usitatissimum* L.) is translated literally as 'most useful linen' [101]. The flax provides high-quality fibre for textiles. Flax is a crop for temperate weather. It is normally grown in areas where the daily temperature remains below 30 °C [102]. Typically, in Western Europe, flax is planted in March to April for harvest in high-quality fibre production regions, From mid-July to August. Flax is a winter crop in warm climates, with seeds sown in November, for the May harvest [103]. Flax production is environmentally friendly in that few chemicals are required for the production of crops. In one of the research about the research of life cycle study of these fibers shoed that the impacts of the flax scenario in Western Europe (dew retting) and central European the hemp scenario (warm water retting) was similar, except that the use of pesticides for flax and water was greater. For hemp, it was higher during processing [104]. The essential fibre/yarn element. However, along with the environmental impacts, consistency was not included in this report. Modern linen in Flax development is rotated between fields, often with a 7 year rotation, to decrease fungal pathogens [105]. The use of flax is in a grass or vegetable rotation method, which enables pathogen reduction or the use of different types of crops. Herbicide forms to monitor unwanted plants. Seeds from high-fiber varieties are densely used for fibre processing. Seeded to offer around 2000 plants per square metre of final plant density [106]. In this, planting in thin-stemmed, straight and tall plants are produced and harvested before full seed maturity, providing thin-stemmed, straight and tall plants Low yield fibre and outstanding properties. As well as quality, the yields of fibre vary with cultivar, climate, But total fibre yields of 25–30% of straw dry mass are possible [107] and agronomic practises. Linseed varieties are sown at low densities (about 750 plants per square) as opposed to the production of flax fibre. Meter) to optimise branching for higher development of seeds. Linseed when harvested at full seed maturity Plants also have thick stems that are poor in fibre output and efficiency [108]. Table 7 shows the chemical composition of flax fibres

Table 7 Chemical composition of flax fibres [4]

Fibre	Hemicellulose	Pectin	Lignin	Wax (%)	Moisture content (wt.%)
64.1	16.7	1.8	2.2	1.5	10
67	11	–	2.2	–	–
73.8	13.7	–	2.9	–	7.9
65	–	–	2.5	–	–
62–72	18.6–20.6	2.3	2–5	1.5–1.7	8–12
71–75	18.6–20.6	2.2	2.2	1.7	10

Table 8 Factors affecting the mechanical properties of flax fibres [4]

Plant growth	Specimens of plant, crop cultivation, crop geographical origin, fibre location in plant, local climate, e.g. rainfall and temperature during growth
Harvesting stage	Fibre ripeness, which effects: cell wall thickness, coarseness of fibres, adhesion between fibres and surrounding structure, size, and shape of lumen, porosity, microfibril angle
Fibre extraction stage	Decortication process, type of retting method, separating conditions
Supply stage	Transportation conditions, storage conditions, age of fibres
Measurement conditions	Tensile speed, initial gauge length, moisture, temperature, different cross-section of fibres at different points
Surface treatment	Chemical treatment, upgrading treatment, water treatment, drying treatment, etc.

[4] and Table 8 shows the factors affecting the mechanical properties of flax fibres [4].

3.4 Abaca

The output of abaca, at approximately 80,000 t per year, is marginal compared with other natural fiber [109]. It is only produced in two countries, mostly in the Philippines and to a limited extent in Ecuador. It's being cultivated in the mid-mountain regions up to approximately 500 m above sea level, primarily as an integrated community. In general, no additional inputs are needed in the form of mineral fertiliser [110]. The High tensile strength favours its present use for the processing of special papers such as bank papers. Notes, paper for cigarettes and bags for tea. In addition, a promising new area is a replacement for glass fibres in Materials in composites. Abac'a is considered one of the strongest natural fibres, and salt water is tolerant. Before BeyondWorld War II, it was the Philippines' monopoly. Today, pulp is the main product of abac'a, followed by Cordage, including cords and twines, yarns and fabrics [111]. Table 9 shows the physicomechanical properties of abaca fibers compared to other natural fibers [9].

Fibrecrafts, natural fibres. At present, approximately 85% of the abac'a is supplied worldwide by the Philippines, the rest by Ecuador [112]. A cultivation area of approximately 140,000 ha in 52 Philippine provinces was planted with abac'a in 2008. It Abac'a is one of the cash crops that can grow in steep areas with relatively little input compared to other crops. Abac'a is currently cultivated in almost all of the Philippines' provinces, except Ilocos, Cagayan, Cavite and Batangas. It was, however, implemented in several countries with a climate comparable to that of the US government's Philippines at a time when the US Navy depended solely on abac'a as the source of the marine Cordage. Abac'a was implemented in more than 20 Central and South American countries in 1923. Countries (Dempsey 1963), including several

Table 9 Physicomechanical properties of abaca fibers compared to other natural fibers [9]

Fiber	Density (g/cm^3)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation (%)	Fiber length (m)	Fiberdiameter (μm)	Moisture uptake (%)
Abaca	1.5	980	41	3–10	2–4	150–260	5.81
Hemp	1.48	550–900	30–60	2–4	1–2	16–50	12
Jute	1.46	400–800	20–25	1.8	3–3.5	60–110	13.75
Sisal	1.33–1.45	600–700	17–22	4.3	1	50–300	11
Cotton	1.54–1.6	287–597	6–10	3–10	0.001–0.065	11–22	8.5
Linen	1.4	800	50–70	2.7–3.5	0.9	12–60	10–12

Caribbean Islands. It was founded in Sumatra in 1925, and West and East Malaysia, and Australia's New Caledonia and Queensland [113]. There have also been attempts at incorporating the plant has operations in India, East Africa, Florida and Vietnam. Today, however, only the Philippines and Ecuador supply the global business with abac'a. The development of abac'a fibres has presently been reduced due to virus infections such as bunchy top, which leads to rising prices. Any attempt to prevent the further spread of viral diseases is therefore crucial [114]. The development of Abac'a has a high potential for extension if incorporated, for example, into established coconut development. Plantations, making it ecologically sound and more effective. The virus-free suckers and corms are not, however, Available in appropriate amounts [115]. Therefore, for tissue-based seedling development, great efforts must be made. Farmers include the production and marketing of a compact and easy-to-handle stripping unit, A necessity, even in remote mountainous regions with the ability to manufacture high-quality fibre bundles, For the use of fibres of abac'a, for example, in composites. Joint Research and Technological Efforts [115]. The Philippines is the largest producer of 72,000 t of abaca fibre, comprising 85% of the world's total. Production, and Ecuador is supplying 13,000 t. In the Philippines, about 106,000 ha of abac'a are developed on With an average of 1–2 ha on small farms [117]. Depending on the variety, fertility of the soil and density of the planting, the Yields range from 600 to 1200 kg per hectare of dry fibre. The amount of fibre bundles is 24,000 t of Processed into pulp, cordage, textiles and crafts by the local industry. The fibres of high quality are used for the manufacturing of tea bags, wrappers for cigarettes and bank notes. The quantity of 48,000 t is primarily exported to as a raw material for the pulp and paper industry, the US, the EU and Japan [117]. Abaca fibres have excellent mechanical qualities that are equivalent to synthetic materials. The strong intrinsic mechanical properties of Abaca fibres may explain this. Studies indicate that the interaction of fibre and matrix is unavoidable in order to manufacture composite materials and strong mechanical characteristics. Chemical or physical fibres can do this by Treatment to make the surface of the polymer matrix wettable with Abaca fibres. The composite of Abaca-Glass was found to have greater tensile strength and ductility than single tensile strength. Composites of Abaca material. One of the issues with synthetic materials is biodegradability.

The addition of natural fibres to the synthetic composite mixtures might enhance the resultant material's biodegradability. Abaca fibre strengthened the big challenge. The hydrophilic existence of the fibres of Abaca is a composite [118]. Fibers' incompatibility with fibres the material is fragile and vulnerable to deterioration due to the normal hydrophobic matrix. Treatments of fibre Problems of Abaca fibres in water absorption were found to be resolved. If water issues exist, It is possible to fix absorption in Abaca fibres, it could be tapped as possible reinforcement for products used in wind turbines and in the transport sector [119].

3.5 Sisal

Sisal plays a dominant role in the manufacturing of natural fiber materials in the region of leaf Fibers. Due to some interesting properties of the fibers, Sisal is well suited for scientific applications [120]. It is a leaf fiber derived from a plant that is generally considered indigenous to Central and South America, where it has been grown, harvested, and used for several centuries in the spinning of coarse yarns, twine, and cords. During the late eighteenth to early nineteenth centuries, sisal was also cultivated on the continents of Africa and Asia due to its potential to grow under different ecological and climatic conditions, ranging from hot and humid conditions through Kenya and Tanzania to the tropical climates of Mexico, the United States and the Caribbean coasts of Florida and Hawaii. China has become a sisal-producing country with an annual production of about 20,000 metric tonnes in 2006.

A single sisal plant can produce 200–250 leaves in which you can harvest 150 kg of fibers in a year [121]. The sisal plant is normally extracted first after 2–3 years and then at intervals of 6–12 months during its lifetime of 7–10 years. Figure 1 shows the pictorial view of sisal plant.

And each leaf comprises about 1000 bundles of fibers on average. Sisal is the world's top grown leaf fiber, accounting for about 70% of all commercial production of these fibers. As per Food and Agriculture Organization Statistics published in 2006, the worldwide production of sisal is estimated at around 427,000 tonnes. Brazil is one of the largest producer with highest production of 247,000 t, therefore produces almost 75% of world's sisal production [122]. The other countries like Mexico, Columbia, Cuba, Haiti and Nicaragua, Tanzania and Kenya contribute about 10% to the continent of Africa and about 5% to China. It is estimated that more than 80% of the production of sisal in Brazil is exported to over 50 countries, the United States, China, Mexico, and Portugal being the main importers. They are nursed up to a height of 15 cm and then transferred by hand to the field in marked-out rows [123]. For the growth of the sisal plant the land must be free of weeds to planting the seedlings. The first harvesting normally takes place 3–5 years after the establishment of the crop. Approximately 120–125 leaves are available for harvesting at about 1.5 m of height. Sisal harvesting is a field operation in which the outer leaves are cut so that approximately 30 leaves are left on the plant so that the plant can grow up to the next harvest cycle after 15–18 months. This process of harvesting is continued until

Fig. 1 Photograph of sisal plant (http://www.flickriver.com/photos/40295335@N00/5219408347)

the end of the life of the plant [124]. After this, cutting of the leaf is carried, and leaves are packed together to load them into a truck and to carry them to the factory. A large-scale automatic decoration machine that can treat nearly 25,000 leaves or 10–20 tons of leaves per hour is ideal for large plantations, but hand-decorticators are suitable for small-scale or pilot testing. Produce approximately 150–200 kg dry fiber bundles in a 10-h change (Snyder et al. 2006). Different fibers are divided into different categories based on the size, colour, and presence of impurities in the grading process [125].

Most plant fibers, like sisal, are primarily composed of cellulose and lignin, but they also contain a variety of other minor constituents, such as pectin, wax, inorganic salts, nitrogen and pigments. The total sisal fiber content of cellulose and lignin is about 67% and 12% respectively and the sisal leaf comprises nearly 4% fiber, 0.75% cuticule, 8% dry matter and 87.25% water[126]. Moreover the fibers being multicellular, with small single cells connected together. On average, the single fiber is around 20 μm thick and 3 mm long and the fiber bundle can achieve a thickness of over 400 μm and a length of over 1000 mm. Such cells serve as reinforcement to matrices of hemicellulose and lignin. The cell wall is therefore a composite structure of lignocellulosic material, supported by helical microfibrillary cellulose band [127]. Fibers of various ages, from different origins and from different parts of the sisal plant exhibit different structures, and hence often vary in their properties. The sisal leaf comprises three fiber types: mechanical, rope, and xylem. The mechanical fibers, also classified as structural Fibers, are mostly situated along the periphery of the leaf, while the ribbon fibers are aligned with the conductive tissues in the median line of the leaf, and the xylem fibers are aligned towards the ribbon Fibers [128]. These Fibers are rarely circular but mainly thick and horseshoe-shaped in cross-section therefore

Table 10 Chemical composition and moisture content of sisal fiber

Cellulose (%)	Hemicellulose (%)	Lignin (%)	Moisture content (%)
65–68	10–22	9.9–14	10–22

it is very difficult to separate in the extraction process. Moreover these fibers are finer therefore grading of these fibers is very important [129]. Ribbon fiber bundles, also known as arch fiber bundles, extend from the foundation to the plant's tip and expand along the median line of the leaf with the conductive tissues as shown in the cross-section. The arrangement of the ribbon fibers gives them strong mechanical strength and they are also the longest bundles of Fibers, which can be easily separated longitudinally during the extraction [123]. Table 10 shows the Chemical composition and moisture content of sisal fiber.

Xylem fibers form a composite bundle around the median line opposite the ribbon Fibers, and when isolated from the vascular bundles they have an irregular shape. Xylem fibers have thin cell walls, which makes the extraction process easy to crack. The mechanical properties of sisal fibers and fiber bundles vary from plant to plant and from cultivar to cultivar, as well as depending on the climatic conditions and soil quality of the region where sisal is made.

The length of the sisal fiber bundles collected varies from 1.0 to 1.5 m, with a diameter of 100–300 μm, with an average fiber density of 1.26} 0.03 g/cm^3 [129]. Lot of research is going on these days on these Fibers to efficiently use them in vehicles, such as internal engine coverings, door panels, hat racks, bottle trays and seat backs.

3.6 Coir

Coir is a natural fibre derived from the husk covering the seed of a coconut as fibre wraps. The Seed, the Seed for the extraction of the oil-rich kernel for various food products such as fresh products, it is removed from the husk for Coconut kernel, copra, and desiccated. The husk is thus the by-product of the processing of copra or desiccated coconut [131]. Originally, coir mining was a domestic industry that may have developed along the East Coast centuries ago. South India and along Sri Lanka's southern and north-western coastal line [132]. Traditionally, coir used to be extracted from husks which have been immersed (retted) in sea water or lagoon water for 6–9 months, and then Beaten with a wooden mallet. Over time, the methods of coir extraction have greatly enhanced the consistency either wet processing (retting procedures) or mechanical decortication extracts coir fibre (bundles) Without being saturated [133]. The quality and quantity of fibre/fibre bundles are dependent on the extraction process. The sum obtained from a given number of husks will vary. In the past, coir has been viewed as a low-quality, low-value commodity with coir being its key uses. Yarn, coir nets, white coir for doormat and floor covering yarn, brown coir for rubberized coir, Coir pads and mattresses and bristles for brooms and brushes. Coconut coir is highly immune to the sea, Therefore, for marine uses (shipping and fisheries), water and corage have great value [134]. Gradually, the launch of synthetic polymer products took over the market for natural hard fibres in Application of cordage and twine. The application of coir has increased tremendously in the last three decades [135]. For the manufacture of automotive and upholstery rubberized coir goods and subsequently as woven Geotextiles and knitted geotextiles to manage erosion and as a foundation for binding earth on sloping lands. In recent decades, developments in coir studies have led to a better understanding of the systemic, Coir's chemical and mechanical properties. A single fibre of coir has a mean width of 0.02 mm and a mean width of 0.02 mm. 2.5 mm in length, and as aggregated fibre bundles, these small fibres exist. Such a kit would be popular in terms of the use of a 'strand' is alluded to. Compared to coir fibre, coir fibre has the largest content of lignin. Other agro-based fibres which are widely used. Any of the benefits of coir are that coir is non-abrasive, rigid, durable, hydroscopic, biodegradable, compostable and combustible, viscoelastic, And a natural product which is resistant to chemical modifications. Coir, as a fibre, has a high aspect ratio and a high aspect ratio High strength-to-mass ratio, low conversion of energy and strong insulation properties [136–139]. A big drawback of coir, however, is the great thickness of fibre bundles when compared to other fabrics, such as wool, hemp and flax. Therefore, large volumes of insulation are needed. Applications. Some benefits of coir are high rigidity, strength, flexibility and elasticity of twisted coir. Rope. Cordage. Recent advances in material sciences have been made in European countries and in the Philippines through research Highly technological and advanced coir applications have been made possible, such as coir composites, fibreboards, coir-based applications Materials for housing, insulation materials, etc. With the importance of eco-friendly natural products being realised, The planet is increasingly moving towards the growing use of natural resources/materials that are renewable. Coir is a year-round commodity available, and cheaper in cost than other agro-based fibres [139–141]. Just Simple Methods of extraction, advanced machinery introduced in recent decades and fresh and flexible applications As a result of technological advances, coir has been the primary milestones that allow this industry to achieve From its humble beginnings, to growth. The coconut palm (*Cocos nucifera* L.) is proud of its place among the palms that grow in the tropical region. Because of the world's versatility and myriad uses. It is the most economically important palm grown, The tropical coastal ecosystem of the world provides more than 200 products in over 93 countries. It occupies an area of approximately 12.17 million hectares worldwide, with an area of about 12.17 million hectares. Approximately 57 billion nuts in annual production. The Philippines is the world's biggest coconut maker, Indonesia, India and Sri Lanka were ranked second, third and fourth, respectively. Total of exports there were 172,928 million t and 172,928 million t of unfinished coir and coir products from developing countries in 2003 and 2004. 194,926 million tonnes (APCC 2006), respectively. World exports of coir and coir products were recorded in 2005 and 2006 [142]. India is the world's major producer of coir, while Sri Lanka and Thailand are the second and third producers of coir. Indonesia, China, the Philippines, Vietnam, Mexico, Venezuela and Tanzania are the other world's coir-producing nations. Coir is imported by around 67 countries around the world Coir-based materials. The United States, the European Union, the main importing countries. The Netherlands and Germany are leading countries in the manufacture of coir products in Europe [143, 144]. Asia and the Pacific account for 90% of the world's total coconut production and production. However, the use of coconut husk for the extraction of coir is restricted to a few nations, While coconut is used primarily by others for its kernel products, such as copra, oil, or coconut desiccated. Major–Major Countries producing coconuts, such as the Philippines, Indonesia and the Pacific, such as Papua New Guinea and to produce copra, Fiji uses coconut husks and shells as an energy source [145]. Because of the economic situation, The significance and versatility of coconut and its many uses as a crop of food, oil, fibre and timber, and one with. It is commonly referred to as the 'tree of life' or 'tree of heaven' because of its aesthetic value. One of the oldest traditional, export-oriented and agro-based industries focused alongside the coir industry is the coir industry South and East Asian countries' coastal belt [143]. This sector offers opportunities for poor people to live Without gender bias, rural individuals. Coir was exported as raw from producing countries several decades ago, Material in the form of mattress ballots and bales, fibre bundles of bristle or omat or as yarn, and the value in the countries of coir-utilising, addition took place [144]. Table 11 shows chemical composition of plant fibres in (% of dry mass) [145].

Consequently, the coir industry has grown significantly in the past two decades, earning more Foreign exchange and creating more opportunities for employment with the least environmental damage. Coir is a product that is eco-friendly, natural, biodegradable, durable, renewable, inexpensive and sustainable.

Table 11 Chemical composition of plant fibres in (% of dry mass) [145]

Fibre	Cellulose	Hemicellulose	Pectin	Lignin	Extractives	Fat and waxes
Cotton	91.8	6.3	–	–	1.1	0.7
Flax	71.2	18.5	2	2.2	4.3	1.6
Hemp	78.3	5.4	2.5	2.9	–	–
Jute	71.5	13.3	0.2	13.1	1.2	0.6
Coir	35.6	15.4	5.1	32.7	3	–
Coir	36.7	15.2	4.7	32.5	3.1	–
Coir	19.9	11.9	7	53.3	0.3	–
Sisal	73.1	13.3	0.9	11	1.3	0.3
Abaca	70.2	21.7	0.6	5.6	1.6	0.2

3.7 Cotton

Among all natural fibre crops, cotton is the most important. In 1960, 68% of all the fibre consumed was cotton. And, though non-cotton fibres have benefited from recent technological advances and developments in the world, Cotton has continued to erode its market share, with cotton remaining to account for no less than 38% as of 2009. Of all the fibre consumed at the stage of end-use [146]. Man-made industrial fibres can now be produced and sold at rates well below the price of man-made fibres. There are, however, a range of characteristics that are highly valued by consumers and it is exclusively found in cotton. Cotton is exceptional in characteristics such as its biodegradability, absorption of water, Convenience and thermostatic capability [147]. New quality features are emerging in the man-made fibre industry. Renewable resource polyesters such as PLA can be produced and produced, but man-made fibres have so far not been able to compare cotton characteristics and, in all likelihood, would hardly be able to exceed cotton in those fields. Each year, over 50 countries plant cotton on at least 10,000 ha. Just about thirteen per cent of cotton the region is located in developed countries, so cotton is really a crop for developing countries. The Cotton International an intergovernmental organisation founded in 1939, the Advisory Committee (ICAC) maintains world cotton. Accessible data on the region planted with cotton, It indicates that cotton has never been cultivated on more than 37 million hectares since 1920/21. Since the ICAC began harvesting cotton, the cotton region has exceeded 36 million hectares on just two occasions [148]. About statistics. On the other hand, less than 30 million hectares of cotton were planted after the 1950/51 season [148]. In 1986/87, just once. So, between the 1950/51 season and the present, the world in the years that followed, Between 30 and 36 million hectares of cotton area remain (ICAC 2008a). The world's cotton industry is aware of the need for the industry to continue developing the Sustainability of processing cotton. The production practises not only have to be sustainable, but the production practises have to be sustainable. Cotton manufacturing, beginning from ginning to finished goods, should also be environmentally friendly. Efforts to enhance the economic, environmental and social sustainability of cotton production and cotton production are under way. Obtaining intake. Organic cotton production and no-tillage production are seen as one way of enhancing sustainability. Techniques of minimum-tillage and. At the same rate as production, cotton consumption has increased. Just about 3 million back in the 1950s T of the overall output of cotton was sold on the foreign markets. Increased foreign trade in raw cotton. In 2005/06, up to 9.8 million t. The combined use of declining mills in the European Community and the United States. The amount of cotton traded on the international market has risen with the risen use of mills in others [149, 150]. The roots of the word cotton are still a mystery in v. In specialist literature, however, there is a consensus that the Arabic word al qatan is derived from cotton. The oldest documented record of cotton use has been discovered. In a Hindu holy text known as the Rig-Veda. Excavations in Mohenjo-daro, Pakistan, have shown that human beings As far back as 3000 BC (Gulati and Turner 1928), human beings used cotton cloth [151]. In Peru, other findings show that people over

4500 years ago were using cotton there. The push to embrace cotton seems apparent. As a fibre seed, the quest for a fibre from which to produce clothing stems from people. It is fair to assume that diploid cottons were used in the Indian subcontinent while tetraploid cottons were used in the Indian subcontinent. Before spreading to other parts of the world, cotton prevailed in South America (in Peru and Mexico). Flax, Flax Long before cotton, silk and wool were used, and literature shows that the term was used in the earliest days. For several different kinds of fibre, cotton was used. No one has a unanimous opinion as to how cotton was Domesticated by humans and placed into widespread use, but much of the study on cotton origin is in Agreement that man has altered cultivated species of cotton [161]. So far 50 species have been found, 19 of which have not been found. It is very difficult to propagate some of them, and many species do not even have the Outgrowth (fibre) on each of the seed coats. There are only four, in spite of the many recognised organisms, Recognized cultivated cotton varieties: Gossypium arboreum and Gossypium herbaceum, two diploid varieties, and Gossypium herbaceum Gossypium hirsutum and Gossypium barbadense are two tetraploids. Often referred to as the $2n = 26$ diploid cottons are Short cotton staples. G. Upland cotton and all extra-long staple/extra-fine cotton are commonly referred to as hirsutum. Cottons (also referred to in Egypt as pima or giza types) belong to G. Barbadense, Barbad. (The organisms referred to as the Sea G. barbadense also belongs to Island cotton) [153–156]. Upland cotton accounts for almost 97% of all cotton produced around the globe, with the remainder Just 3% of world production is composed of all other animals. Usage of inter-specific and intraspecific industrial composites. The most significant natural fibre is cotton. Many cotton species are recognised, but only four of them are cultivated. On a trade scale. Around 97% of all the cotton produced belongs to the G genus. Hirsutum, with 3% to G. Barbadense, and less than 1% is G. G. and Arboreum. Uh, herbaceum. Naturally, the cotton plant is susceptible to a range of pests, particularly insects. After the widespread use of insecticides in cotton for over two decades. The number of insecticide applications for cotton is being reduced by integrated pest control. Immune to Insects As a promising option for handling lepidopteran insects, biotech cotton has arisen. Consciousness [157–161].

The production and processing of cotton using sustainable techniques is rising. Nearly half of the cotton that is produced in the planet, irrigation is guaranteed, while the other half comes from conditions that are rain-fed. Cotton is mainly Computer picking, always selected by hand, is only adopted if labour is not available or costly [160, 162–164]. Table 12 shows the chemical composition of the cotton plant parts [165].

4 Conclusions

The material revolution of this century with an emphasis on ecological balance could be bio composites made from 100% renewable and low-cost resources compared to traditional materials. To improve performance for long-term durability, the success

Table 12 Chemical composition of the cotton plant parts [165]

Plant part	Nitrogen in %	Phosphorus in %	Potassium in %	Calcium in %	Magnesium in %	Sulphur in %
Root	0.82	0.12	1.06	0.45	0.25	0.06
Stem and branches	1.06	0.08	1.6	0.69	0.25	0.05
Leaves	2.3	0.15	2.49	3.15	0.52	0.42
burr	1.08	0.18	3.5	1.28	0.26	0.17
Seed	3.13	0.43	2.1	0.18	0.33	0.33
Fiber	0.18	0.28	2.28	0.08	0.05	0.05

of these materials will depend on the proper manufacturing techniques and different treatments as these materials provide realistic answers to increasing environmental and economic apprehensions for the expansion of novel products.

However, the manufacture of green materials by compression moulding and thermoforming varies mainly from traditional polymer composites due to improvements in rheological behaviour, thermal instability, and chemical and morphological alterations in natural fibres and biopolymers. For the manufacture of these materials, precise manufacturing guidance principles must also be followed. These materials are processed based on their selection, the pre-processing of the fibre to be used, the manufacture of semi-finished goods and the manufacturing of components. Raw materials must be carefully chosen in the selection of materials on the basis of useful properties and material processability. Characteristics such as melt viscosity, specific heat power, thermal conductivity and crystallinity of materials are considered for processability. Fiber and polymers are pre-processed until the materials are picked. Pre-processing includes pre-treatment of fabrics, biopolymer modifications and drying. The next step is to manufacture semi-manufactured products through compounding or fibre mat technology, such as granules, prepregs, sheets, or laminates. Detailed consideration is taken in the final step with respect to the moisture and thermal degradation of the green composite.

Acknowledgements No conflicts exist for the present work.

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Hierarchical Vegetal Fiber Reinforced Composites

Usha Kiran Sanivada, Gonzalo Mármol, and Raul Fangueiro

1 Introduction

Composite materials can be produced from different sources such as ceramics, metals, and polymers. PMC's played a crucial role in several applications in both household and manufacturing sectors [1]. Composites are a combination of two or more elements with discrete properties and are produced with reinforcements of a matrix structure [2]. The composite has superior properties when compared to the base material as a consequence of the addition of reinforcing material and properties of the composite can be modified by changing the amount of reinforcing material [3]. The matrix is a continuous phase while the reinforcement may be in the dispersed phase [1]. Composite materials may sometimes incorporate fillers, additives that have different properties from the base materials that are used for the manufacture of the composites themselves [2]. Composite materials are classified as having a metal matrix, ceramics matrix, and polymer matrix [4]. Epoxy, polyester, and vinyl ester are popular thermoset resins whereas carbon, aramid, and glass fibers are the most common reinforcements [2].

U. K. Sanivada (✉) · R. Fangueiro
Department of Mechanical Engineering, University of Minho, Azurém Campus, Guimarães 4800-058, Portugal

R. Fangueiro
e-mail: rfangueiro@dem.uminho.pt

U. K. Sanivada
Mechanical Engineering and Resource Sustainability Centre (MEtRICS), University of Minho, Azurém Campus, Guimarães 4800-058, Portugal

G. Mármol · R. Fangueiro
Centre for Textile Science and Technology (2C2T), University of Minho, Azurém Campus, Guimarães 4800-058, Portugal

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_17

Although PMCs present a lot of advantages, the lack of degradation is a limitation regarding sustainability. Usage of synthetic polymers and conventional fibers has raised a lot of concerns. Air and water pollution has increased with the usage of non-biodegradable polymers in PMCs [5]. Manufacturing of polymers such as polypropylene, polyethylene needs oil-based resources that are non-renewable. Declining of oil reserves due to consumption for producing polymers, increased pollution, need for reduction of carbon dioxide, new laws and regulations have made scientists exploring alternatives that are renewable and eco-friendly in nature [1, 6]. Considering these facts, green composites have evolved as a new eco-friendly material having its applications in various engineering applications [1]. The constituents of green composites, both the reinforcement and matrix are derived from renewable resources. These composites are biologically degradable and hence do not have any significant adverse effect on the atmosphere, from their inception until the end of their life.

2 Natural Fibers

Natural fibers are considered as renewable and sustainable as they are obtained from renewable resources. Properties such as less density (1.25–1.50 g/cm^3) and high specific properties, biodegradable in nature, availability at large scale, and low cost have gathered a lot of attention for utilizing them and replacing synthetic fibers when producing the composites [7]. Cellulosic fibers such as jute, sisal, jute, kenaf, ramie, bamboo fiber, coconut coir, and pineapple leaf fibers, etc. are some of the noted fibers that are used in producing biocomposites [8]. Figure 1 presents the classification and sub-classification of natural fibers.

Natural fibers are mainly composed of cellulose, hemicellulose in large proportions and lignin, waxes in smaller proportions. Their chemical compositions are enlisted in Table 1. The presence of cellulose is responsible for the strength and stiffness of plant-based fibers [10]. Microfibrillar angle, amount of cellulose, the process of fiber extraction, age of the plant, location of the plant from where fibers are obtained and environmental conditions where plants are grown are some of the factors that influence the mechanical properties of the natural fibers [9, 11]. Strength requirements are the main criteria for the selection of fibers and their usage in numerous applications. Table 2 lists out properties of natural fibers such as density, tensile strength, tensile modulus, elongation at break, and moisture absorption [12].

It is evident from Table 2 that the mechanical properties of the cellulosic fibers are inferior in comparison with man-made fibers. Moreover, significant research is taking place in the direction of enhancing the properties of plant-based fibers and obtain comparable values with those of man-made fibers by suitable surface modification treatments. Some of the natural fibers such as flax, hemp, ramie have comparable Young´s modulus value when compared with glass fibers. The lesser density of natural fibers has led to the higher specific properties and this tendency has attracted much of the industries to use them as reinforcements in green composites [13]. Besides natural fibers also have few limitations like poor wettability, high moisture

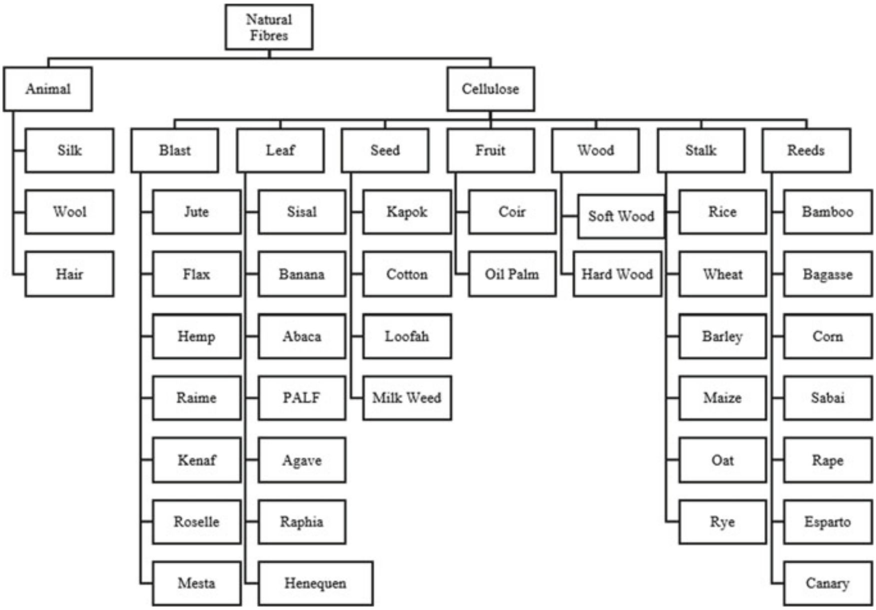


Fig. 1 Classification and subclassification of natural fibers source. Adopted From [9]

absorption, and incompatibility with hydrophobic polymers, which obstruct their usage in PMC's. Table 3 reports the pros and cons of natural fibers.

Absorption of moisture was considered as one of the major drawbacks in the usage of these fibers as reinforcements in composites [14]. Altogether bast fibers have almost similar structures that consist of cellulose and hemicellulose. A large hydroxyl (OH)-to-Carbon (C) ratio is present in cellulose and hemicellulose. The water molecules that diffuse into the amorphous region of the cellulose and hemicellulose break the inter-molecular hydrogen bonding. Hence there is an increase in the inter-molecular distance of the cellulose chains and causes swelling [15]. The stiffness of the natural fiber is highly influenced by the presence of moisture content [16]. Frequent moisture absorption/desorption cycles tend to lower the strength of fiber [17]. The structure of the fiber changes when it is exposed to high humidity levels [18].

When using natural fibers as reinforcements in Natural Fiber Reinforced Composites (NFRC), lack of proper fiber-matrix adhesion emerges as one of the major limitations and results in obtaining lower mechanical properties. High-performance fiber-reinforced composites cannot be produced without achieving proper adhesion between fiber and matrix. Certain methods (physical and chemical) are utilized by the researchers to improve the properties of NFRC [19]. Likewise, hydrophilicity is also one of the major drawbacks of natural fibers [9]. To minimize the hydrophilic nature of the natural fibers, improve the properties of the composites, treatments such as silane, acetone, and alkaline, etc. have been successfully used [20].

Table 1 Chemical composition of several natural fibers

Fibers	Cellulose (wt%)	HC (wt%)	Lignin (wt%)	Pectin (wt%)	Ash (wt%)	Waxes (wt%)	MC (%)	MFA (deg)	References
Abaca	56–63	20–25	7–9	–	3	3	5–10	–	[21]
Bagasse	55.2	16.8	25.3	–	1.5–5	–	8.8	–	[9]
Bamboo	73.83	12.49	10.15	0.37	9.6	–	3.16	–	[9]
Banana	60–65	6–8	5–10	–	2.7–10.2	–	10–15	11	[9]
Coir	32–43	0.15–0.25	40–45	–	–	–	10–12	30–39	[9]
Cotton	82.7	5.7	–	–	–	–	1	20–30	[9]
Curaua	73.6	9.9	7.5	–	3.9–9.6	–	–	–	[22]
DP	30.3–33.5	59.5	27–31.2	–	5	–	–	–	[23]
EG	45.6	–	17.7	–	4.23	–	–	–	[24]
Flax	71	18.6–20.6	2.2	2.3	–	1.7	8–12	5–10	[21]
Hemp	68	15	10	1	0.8	0.8	6.2–12	2–6.2	[9]
Henequen	77.6	4–8	13.1	–	–	–	–	–	[21]
Jute	61–71	14–20	12–13	–	0.8	0.5	13.7	8	[9]
Kenaf	45–57	21.5	8–13	3–5	2–5	–	–	–	[9]
Oil-palm	65	–	29	–	2.4	–	–	46	[9]
Pineapple	70–80	18.8	12.7	1.1–1.2	0.9–1.2	3.2–4.2	11.8	8–15	[9]
Ramie	68.6–76.2	13–16	0.6–0.7	1.9	–	0.3	7.5–1.7	7.5	[21]
RH	35–45	19–25	20	–	–	14–17	–	–	[22]
RS	41–57	33	8–19	–	–	8–38	–	–	[22]
Sisal	65	12	9.9	10	0.6–1	2	10–12	10–22	[9]
SP	53.41	7.45	24.92	–	4.27	–	8.7	–	[25]

(continued)

Table 1 (continued)

Fibers	Cellulose (wt%)	HC (wt%)	Lignin (wt%)	Pectin (wt%)	Ash (wt%)	Waxes (wt%)	MC (%)	MFA (deg)	References
WS	38–45	15–31	12–20	–	6.8	–	10	–	[9]

DP Date Palm; *EG* Elephant Grass; *HC* Hemicellulose; *MFA* Micro-fibrillar Angle; *MC* Moisture Content; *RH* Rice Husk; *RS* Rice Straw; *SP* Sugar Palm; *WS* Wheat Straw

Table 2 Physical and mechanical properties of natural and synthetic fibers

Fibers	Density (g/cm^3)	Tensile strength (MPa)	Youngs modulus (GPa)	Elongation (%)	Moisture absorption	References
Abaca	1.5	400	12	3–10	–	[22]
Banana	1.35	721.5–910	29	2	–	[26]
Chicken Feathers	0.89	100–200	3–10	–	–	[27]
Coconut	1.15	131–175	4–6	15	–	[28]
Coir	1.2	175–220	4–6	15–30	10	[9]
Cotton	1.5–1.6	287–597	5.5–12.6	3–10	8–25	[21]
Curaua	1.4	500–1150	11.8	3.7–4.3	–	[22]
Flax	1.4–1.5	345–1500	27.6–80	1.2–3.2	7	[9]
Harakeke	–	440–990	14–33	–	–	[29]
Hemp	1.48	550–900	70	1.6	8	[9]
Henequen	1.4	500	13.2	4.8	–	[26]
Jute	1.3–1.46	393–800	10–30	1.5–1.8	12	[21]
Nettle	1.51	650	38	1.7	–	[26]
Pineapple Leaf	1.07–1.50	413–1627	34.5–82.5		11.8	[30]
Ramie	1.5	220–938	44–128	2.0–3.8	12–17	[21]
Sisal	1.33–1.5	400–700	9–38	2–14	11	[9]
Spartium Juncem L	1.55	986.46	17.86	–	–	[31]
Softwood	1.5	1000	40.0	–	–	[9]
E-Glass	2.5	2000–3500	70.0	2.5–3	–	[21]
S-Glass	2.5	4570	86.0	2.8	–	[21]
Aramide (normal)	1.4	3000–3150	63–67	3.3–3.7	–	[9]
Carbon (standard)	1.4	4000	230–400	1.4–1.8	–	[9]

Table 3 Pros and cons of natural fibers

Pros	Cons
Lower density results in higher specific properties	Inferior mechanical properties specifically impact resistance
Produced from renewable sources	High moisture absorption
Biodegradable	Poor fiber-matrix adhesion

Adopted from [32]

2.1 Flax

The flax plant (Linum Usitatissimum) is the source for producing flax fibers. It is grown in a moderate climate region and extensively in western parts of Europe where the temperature is under 30 °C. It is also cultivated in southern Europe, Argentina, India, China, and Canada [33]. The life cycle of the flax plant is 90–125 days and consists of vegetative, flowering, and maturation periods. The extraction of fibers is done by retting and scorching [26]. It was reported from the previous studies that the enzyme treatment for the extraction of fibers causes less damage when compared to a mechanical process [34]. The diameter and height of the flax stem are 1–2 mm and 80 cm respectively [6, 33]. The length and diameter of elementary fibers of flax vary between 2 and 5 cm and 19–25 μm respectively [6]. The classification of flax stem and the diameters of different fibers are shown in Fig. 2.

2.1.1 Structure of Flax Fiber

Figure 3 displays the three layers of the flax stem. i.e., bark, bundle, and xylem. The external layer bark acts as a shield from exterior attacks however, necessary elements like water and nutrients are allowed through the layer [33]. The inner bark of the plant stem consists of fibrous bundles from which bast fibers are collected [14]. Figure 4 depicts the different layers present in a flax fiber structure [36]. The first layer is of 0.2 μm thickness, a thin primary wall that contains cellulose and hemicellulose [37]. The second layer is known as the secondary wall and it is made up of three layers which consist of helically wound highly crystalline cellulose chains called microfibrils. The middle layer is wider than the other two layers and significantly contributed to fiber strength. Microfibrils include 30–100 cellulose molecule chains

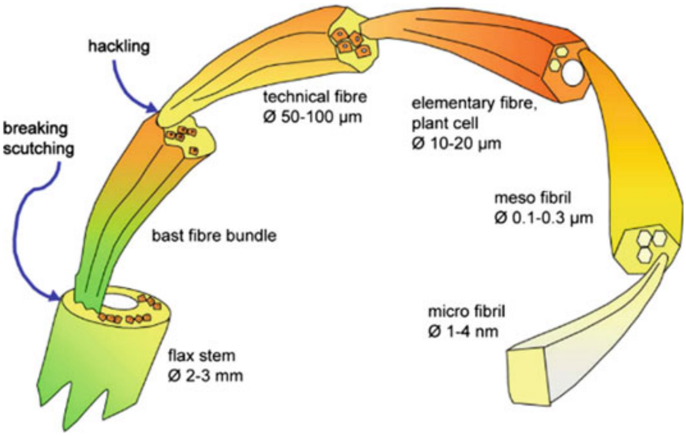


Fig. 2 Fiber classification in flax stem. Reproduced from [35]

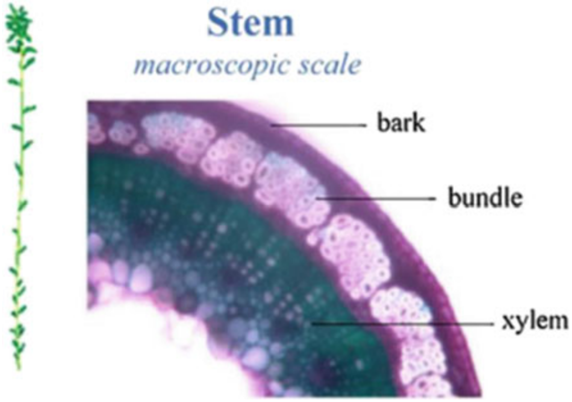


Fig. 3 Composition of flax stem. Reproduced from [33]

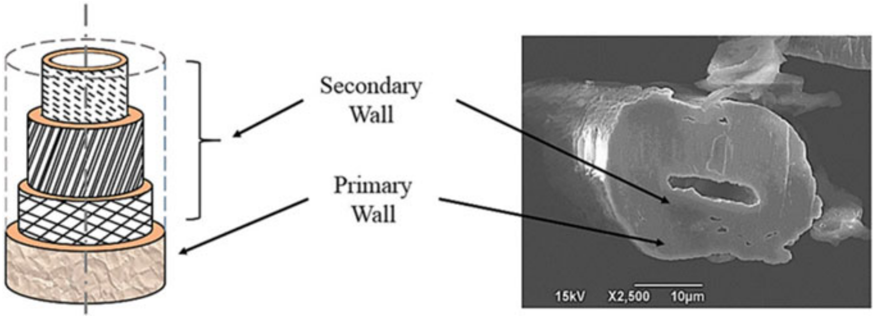


Fig. 4 Structure of flax fiber. Reproduced from [38]

and are aligned approximately at an angle of 10 °C with the fiber axis. A smaller microfibrillar angle results in a stiffer fiber [37, 38]. 70% of the fiber Young´s modulus is due to the secondary wall. The tensile modulus of the fiber is affected by the amount of cellulose content [3]. The chemical composition, physical and mechanical properties of the flax fiber are shown in Tables 1 and 2 respectively.

2.1.2 Factors Influencing the Properties of Flax

The mechanical properties of flax fibers are dependent on the position in the flax stem from where they are extracted and their extraction methods. Fibers extracted from the bottom exhibit inferior mechanical properties, while flax fibers situated in the middle exhibit better mechanical performance [14]. It was revealed that manually isolated fibers are stronger when compared to mechanically isolated fibers. Kink bands are induced in the fibers as a result of the mechanical process of fiber extraction, thus reducing their tensile strength [39]. The strength of the fiber is significantly reduced due to the presence of kink bands and micro-compression defects [40].

2.1.3 Flax Fiber as Reinforcements

Because of its unique properties, flax is recognized as the most significant member of the bast family to be utilized as reinforcements in NFRCs [41]. The vital characteristics of flax fiber that attract researchers in composite research are its high strength, stiffness, and low elongation to failure [14]. Elementary flax fibers in the form of yarns, fabric mats, and roving's, are used in the fabrication of composites. They are combined with the matrix material and by using a suitable technique, composites are manufactured [14].

2.2 Jute

Jute belongs to the genus *Corchorus* and *Tiliaceae* family. There are more than forty Corchorus species out of which white jute (*Corchorus Capsularis*) and Tossa jute (*Corchorus Olitorius*) are extensively known [42, 43]. It is also known as gold fiber [42]. The leading producers of jute are India, Bangladesh, Nepal, China, and Thailand [42]. Other countries include Myanmar [26] and Brazil [44]. Among these two varieties, the chemical compositions are very much similar and grow to a height of 2.5–3.5 m [45]. The fibers are situated between the outer bark and central pith or stick [46]. The jute plant has fewer branches and the stems measure about 1–2 cm in diameter [47]. Jute is cultivated in a warm and wet environment where the temperature is between 20 and 40 °C and relative humidity of 70–80% [42, 48]. A few of the methods to extract jute fibers include steeping in water (retting) [46], biological retting [25, 26]. The cementing materials suffer bacterial decomposition and result in the loosening of the fiber from the neighboring cortical tissue thus helping the fiber to get detached from the plant [46]. The thickness of jute fiber varies between 40 and 30 μm and can withstand up to 100 °C without any decomposition [48]. The general structure of plant fiber is shown in Fig. 5 [49].

2.2.1 Structure of Jute Fiber

As shown in Fig. 6, jute fiber is multicellular and comprises a bundle of ultimate cells that are spindle-shaped. The layer of natural gum existing between the ultimate cells is known as middle lamella. Each ultimate cell has a thick cell wall and central canal named the lumen. Each cell wall is composed of an outer thin primary wall and an inner thick secondary wall where both walls are composed of ultra-fine microfibrils. The fibrils in the primary wall lie in a crisscross manner and are arranged almost parallel as right-handed spirals in the secondary wall. The fibrils are arranged in

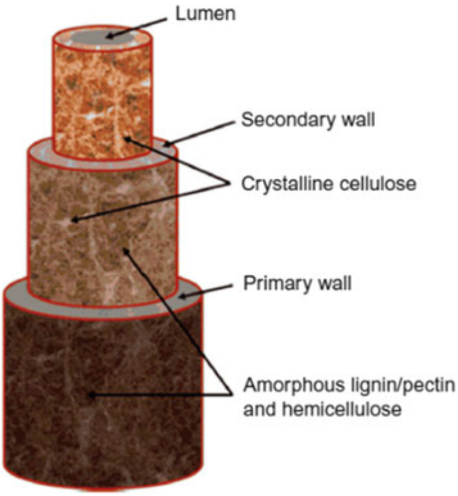


Fig. 5 Structure of a plant fiber. Reproduced from [49]

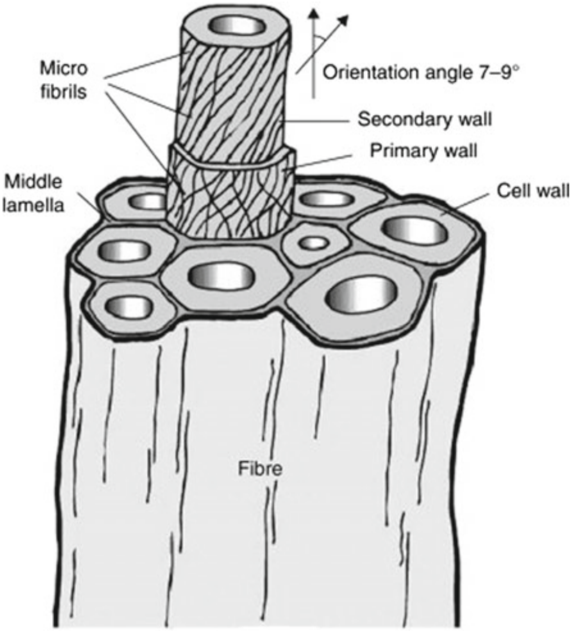


Fig. 6 Structure of jute fiber. Reproduced from [47]

a right-handed spiral forming an angle of 7–9° with the cell axis [47]. There are three core elements known as cellulose, hemicellulose, and lignin [50]. Cellulose and hemicellulose are the main elements in the primary and secondary walls [46]. Higher portions of lignin are found in the middle lamella [50]. The main reinforcing component in jute fiber is cellulose and hemicelluloses while lignin serves as the cementing material [50]. Lignin content in Tossa jute is higher compared to white jute. The presence of more lignin content in Tossa jute is the reason for the dark grey color [46]. The chemical composition and physical and mechanical properties of jute fiber are shown in Tables 1 and 2 respectively.

2.2.2 Factors Influencing Its Properties

The properties of jute fiber depend mostly on the nature of the plant, the area in which it is grown, the age of the plant, and the adopted methods for extraction [45]. Factors like size, maturity as well as the processing methods adopted have their influence on the quality of the fibers. Properties such as size, density, electrical resistivity, ultimate tensile strength depends upon the internal structure and chemical composition of the fibers [50]. Fiber properties depend on the cellulose content and value of microfibril angle. To utilize fiber as reinforcement in the polymer matrix, it is desirable to have more cellulose content and lesser microfibril angle. Jute has high cellulose content and low microfibril angle (~8.0°) [51]. Rigidity, good tensile and flexural strength are provided by cellulose fibrils. The stiffness of the fiber is decided by the microfibrillar angle. Low microfibril angle enhances the rigidity of the fiber and makes fiber mechanically strong [42]. Hydroxyl groups in cellulose are accountable for poor compatibility and dimensional instability of fiber [51].

2.2.3 Jute Fiber as Reinforcements

High specific properties, good stiffness, lower density have made jute a substitute to natural fiber for synthetic fibers in polymeric composites as reinforcements [45, 48]. High moisture absorption and degradation of jute fiber at higher processing temperatures and variations of the properties within the same fiber are some of the barriers to overcome for widespread use of fibers in polymer matrix composites [52]. To overcome these limitations various surface modifications methods such as grafting and mercerization have been used. Enhancement of mechanical properties is observed with the modification of fiber surfaces [45].

2.3 Hemp

Hemp fibers are one of the dominant class of bast fibers. These fibers are derived from the hemp plant under the species of *Cannabis* [53]. It is a plant that grows about 2–5 m in height which is sown in spring and harvested in autumn [54]. It is cultivated across the world (especially Europe) in different climatic conditions [55]. The fiber bundles spread from bottom to top of the plant. Hemp is composed of lignin, cellulose, and hemicellulose and the composition varies with the types and portion of the plant [54].

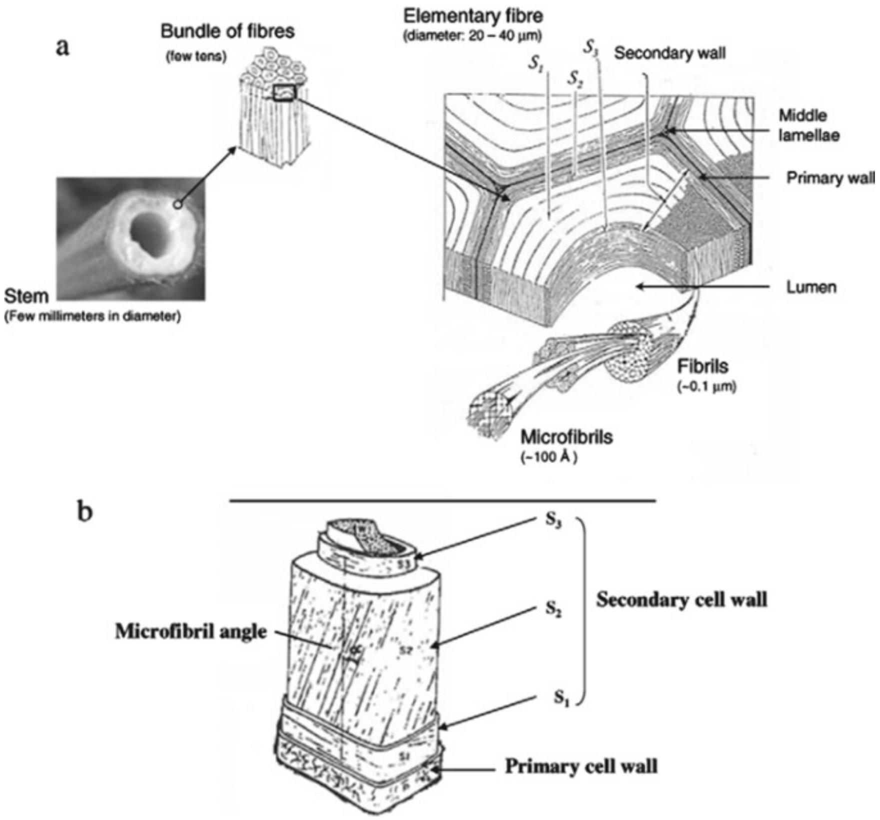


Fig. 7 **a** Structure of hemp fiber from plant stem to microfibrils, **b** schematic structure of a natural fiber cell wall. Reproduced from [56]

2.3.1 Structure of Hemp

Hemp fiber has a multi-celled structure. Figure 7 [56] represents the hemp structure from plant stem to microfibrils. The cell wall contains a primary wall and a secondary wall (S). The primary cell wall is composed of cellulose, hemicellulose, and pectin. The secondary wall is made up of three layers (S_1, S_2, and S_3) and it is composed of cellulose and lignin. L_2 layer is the thickest layer among them. The fibers are glued together due to the lignin-rich region known as the middle lamella and it covers both primary and secondary walls [54, 56].

2.3.2 Hemp Fiber as Reinforcements

Hemp fibers have become the most promising reinforcements in PMC´s owing to their good mechanical, thermal, and acoustic properties [57]. Biodegradability and low density are some of the reasons for their wide acceptance [53]. These fibers are used to reinforce different types of synthetic polymers and biopolymers. Fibers undergo chemical treatments for enhancing the performance of the composite.

2.4 *Sisal*

Sisal fibers are derived from Agave sisalana and the fibers are extracted from the leaves of the plant. This plant is cultivated in the tropical and sub-tropical regions such as north and south America, Africa, West Indies, Brazil, Tanzania, India, and the Far East [58]. Like all fibers, the chemical composition of the sisal fiber is composed of cellulose, hemicellulose, lignin, waxes, and ash [59]. The fibers are extracted from the leaves by different processes such as retting, scraping, or mechanical decortication [59]. The length and diameter of the fiber are between 1.0–1.5 m and 100–300 um respectively [58].

2.4.1 Structure of Sisal

The fiber consists of a bundle of hollow sub-fibers. The cell walls are reinforced with spirally oriented cellulose in a hemicellulose and lignin matrix [59]. Middle lamellae are composed of hemicellulose, lignin, and pectin, and all the fibers are bonded together due to the lamellae. The structure of sisal fiber is shown in Fig. 8. The fiber cell is composed of several numbers of walls and those walls are arranged with fibrillae and the shape of the fibrillae depends upon the location of them. The fibrillae located in the outer wall are in a reticulated structure whereas, in the outer

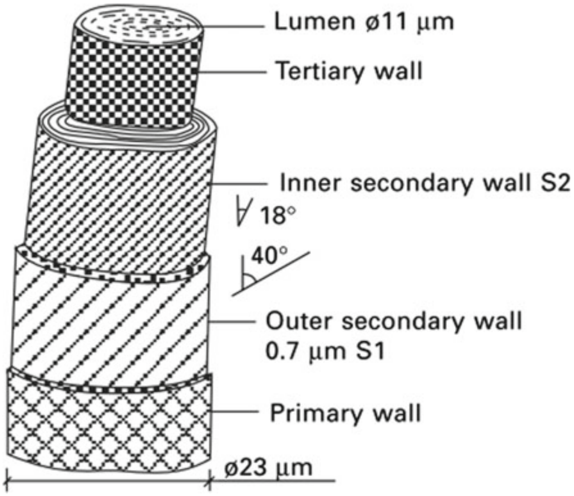


Fig. 8 Structure of sisal fiber. Reproduced from [58]

secondary wall S1, they are organized in spirals with a spiral angle of 40° to the longitudinal axis of the cell. In the inner secondary wall, S2 has a sharper slope i.e., 18º. The tertiary wall which is the innermost wall has a reticulated arrangement of fibrillae [58].

2.5 Kenaf

Kenaf fibers are derived from a warm-season crop that belongs to the family of Malavaceae. In six months, the kenaf plant grows to a height of 12–18 feet and the fiber is concentrated in the lower portion of the plant [60]. It can be grown in tropical and subtropical areas [61]. Southeast and East Asian countries like India, Bangladesh, China, Thailand, Indonesia, Vietnam, Nepal, Myanmar, Cambodia, and other countries such as Brazil, Cuba actively cultivate these plants [62].

2.5.1 Structure of Kenaf

Kenaf fiber is a combination of multicellular bonded with non-cellulose materials [62]. The fiber bundle is composed of many elementary fiber cells that are polygonal in shape. The elementary fiber consists of microfibrils with angles varying between 7 and 12°. Tensile strength, stiffness, flexibility, and elongation depend upon the chemical composition of the cell wall and the microfibril layered structure of the oriented cellulose crystals. The structural composition of the kenaf stem is shown in Fig. 9 [63] and it consists of the stem which has 20–45 mm, bast fiber bundle of 60–120 μm, elementary fiber 14–33 μm, and microfibril 4–10 nm [64].

3 Hierarchical Composites

The composites that accommodate microscopic continuous fibers and nano reinforcements at the same time are termed as hierarchical composites. The purpose of the addition of nano reinforcements is to induce new functionalities into the composite without compromising their performance [65]. Biological materials available in nature have inspired the researchers and they have realized the importance of nanoscale features in the materials [66]. Hierarchical structure and the astonishing performance of biological materials has motivated research towards new man-made materials using the same principles [65]. Weaker but more environmentally friendly, abundant, and bioresorbable materials can be incorporated when introducing hierarchy in man-made composites and achieving the properties in comparison with existing synthetic materials. However, mimicking these bioinspired architectures and obtaining hierarchical design is challenging [67].

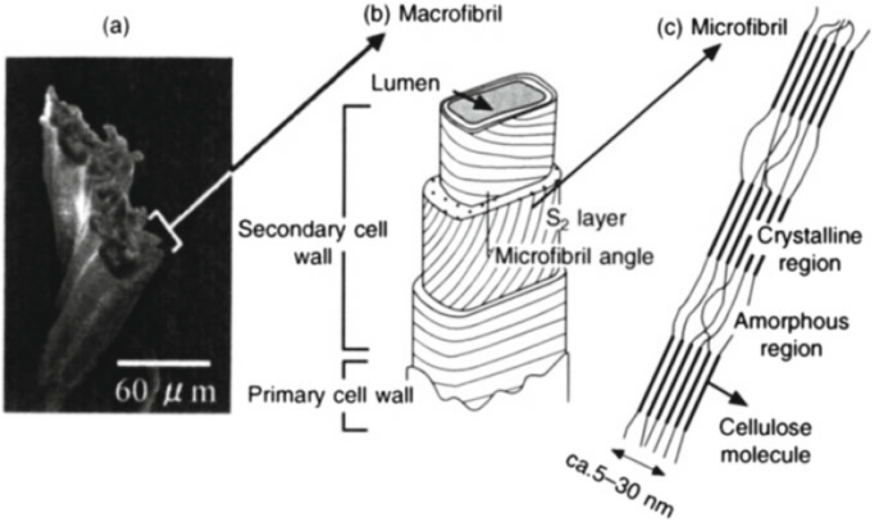


Fig. 9 **a** SEM of Kenaf bark fiber, **b** schematic representations of macrofibril and, **c** schematic representations of microfibril of natural plant. Reproduced From [63]

Control of size, geometry, and alignment of nanostructures are the major challenges in the biomimetic synthesis of composites. Without getting a proper understanding of the interactions of the constituents over various scales of length, it will be difficult to obtain an effective load transfer between the matrix and the reinforcements. A lot of attention is given to reinforce micro or nano fibrillated cellulose, cellulose nanofibrils, or nano-cellulose crystals along with the natural fibers [68].

3.1 Cellulose

Cellulose was discovered and extracted by Anselme Payen in the year 1838 [69, 70]. It is a natural biodegradable polymer that can be obtained from renewable sources and abundantly available across the globe [71]. It is the main constituent of the plant cell wall and can be extracted from various resources such as wood, bast fibers, grasses, seed fibers, marine animals, algae, fungi, and bacteria, etc. [21, 71]. Applications of cellulose include food, pharmaceutical, paint, and textile industries [72]. The tendency to absorb, retain moisture and difficulty in melting have restricted its usage in some applications. However, these days cellulose production at the nanostructure level has been proposed for its wider application [71].

3.2 Nanocellulose

Nanocellulose is a natural fiber that can be extracted from cellulose and its size is generally less than 100 nm in diameter and several micrometers in length [73]. The cellulosic materials having at least one dimension in the nanometer can be referred to as nanocellulose [74]. The mechanical properties can be increased by decreasing the cellulose fiber size [75]. It has gained a lot of interest in a variety of applications such as material science and biomedical engineering [71]. The characteristic properties of nano-cellulose such as crystallinity, surface area, and mechanical properties vary with the extraction methods and processing techniques [76]. Applications in the field such as photonics, medical devices like scaffolds for tissue generations, flexible optoelectronics, films, and foams surface modifications, and nanocomposites are still under investigation [71].

3.2.1 Extraction of Nanocellulose

A top-down approach and a bottom-up approach are used to produce nanocellulose. The top-down approach comprises of the chemical or mechanical process to isolate nano-cellulose from its resources. In the bottom-up approach, nanocellulose is obtained from glucose by bacteria. Nanocellulose is categorized into three types; Nanocrystalline Cellulose (NCC), Nanofibrillated Cellulose (NFC), and Bacterial Nanocellulose (BNC). They have similar compositions however, they don't have the same morphology, particle size, crystallinity. Figures 10 and 11 show the extraction of NCC and NFC by chemical and mechanical methods such as homogenization, grinding, and milling [71]. Some of the properties may be varied depending on the

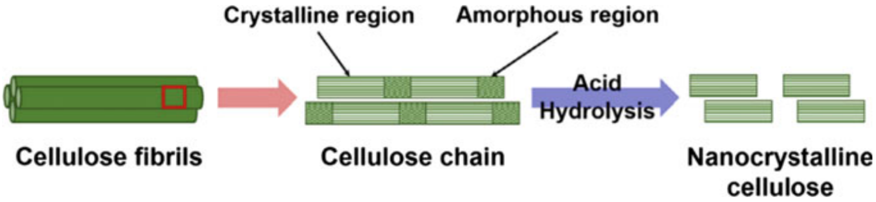


Fig. 10 Extraction of nanofibrillated cellulose by chemical process. Reproduced from [73]

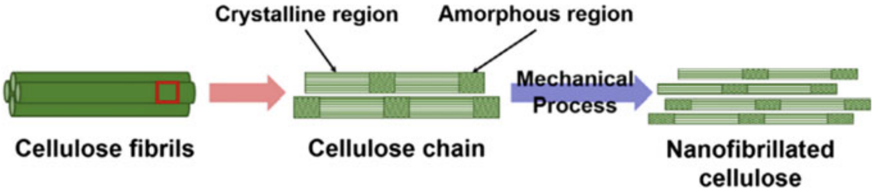


Fig. 11 Extraction of nanocrystalline cellulose by mechanical process. Reproduced from [73]

production methods and the source from where it is obtained [73, 77]. The first two categories are produced by a top-bottom approach and the latter is produced by a bottom-top approach [78]. Wood, cotton, hemp, flax, wheat straw, sugar beet, potato tuber, mulberry bark, ramie, algae, and tunicin are the sources for extraction of CNC and Cellulose Nanofibrils (CNF) [79]. Information related to different types of nanocellulose is presented in Table 4. Figure 12 presents a Transmission Electron Microscope (TEM) image of CNC and CNF and a Scanning Electron Microscopy (SEM) image of BC.

Table 4 Types of nanocellulose

Nanocellulose	Synonyms	Typical resources	Average size	Method	References
Nanocrystalline Cellulose (NCC)	Cellulose nanocrystal (CNC), Whiskers, rod-like cellulose, microcrystals	Wood, cotton, wheat straw, hemp, flax, rice straw, mulberry bark, ramie, tunicin, algae, and bacteria, etc.	Diameter: 5–70 nm Length: 100–250 nm (for plant) Several micrometres (from the cellulose of tunicates, bacteria)	Acid hydrolysis	[74, 86, 87]
Nanofibrillated Cellulose (NFC)	Cellulose nanofibrils (CNF), Microfibrillated Cellulose (MFC)	Wood, Potato, tuber, sugar beet, hemp, and flax, etc.	Diameter: 5–60 nm Length: several micrometres	Mechanical treatments	[20, 74, 87]
Bacterial nanocellulose (BNC)	Bacterial Cellulose (BC), microbial cellulose	Low molecular-weight sugars and alcohols	Diameter: 20–100 nm	Bacteria synthesis	[71, 74, 81]

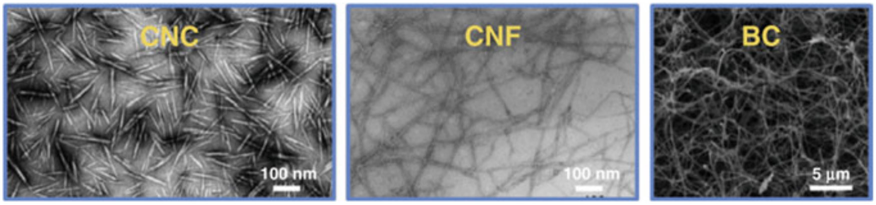


Fig. 12 TEM images of CNC and CNF and SEM image of BC. Reproduced from [80–82]

Table 5 Comparison of nanocellulose properties with other materials

Material	Tensile strength (GPa)	Youngs modulus (GPa)	Density g/cm^3	References
CNC	7.5	145	1.6	[88]
Glass Fiber	4.8	86	2.5	[88]
Steel Wire	41	207	7.8	[88]
Kevlar	3.8	130	1.4	[88]
Graphite	21	410	2.2	[88]
Carbon Fiber	1.5–5.5	150–500	1.8	[89]
Carbon Nano Tubes	11–73	270–970	1.0	[88]

3.2.2 Properties of Nanocellulose

Nanocellulose has a low-density value of around 1.6 g/cm^3, stiffness of 220 GPa which is higher than Kevlar fiber. The tensile strength of nanocellulose is around 10 GPa higher than cast iron and when comparing the ratio of strength to weight it is observed to be 8 times higher than stainless steel. It is transparent and the presence of hydroxyl groups has given a possibility to functionalize and obtain various surface properties. Table 5 reports the comparison of mechanical properties of nanocellulose in various forms.

3.2.3 Nanocellulose as Reinforcement

A novel design approach of incorporation of small amounts of high-stiffness, high-aspect-ratio nanometer-size filled into polymers has emerged for the creation of new materials with tailored mechanical properties [83]. Due to their fascinating mechanical properties and abundant availability, crystalline nanocellulose fibers are attracting significant interest. The addition of stiffer nanoparticles as reinforcements in polymeric nanocomposites has increased these days [84]. Nanocellulose in the form of CNC, CNF, and BNC is used as reinforcement in the polymeric matrix composites [85].

4 Inducing Hierarchical Nature into the Vegetable Reinforced Composites

From the literature, it can be observed that Natural Fiber Reinforced Composites (NFRC) have always fallen short regarding mechanical performance when compared with synthetic composites. The main reason for this is poor interface compatibility between polymer matrix and natural fibers. Although a lot of studies have been taken place to enhance the compatibility (surface modifications) between reinforcements and matrix there is still room for improvement. Inducing the hierarchical nature of the composite materials can reduce the gap in the mechanical performance of the NFRC´s compared with synthetic polymer composites.

The strategies that are available in the literature to induce hierarchical nature in the composite materials are (i) surface microfibrillation of lignocellulosic fibers, (ii) dispersion of microfibrillated cellulose within the matrix of conventional fiber-reinforced composites, (iii) attaching nano-sized bacterial cellulose onto natural fibers [90].

4.1 Surface Microfibrillation of Lignocellulosic Fibers

The fiber surface microfibrillation is one of the methodologies to induce the hierarchical nature, this procedure can be accomplished with the help of a pulp refiner. The degree of surface microfibrillation can be varied by the adjustment of the gap between rotor and stator discs. Hairy fibers are produced using the refiner and Schopper-Reigler (SR) values are used to quantify the degree of microfibrillation [90]. In a study, hierarchical nature was induced by adopting surface microfibrillation onto the sisal fiber. Surface microfibrillation was achieved by utilizing a pulp refiner and several degrees of microfibrillation was attained by regulating the gap (3 mm, 1 mm, and 0.5 mm) between the rotor and stator disks of the machine. Different degrees of microfibrillation were obtained for sisal fibers i.e., 18° SR, 24° SR and 32° SR. The morphology of the surfaces is shown in Fig. 13. Sisal and aramid fibers were reinforced with phenolic resin to produce a composite. The results (Table 6) showed that the tensile strength was improved by 88%, 93%, and 102% for 18° SR, 24° SR and 32° SR respectively when compared to the composites produced with non-microfibrillated sisal fiber. This improvement was due to the effective load transfer at the interface. A larger contact area was provided due to the larger number of microfibrils and hence mechanical interlocking was improved [91]. A similar kind of study was made by a team where they have reinforced microfibrilatted sisal fibers with phenolic resin to produce the composite and observed enhanced mechanical properties when compared to the normal sisal fiber composite and the tensile results are shown in Table 7 [90].

The shake test method was used in another study to produce hairy fibers and to induce hierarchical nature into the materials. Lyocell fibers were placed in a vessel that contained distilled water and they were subjected to mechanical treatment by shaking them for either 3 or 9 h. After treatment, it was observed that Lyocell fibers underwent significant fibrillation (Fig. 14) and thus created hairy fibers. Single fiber composite samples were prepared by placing a fiber between two polyethylene films and hot-pressed at 140 °C for 2 min. These samples underwent a single fragmentation test and subsequently found that there was an improvement in IFSS (Interfacial Shear Strength) by 75% when compared with the neat fibers [91].

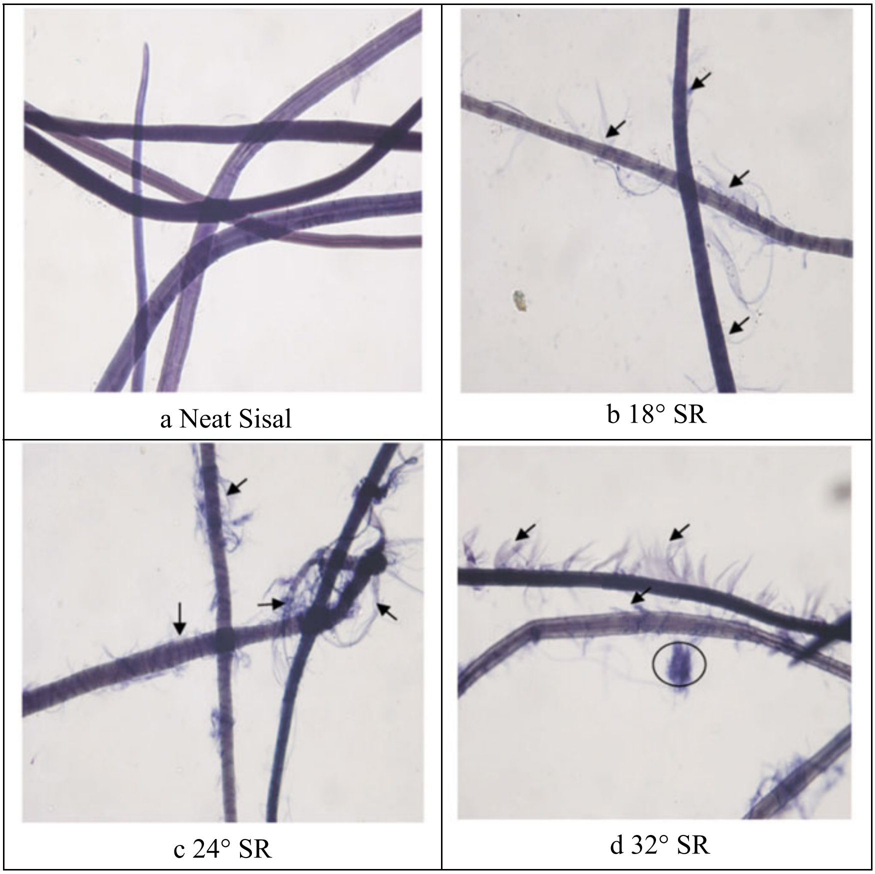


Fig. 13 SEM Images showing different degrees of microfibrillation. Reproduced from [91]

Table 6 Tensile properties of hybrid composite (Sisal/Aramid)

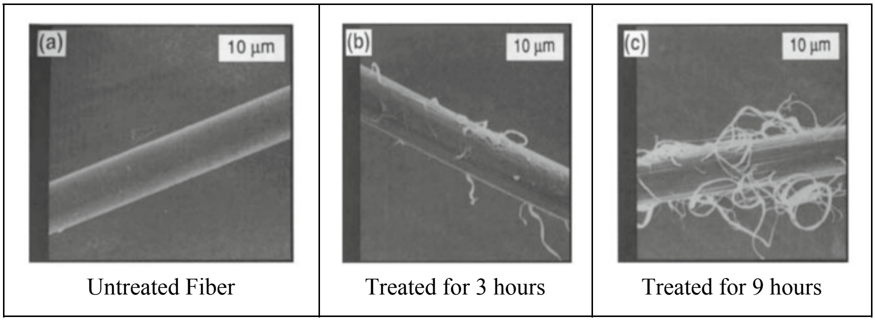
Types of sisal fibers	Tensile strength (MPa)	Youngs modulus (GPa)
Neat Sisal	13.3	1.50
18° SR	25.1	2.50
24° SR	25.7	2.38
32° SR	26.9	2.25

Reproduced from [90]

Table 7 Tensile properties of sisal composite

Degree of microfibrillation	Tensile strength (MPa)	Youngs modulus (GPa)
12° SR	13.0 ± 1.5	0.74 ± 0.10
14° SR	18.0 ± 1.5	1.02 ± 0.11
16° SR	24.5 ± 2.2	1.24 ± 0.14
21° SR	24.3 ± 2.0	1.30 ± 0.13
32° SR	23.5 ± 2.0	1.46 ± 0.15
46° SR	22.8 ± 2.3	1.62 ± 0.14

Reproduced from [90]



Untreated Fiber
Treated for 3 hours
Treated for 9 hours

Fig. 14 Hairy fibers after shake test. Reproduced from [92]

4.2 Dispersion of Microfibrillated Cellulose Within the Matrix Conventional Fiber Reinforced Composites

The other method to incorporate hierarchical nature into the composites is by the addition of nano or micro-sized cellulose into NFRC [90]. Uniform dispersion of the nanofiller is essential to increase the properties of the NFRC´s. However, obtaining uniform dispersion is challenging due to improper compatibility between nanocellulose and polymer [93]. Surface modification techniques can be employed because of the existence of the hydroxyl groups in nanocellulose to change the hydrophilicity nature [94]. This kind of approach was employed in a study where MCC was dispersed in a matrix. The MCC was dispersed by using a short ultrasonication process. The main intention of this approach was to improve the interface and to induce hierarchical nature into the composites. In this work, jute fibers were reinforced with matrix (MCC dispersed epoxy) and the obtained hierarchical composite was studied for the mechanical, dynamic mechanical, and thermal performances along with the improvement in the fiber/matrix interface. The results showed that interfacial shear strength (IFSS), tensile strength, flexural strength, impact energy and loss moduli were improved by 18.4%, 21.5%, 28.3%, 67% and 49.5% respectively. The improvement in adherence at the interface was confirmed by SEM images (Fig. 15). It was

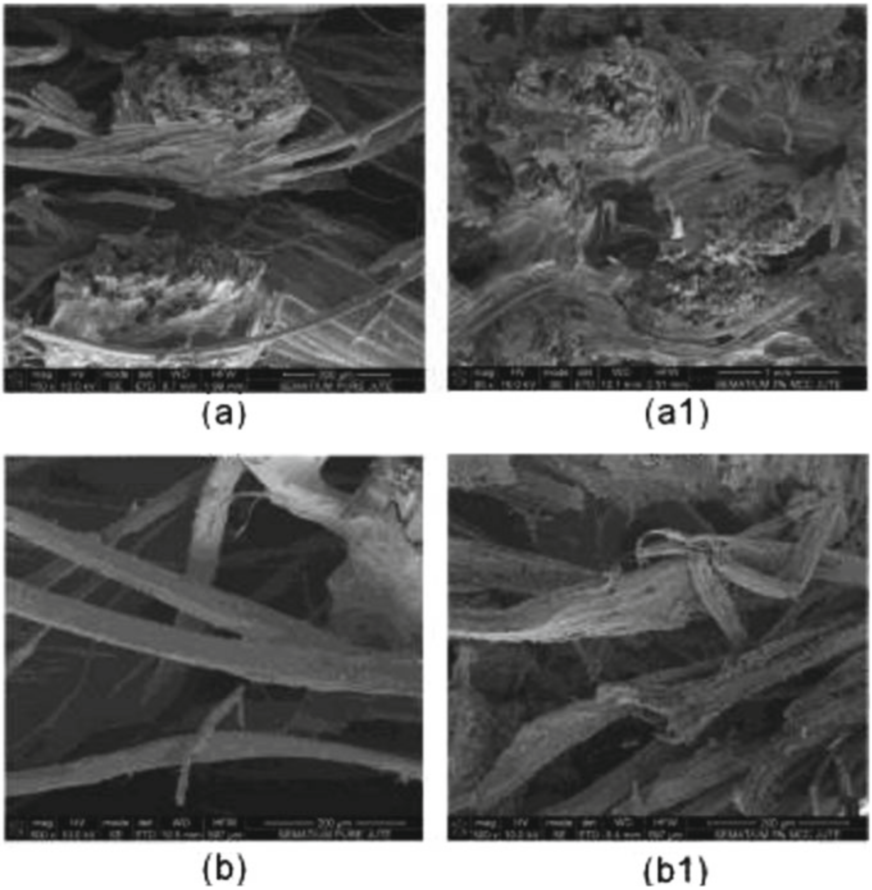


Fig. 15 Showing the fracture surface a, b Neat Jute and a1, b1 hierarchical composite. Reproduced from [95]

found that when MCC concentration was more than 1% the tensile strength and Young´s modulus got reduced. This was attributed due to the agglomerations (Fig. 16) of MCC at higher concentrations [95].

4.3 Coating of Cellulose onto Natural Fibers at Nano Scale

4.3.1 Coating of Nano Cellulose

A similar kind of approach was employed in a study where nanocellulose was coated using a Bandelin ultrasonic probe on the jute fabric surface at room temperature (Fig. 17). The nanocellulose coated woven jute was reinforced with epoxy to produce

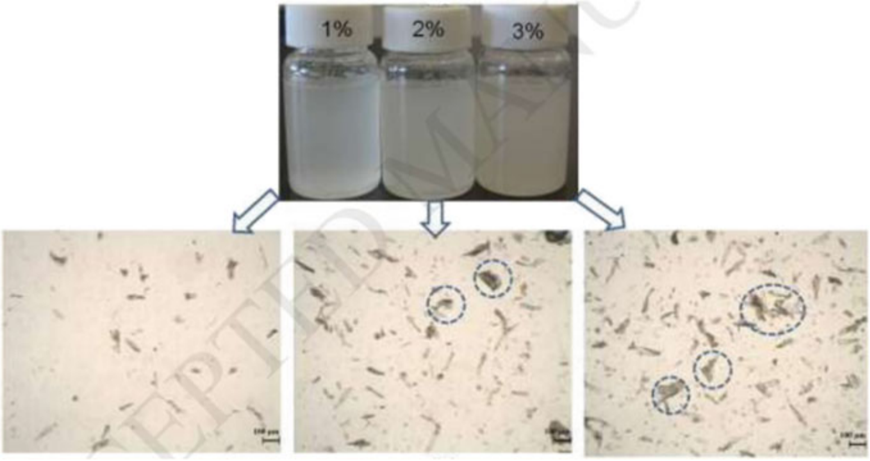


Fig. 16 Dispersion of MCC in epoxy resin at various concentrations. Reproduced from [95]

composite by compression molding method. In this work, the effect of nanocellulose coating on the mechanical properties was explored. The study revealed that an improvement was observed in tensile modulus, flexural properties, and fracture toughness. The dynamic mechanical analysis showed that there was an increment in the storage modulus and decrement in tangent delta peak height of nanocellulose coated composites [96].

4.4 Coating of Bacterial Cellulose

4.4.1 Culturing of Bacterial Cellulose in the Presence of Natural Fiber

BC can be cultured on the surface of natural fiber using a suitable culture medium and bacteria via in situ synthesis. This practice was used in a study where such as *Acetobacter xylinum* was used to deposit nanocellulose on to the sisal fibers. The deposition of BC shown in Fig. 18 was confirmed through SEM images (Fig. 19) [97].

It is observed from Fig. 18 that a layer of BC pellicles grew on the natural fiber surface. Sisal fibers were extracted from the culture medium and after purification, it was investigated under scanning electron microscopy and observed a layer of BC nanofibrils attached to the surface of natural fiber (Fig. 19b). It was found out from the weight gain calculations that nearly 5–6 wt% of BC was deposited on the fiber surface. By using BC coated natural fibers as reinforcements, a hierarchical reinforcement is incorporated at the interface between reinforcements and matrix which leads to the improvement in the stiffness of the matrix around natural fibers.

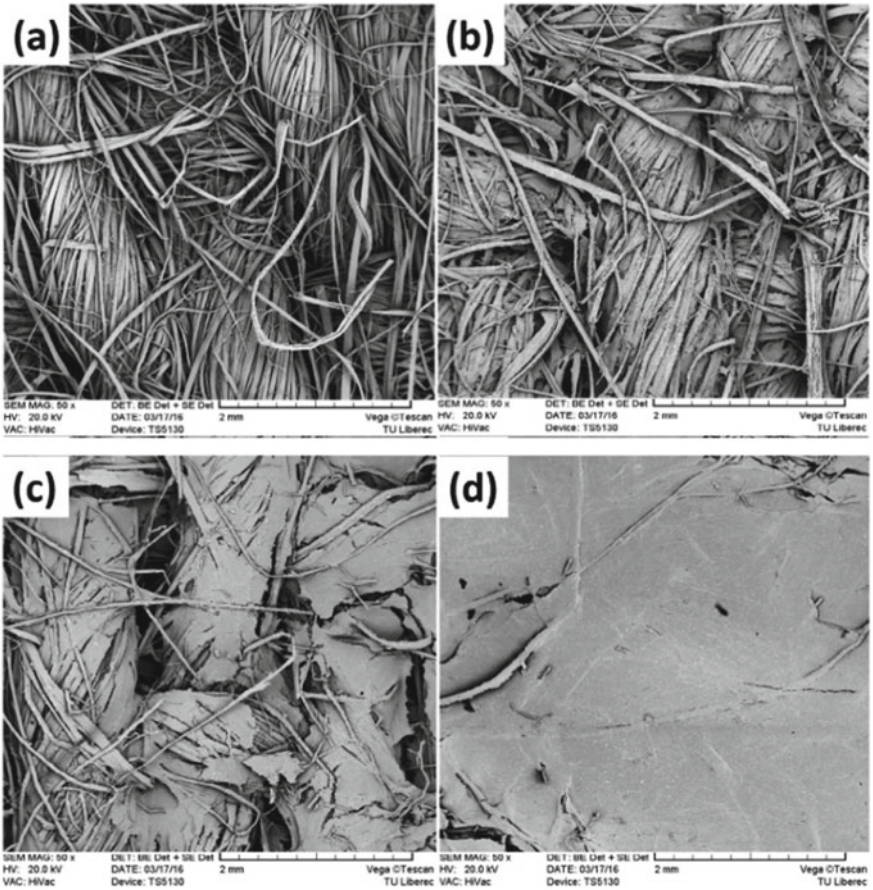


Fig. 17 Surface morphology of nanocellulose coated jute fabric **a** 0 wt%, **b** 2 wt%, **c** 5 wt%, **d** 10 wt%. Reproduced from [96]

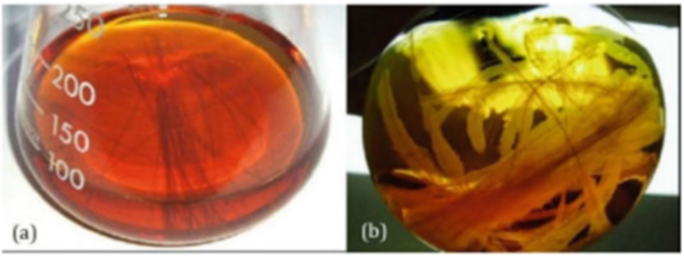


Fig 18 Sisal Fibers placed in culture medium **a** before 2 days, **b** after 2 days. Reproduced from [97]

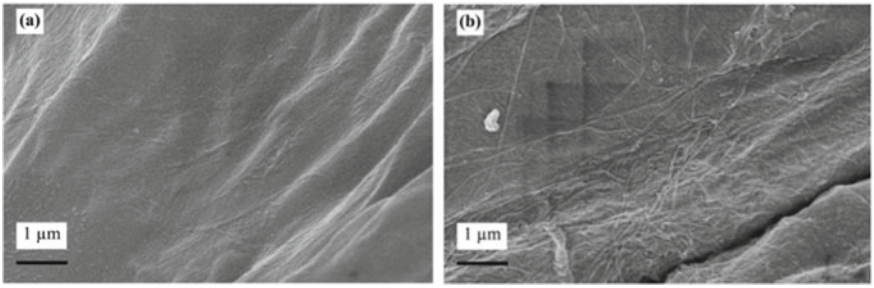


Fig 19 SEM images of sisal fiber **a** Neat, **b** BC modified. Reproduced from [97]

The contraction of fibers was reduced with the coating of BC on to the fibers due to its low thermal expansion (0.1×10^{-6} K^{-1}) of BC [90].

4.5 Coating of Bacterial Cellulose on to the Natural Fibers Surface by Using a Slurry Dipping Method

The slurry dipping method is an easy and profitable method to coat nanosized BC onto the surface of a natural fiber without the need for bioreactors. Natural fibers are immersed into BC dispersions in water, this results in the drawing of water and BC nanofibrils from the medium on to the surface of fibers. BC nanofibrils cannot penetrate through sisal fibers since they are bigger than water molecules and hence BC nanofibrils are settled on the surface of natural fiber [90]. This methodology was used in a work [98] where BC was coated on sisal fibers surface. The morphology of sisal fibers coated with BC using the slurry dipping method was nearly the same as the morphology of the BC coated sisal fibers obtained by culturing Acetobacter while placing sisal fibers in a bioreactor. Two different types of sisal fibers (Fig. 20) were produced: (i) a dense coating around fibers (DCS) (Fig. 20a) and (ii) hairy fibers with BC orientated perpendicular to the surface (HFPS) (Fig. 20b). When undergone single fiber tests, HFPS did not exhibit any major difference in tensile strength and Young´s modulus when compared to neat sisal fibers [98].

In the same study, the researchers produced two composites: (i) PLLA reinforced with BC coated sisal fiber and (ii) PLLA- BC reinforced with BC coated sisal fiber, where the second type of composite contained BC in both constituents (matrix and fiber). The outcomes of mechanical characterizations are shown in Table 8.

From the results (Table 8), it can be observed that the tensile strength of the composites reinforced with sisal and BC coated sisal fibers was reduced when compared to neat PLLA composites. The decrement in the values could be due to the poor fiber-matrix interface. However tensile strength improved with the addition of BC into the matrix. This improvement may be credited to the improved interfacial adhesion between the BC incorporated matrix and BC coated fibers. The tensile

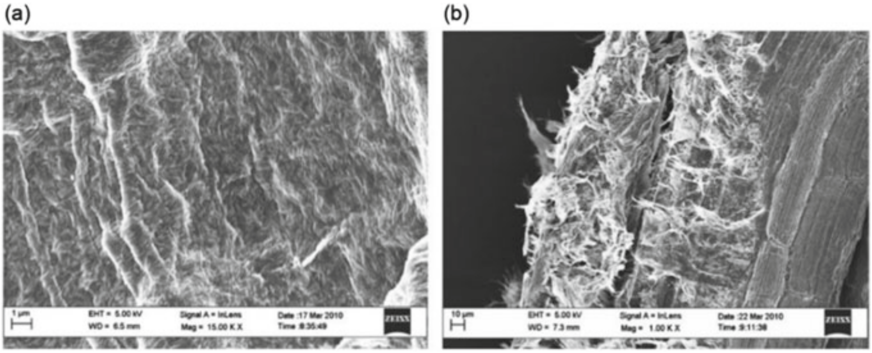


Fig. 20 SEM images of BC coated sisal fiber **a** dense coating around fibers **b** BC orientated perpendicular to surface. Reproduced from [98]

Table 8 Mechanical properties of PLLA composites

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
Neat PLLA	62.6 ± 1.0	0.97 ± 0.02	86.1 ± 6.9	3.70 ± 0.04
PLLA-Sisal	58.7 ± 1.0	1.28 ± 0.03	105.6 ± 1.5	4.85 ± 0.10
PLLA-DCS	57.3 ± 1.3	1.35 ± 0.03	99.2 ± 2.8	5.19 ± 0.07
PLLA-HPSF	57.8 ± 1.6	1.29 ± 0.03	102.0 ± 2.5	4.96 ± 0.16
PLLA-Sisal-BC	60.9 ± 1.9	1.46 ± 0.02	100.0 ± 2.2	5.74 ± 0.05
PLLA-DCS-BC	67.8 ± 1.2	1.63 ± 0.01	95.5 ± 2.3	6.19 ± 0.08
PLLA-HPSF-BC	69.2 ± 1.2	1.59 ± 0.05	96.8 ± 2.0	5.77 ± 0.13

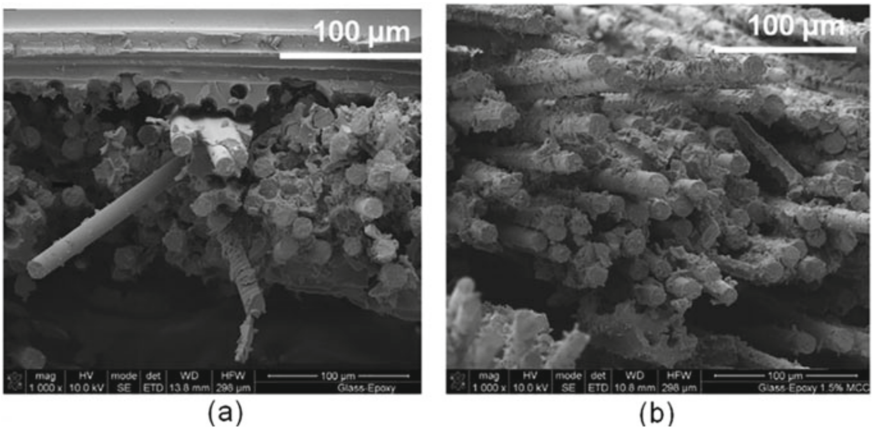
Reproduced from [98]

modulus was improved with the addition of untreated and treated sisal fibers when compared to neat PLLA. The flexural strength of all composites was improved in all composites in comparison to neat PLLA, yet BC coating on fibers or mixed in the matrix has shown no significant change in flexural strength of composites. The flexural modulus was improved in all cases in comparison with neat PLLA. The composites produced where the matrix was modified with BC, have shown more improvement when compared to neat and BC coated sisal fiber composites. It could be attributed to the stiffening of the matrix by the nanosized reinforcement in the PLLA matrix [98].

5 Recent Works in Hierarchical Composites Using Cellulose at Different Scales

In a work that has been reported recently, cellulose microcrystals (CMCs) were used for improving the fiber-matrix interface. Epoxy was reinforced with glass fibers and CMCs were used to progress the composite´s performance by enhancing the fiber-matrix interface. The composite was produced by the vacuum infusion process. In this case, CMCs were dispersed in epoxy resin using an ultrasonic treatment, and homogenous dispersion was observed when 1 wt% was dispersed. Dispersion of CMCs above 1 wt% led to the agglomeration. The properties of the composites drastically improved with addition of 1 wt% CMCs, an improvement of 65% in laminar shear strength, 14% in tensile strength (338 ± 5 MPa), 76% in flexural strength (510 ± 6 MPa), 9.4% in impact energy (1.63 ± 0.03 J), 13.5% in storage modulus (20.02 ± 0.2 GPa) and 21.9% in loss modulus (0.62 ± 0.01) was reported when compared to glass/epoxy composite. Due to the addition of CMCs, a substantial improvement in the interfacial adhesion between epoxy matrix and glass fibers was observed and hence led to enhancements of tensile and flexural strength. The improvement in resistance to crack propagation was due to the hierarchical nature and contributed to the increment of impact energy [99].

When observing SEM images of the fractured surface of neat composites (Fig. 21a) and MCS dispersed composite (Fig. 21b), it is evident that there exists a drastic change. The SEM image of neat composite showed the existence of some fibers with a smooth surface, voids, and holes due to the fiber pull out. This is due to the poor interfacial adhesion between matrix and fibers. On the other hand, in SEM images of fractured surfaces of MCS dispersed composite, it was observed that fibers were well impregnated and embedded into the matrix and hardly there are any voids. Hence it can be concluded from the findings that the dispersion of MCS improved



(a) (b)

Fig. 21 Fracture surface of **a** neat composite, **b** hierarchical composite. Reproduced from [99] the interfacial bonding between matrix and fibers due to the hierarchical nature of the reinforcements in the composites [99].

A similar kind of observation was made in another study where CNC was added in epoxy resin and reinforced with plain woven glass fabric (GF). CNCs were dispersed into the epoxy matrix by ultrasonication. The composite was produced by a vacuum-assisted resin infusion process. The addition of 2 wt% of CNCs improved tensile strength (332 ± 9.2 MPa) by 24%, Young´s modulus (11.7 ± 0.26 GPa) by 14%, and flexural strength (660 ± 20.09 MPa) by 55% in comparison with the values of glass fiber reinforced composite [100].

The improved interfacial strength attributed to the enhancement of tensile strength and increment in Young´s modulus was due to the increment in the stiffness of the CNC matrix and stiffening of the local interface region. High flexural strength was achieved in CNC/GFR composites because the homogeneous dispersion and separation of individual CNCs within the matrix are settled around the surface of the fibers. The CNCs around the surface of fiber facilitate an interface strengthen mechanism by bridging or suppressing the surface microcracks and hence there is a delay in propagation of cracking. This bridging effect minimizes the interlaminar delamination and interlaminar stress concentration between adjacent layers which results in improved interlaminar adhesion which governs flexural strength [100].

After investigating the SEM images (Fig. 22) of the fracture surfaces of glass fiber reinforced composite (GFRC) and 2.0 wt% CNC/GFR composite, the failure noticed in the initial case was due to the poor interfacial adhesion between fiber and matrix which was confirmed by interfacial debonding and fiber pull out. In the latter case, equal straining of both fibers and matrix (concurrent failure) confirmed strong interfacial bonding between fibers and matrix [100].

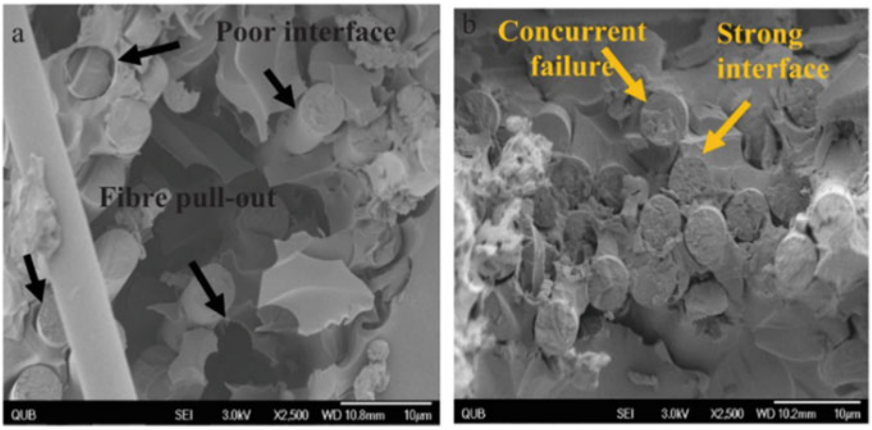


Fig. 22 SEM image of fracture surface **a** glass fiber composite, **b** CNC/GFR composite. Reproduced from [100]

6 Conclusions

Researchers these days are getting inspired by nature. Inducing hierarchical nature into the biocomposites is one of the methodologies to improve the performance of the composites. Hierarchical composites have the potential to be utilized in various advanced applications. However, the addition of reinforcements at various levels and achieving homogenous dispersion of nano reinforcements were a few of the challenges. To maintain sustainability, it is needed to replace the conventional composites (traditional fiber reinforced). In this regard, this chapter has shown the possibilities of producing vegetable hierarchical composites using green nano reinforcements. However, some issues need to be addressed such as optimum concentration, novel technologies to obtain homogenous dispersion, and economical manufacturing methods to utilize these vegetable hierarchical green composites. Considering the promising results in the performance of hierarchical composites, sustainability and biodegradability ignite the researchers for further advancements in this topic in the future.

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Development of Vegetable Fibre-Mortar Composites of Improved Durability

Banjo A. Akinyemi, Daniel O. Oguntayo, and Anish Khan

1 Introduction

To resist propagation of cracks and to improve the ductility behaviour in cement mortar,fibres are used as reinforcement. Fibres are thread like substances which can improve the strength of cement composites, reduce the crack growth, and result to a better strain capacity of the cement composites.

The main types of fibre that have been used in cement-composites are natural and synthetic fibres. These fibres are derived from different materials, for example, natural fibres are gotten from animal, mineral, and plant. However, due to cost and environmental pollution that is associated with the use and production of synthetic fibres, natural fibres have been considered as viable alternative [31]. Being a very cheap and locally sourced material, their application in construction for improving the quality of cement composites will costs a very little and can lead to sustainable development.

Therefore, the utilization of natural fibers is technically beneficial being a material that can be promoted in construction industry [19]. One of such natural fibre that has potentially increased the durability of cement composites is the vegetable fibres (plant based fibres).

Vegetable fibres are bio-based fibres from vegetable origin (plants and wood). These bio-based fibres have continued to generate growing interest due to their

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B. A. Akinyemi (✉)
Department of Agricultural and Biosystems Engineering, Structures and Building Materials Unit, Omuaran, Kwara, Nigeria

D. O. Oguntayo
Department of Civil Engineering, Landmark University Omuaran, Omuaran, Kwara, Nigeria

A. Khan
Center of Excellence for Advanced Materials Research, King Abdulaziz University , Jeddah 21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_18

potential as possible replacement for their synthetic counterparts [20]. Their chemical composition plays a vital role in their performance, cellulose and lignin being the major constituents have tremendous impact on the hydration process and ultimately on strength development in cement composites. Vegetable fibres are readily available, possess low weight and are energy and cost efficient. They require merely a small amount of industrialization for their processing and in contrast with an equivalent weight of nearly all regular synthetic reinforcing fibres, the energy required for their production is small and hence making them to be employed effectively in cement-composite components for weight reduction, strength improvement and crack reduction at low cost [40].

Also, their utilization in cement composites will result in significant reduction in the volume of agro-forestry residues generated by agro-industrial activities, as they have been previously considered as biodegradable waste. This implies that there could be a significant increase in the adoption of vegetable fibre as cementitous material, and this could be achieved by obtaining a material with properties comparable with the conventional construction materials.

2 Relevance of Vegetable Fibre as Reinforcement in Cement-Mortar Composites

The utilization of vegetable-fibres in cement composites has attracted great interest due to the following:

i. The application of vegetable fibre in cement-mortar composites will contribute to the decline of the environmental challenges caused by waste disposal. Vegetable fibres form major proportion of waste produced from agricultural sector, for instance, each tonne of commercially used sisal fibers resulted in three (3) tonnes of residual fibers, whose disposal have created environmental hazards in the neighbouring community [34]. Therefore, their utilization in cement composites will greatly help in addressing the problems of waste management faced in developing nations [27].

ii. They are abundantly available (they are produced in nearly all countries) [45] (Table 1). Due to various countries involvement in different agricultural practices such as growing plants and fruits which are used as raw materials for industries, the supply of vegetable fibres resources are unlimited, freely available and comparatively cheap [8]. More so, vegetable fibres originated from the environment (that is, they grow naturally in the environment), thereby making them to be abundantly available.

iii. Their use in cement composites will help in achieving sustainable construction materials which will support sustainable development, especially in emerging economies. Since, construction sector is a key contributor to climate change and the usage of sustainable materials in this industry have been a key focus

Table 1 Global production of vegetable fibres [42]

Fibres	Quantity (Million tons)	Country of production
Cotton	25	India, China, USA, Pakistan
Jute	2.5	Bangladesh, India
Kapok	0.03	Indonesia
Kenaf	0.45	Thailand, India, China
Flax	0.50	France, China, Belarus, Belgium, Ukraine
Hemp	0.10	China
Ramie	0.15	China
Abaca	0.10	Ecuador, Philippines
Sisal	0.30	Brazil, Kenya, China, Tanzania
Henequen	0.03	Mexico
Coir	0.45	India, Sri Lanka
Wool	2.2	China, Australia, New Zealand
Silk	0.10	China, India

over the years, the utilization of vegetable fibres in construction will drastically reduce the environmental impact caused by the industry [23].

iv. Vegetable fibers are non-hazardous, renewable, and biodegradable, permitting the development of more sustainable construction materials. In a study conducted by [21], it was reported that the process of extraction of vegetable fibers is pollution free and environmentally sustainable. The study further stated that their utilization as fibers-reinforced cement composites as a substitute of asbestos cement composites, would eradicate the dangers of exposure of human lives to infectious diseases like asbestosis, cancer, malignant pleural disease and tumors.

v. Vegetable fibres are as stronger as their synthetic fibres counterpart, cost-effective and above all environmental friendly [30]. Their properties such as low cost, good specific mechanical properties, and their requirements of low energy during production [33] will result in 10% decrease in weight, 80% decrease in energy required for production, and 5% reduction in cost of constituent utilized in contrast to their synthetic counterpart [25]. Though their moderate mechanical properties prevent them from being used in extreme loading conditions, nevertheless, for numerous reasons, they can compete with their synthetic counterpart.

vi. Their tensile performance can compare fairly with synthetic ones [30]. Attentions have been drawn to resilient non-conventional materials with comparable qualities as those presented by construction materials habitually used in civil engineering [32]. According to Da [12], vegetable fibres offer durability and resilience, even in excessive loading situations thereby contributing to infrastructure sustainability through reduced repair events and consecutively extending infrastructure service life.

vii. They have low density, less abrasiveness, and lower cost [28]. Vegetable fibres have mechanical properties which can contribute to sustainable construction materials relevant in construction sector. According to [5], the low density of vegetable fibres help in achieving better efficiency while their low abrasiveness makes their processing easier and more recyclable.

viii. They can be fashioned on site into complicated shapes and can also be easily cut to length on site. For complex shapes construction, vegetable fibres are usually suitable as their in-plane shear ability allows the membrane to seize the complex geometries required [10].

3 Types of Vegetable Fibres Used in Cement Composites

Different types of vegetable fibres exist; as seen in Table 1, these vegetable fibres with varied physical, mechanical, and chemical characteristics have been used in cement composites. The classifications include as seed-fibres, bast-fibres, and leave-fibres, stalk fibre, grass and other fibre crop residue, and wood and specialty fibres [4, 20]. The fibres under these categories which have been found suitable for cement composites are shown in Figs. 1 and 2:

i. Seed fibres:seed fibres are obtained from the seeds and seed cases of various plants. Popular fibres under this category include coir, cotton, kapok and milkweed. The most studied fibre in this group is the coir fibre and it is the extracted husk of coconut. This fibre has been extensively utilized as composite materials in civil engineering; worthy of note is their utilization in cementitious matrices as a very suitable construction material for resisting earthquakes [22]; which meant that their composites have higher impact strength [38].

ii. Bast-fibres: jute, flax, abaca, kenaf, ramie, hemp can be grouped and defined as bast fibres. These fibres are gotten from the exterior of various plants. A common mechanical property possessed by fibres under this category is their

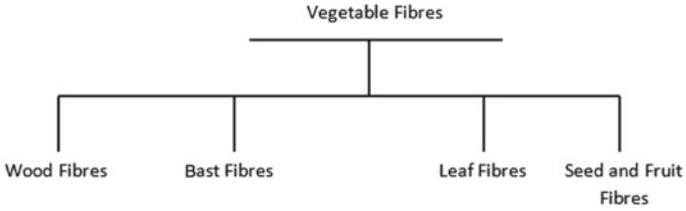

Fig. 1 Classification of vegetable fibres [35]

Bast Fibre Seed Fibre Stalk Fibre

Grass Fibre Leaf Fibre Wood Fibre

Fig. 2 Samples of fibre under different classification [6]

high tensile strength and ability to be a good thermal insulator [44]; therefore, they hold a high prospective, especially where there is a demand for considerable strength.

iii. Stalk fibres: Fibres such as baggasse, rice straw, wheat straw, barley etc. are obtained from the stem/stalks of plants. These fibres are usually bigger in diameter and showed significant differences in potassium and galacturonic acid content, strength, and rigidity [26]; there is no doubt that they will play a crucial role in the improvement of cement composites.

iv. Grass and other fibre crop residue: Grass fibers such as bamboo, elephant grass, peanut shell, corn husk, millet stover, hazelnut husk etc. are those fibres that originated from tall grasses. They have also been studied as component in cement composites [1].

v. Wood and specialty fibres: Wood fibres are sourced from a wide variety of trees while specialty fibres are industrially processed vegetable fibres with unique attributes such as bond enhancement and alkali resistance features. The fibres under this group have shown great potential in improvement of cement composites; for example, in a study conducted by [15] in which cement content was replaced with wood fibres using 1% by weight of cement, it was reported that significant improvement in the compressive strength by more than 40% with 1% by weight of the wood fibers was obtained.

Leaf fibres: the fibres in this group are gotten from the leaf of plants and they include sisal fibres, banana fibres, pineapple fibres, caroa fibres and henequen fibres. They are usually obtained by mechanically scrapping them away from the leaf of plants. Several experimental studies have recognized the positive effects of the inclusion of these types of vegetable fibres on the properties of cement composites. However, the most studied fibre in this group is sisal because of its strength, durability, ability to stretch, affinity and resistance to deterioration in salt water [2, 29] (Table 2).

Table 2 Vegetable fibre Types and Properties [14]

Fibre	Density (g/cm^3)	Diamater (um)	Length (mm)	Elongation (%)	Tensile modulus (GPa)	Tensile strength (Mpa)	Specific modulus	Cellulose (wt%)	Hemi-cellulose (wt%)	Lignin (wt%)	Pectin (wt%)
Alfa	0.89	–	–	5.8	22	35	25	45.4	38.5	14.9	–
Abaca	1.5	–	–	1.0–10	6.2–20	400–980	9	56–63	20–25	7–13	1
Bamboo	0.6–1.1	25–40	1.5–4	2.5–3.7	11–32	140–800	25	26–65	30	5–31	–
Bagasse	1.25	10–34	10–300	1.1	17–27.1	222–290	18	32–55.2	16.8	19–25.3	–
Banana	1.35	12–30	300–900	1.5–9	12	500	9	63–67.6	10–19	5	–
Coir	1.15–1.46	10–400	20–150	15–51.4	2.8–6	95–230	4	32–43.8	0.15–20	40–45	3–4
Cotton	1.5–1.6	10–45	10–60	3–10	5.5–12.6	287–800	6	82.7–90	5.7	<2	0–1
Curaua	1.4	7–10	35	1.3–4.9	11.8–96	87–1150	39	70.7–73.6	9.9	7.5–11.1	–
Flax	1.4–1.5	12–600	5–900	1.2–3.3	27.6–103	343–2000	45	62–72	18.6–20.6	2–5	2.3
Hemp	1.4–1.5	25–500	5–55	1–3.5	23.5–90	270–900	40	68–74.4	15–22.4	3.7–10	0.9
Henequen	1.2	–	–	3.7–5.9	10.1–16.3	430–570	11	60–77.6	4–28	8–13.1	–
Jute	1.3–1.49	20–200	1.5–120	1–1.8	8–78	320–800	30	59–71.5	13.6–20.4	11.8–13	0.2–0.4
Kenaf	1.4	–	–	1.5–2.7	14.5–53	223–930	24	31–72	20.3–21.5	8–19	3–5
Oil palm	0.7–1.55	150–500	–	17–25	0.5–3.2	80–248	2	60–65	–	11–29	–
Palf	0.8–1.6	20–80	900–1500	1.6–14.5	1.44–82.5	180–1627	35	70–83	–	5–12.7	–
Ramie	1.0–1.55	20–80	900–1200	1.2–40	24.5–128	400–1000	60	68.6–85	13–16.7	0.5–0.7	1.9
Sisal	1.33–1.5	8–200	900	2–7	9–38	363–700	17	60–78	10–14.2	8–14	10

4 Improvement of Durability of Vegetable Fibre-Cement Mortar Composites

Alkaline pore solution within the cement matrix has been reported to be the major cause of degradation of vegetable fibres leading to a reduction in their durability, subsequently resulting into untimely failure of the cement composite [43]. It is therefore imperative that the durability issues surrounding vegetable fibers as reinforcement in cement composites be urgently addressed so that they could be widely accepted for use in various applications.

Three methods have been identified:

(1) Fibre impregnation with blocking agents and water-repellent agents
(2) Fibre treatment with alkaline and acidic chemicals, coating agents and hornification process
(3) Cement matrix modification.

(1) Fibre impregnation with blocking agents and water-repellent agents

The findings of [16] on the treatment of a vegetable fibre with sodium sulphite, sodium silicate, barium, sulfite salts, magnesium sulfate, iron and copper compounds showed that noticeable effect on the durability of the fibre reinforced cement composite was achieved with the blocking agents used. In the same study also, the adoption of water repellent additives which include PVA, rubber latex, formine and stearic acid, amide wax, tar, asphalt, silicon and oil were used to impregnate the vegetable fibre. The results indicated that only reactions from the interactions of formine and stearic acid with the vegetable fibres resulted into significant reduction in fibre embrittlement of the cement composites.

(2) Fibre treatment with acidic, alkaline chemicals and coating agents

The most widely accepted and used acid for vegetable fibre treatment is the sulphuric acid because of its economic and environmental advantages. However, other acids that could be used include fluoridric and chloridric acids [7].

The report of durability studies performed on some vegetable fibers such as sugar and coir fibres used as reinforcement in concrete samples by subjecting them to sulphuric acids revealed that, mass and compressive strength losses are determined by the type of vegetable fibre used as reinforcement. Coir fibre reinforced cement composite recorded 14, 22 and 28% losses in mass after 30 days, 1 and 2 years immersion in the acid while sugarcane fibre concrete suffered losses of 14.5, 23.5 and 30.8% after similar duration of immersion in the same medium [37].

Some common alkaline chemicals used are sodium hydroxide, lithium hydroxide, calcium hydroxide, hydrogen peroxide, potassium hydroxide and ammonia. Of all these chemicals, sodium hydroxide is commonly used to treat vegetable fibers. As seen in Fig. 3, sodium hydroxide alters the orientation of highly packed crystalline cellulose order and forming an amorphous region thereby providing more access

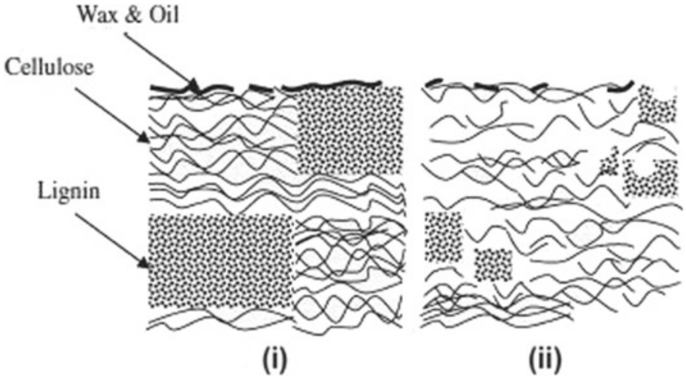

Fig. 3 Arrangement of (i) raw and (ii) treated fibre [18]

for penetration of the chemicals [18]. The investigations conducted by [41] on the assessment of durability of coir and sisal fibre reinforced cement composites revealed that more loss of durability was obtained from immersion in the calcium hydroxide compared with that from sodium hydroxide solution. For sodium hydroxide's effect on durability of the vegetable fibre cement composites, 70% of the original strength was retained after immersion in the solution for 420 days while after 300 days immersion in calcium hydroxide, a significant loss in strength was reported by the authors.

Coating involves the process of improving the surface of the vegetable fibre either by dipping, brushing or immersion in agents capable of forming thin layers of water-resistant films on the fibre surface. Some of the methods that have been used include silane coating and polymer coating of vegetable fibre reinforced cement composites. The coating method also assists in enhancing the interface between the matrix and the fibre thereby creating a stability and improved adhesion of the vegetable fibers to the cement-mortar matrix [9]. In a study by [9] it was concluded that 6% weight of silane is capable of reducing water absorption potential of vegetable fibers, hence improving the durability.

Hornification is also known as wetting and drying cycles which is recommended to be done prior to inclusion of vegetable fibre in cement composites. This process helps to improve the dimensional stability while reducing the possibility of fibre mineralization from $Ca(OH)_2$ on the fibre surface [17]. Claramunt et al. [11] reported that 20 and 13% higher enhanced compressive and flexural strength after 4 wet and dry cycles were obtained from previously hornified kraft pulp fibres on comparison with untreated fibre reinforced cement composites

(3) **Matrix modification**

For matrix modification, polymer based materials and pozzolanic materials have been suggested by some authors to improve the cement mortar in the composite prior to vegetable fibre inclusion.

The use of polymer chemical admixtures help to improve the bonding between the vegetable fibers and it is usually accompanied by a decrease of permeability due to low porosity [36]. The low porosity is caused by the development of thin films within the polymers which is capable of effectively blocking the pores developed during cement hydration. Hence, movement of moisture and heat which are elements majorly responsible for degradation through the pores are significantly reduced. A study by [3] on the durability of vegetable fibers with polymer modified cement matrix showed enhanced dimensional stability after 50 numbers of wet and dry cycles. As reported by the authors, this improvement was caused by the limitations imposed on the pores/voids during the cycles which resulted into enhanced microstructural network of the cement composite. The polymer admixtures also facilitated the reduction of interfacial debonding at the transition zone which ultimately improved the compactness of the vegetable fibre-cement matrix.

Modification with pozzolanic materials such as fly ash, blast furnace slag and silica fume etc. have been reported to improve the durability of the composite as well by reducing the calcium hydroxide which is responsible for the formation of alkaline environment that degrades the vegetable fibers [13]. Due to the high pozzolanic activities attached to their reaction in the matrix, they are capable of effectively consuming the formed calcium hydroxide within the cement matrix thereby enhancing the durability of the vegetable fibre cement composites [24, 39].

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The Roles of Vegetable Fibres in Green Chemistry

A. T. Ajiboye, K. O. Otun, H. F. Babamale, and L. B. Abdulra'uf

1 Introduction

Green chemistry holds a prominent position in the fabrication of chemical products and processes that lessen or wipe out the utilization and production of harmful substances [1]. In turn, this has provided chemists and researchers worldwide with a captivating technology for groundbreaking research and numerous applications including nanomedicine, drug delivery, nanotechnology, textile technology, catalysis, etc. About 20 years ago, Paul Anastas and John Warner [2] put forward the 12 golden principles that drive green chemistry and which contribute immensely towards sustainable development. These principles, which are summarized in Fig. 1, recommend environmentally benign measures right from the preparation of the material to its synthesis, modifications, analysis, and final use. The key aim is to reduce the environmental and work-related risks associated with industrial operations. Since then, different terminologies have been ascribed to the concept of green chemistry, and these include but not limited to eco-friendliness, cleaner production, atom efficiency, atom economy, sustainable chemistry, renewable energy sources, process integration, and environment-friendliness, among others [3].

Fast-forward to today, the concept of green chemistry has advanced from quantifying the greenness of a chemical process to measurement of variables that include

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A. T. Ajiboye (✉) · K. O. Otun · L. B. Abdulra'uf
Chemistry Unit, Department of Chemical, Geological and Physical Sciences, Faculty of Pure and Applied Sciences, Kwara State University, PMB 1530, Ilorin, Kwara, Nigeria
e-mail: abdulfatai.ajiboye@kwasu.edu.ng

K. O. Otun
Department of Chemistry, University of South Africa, P Bag X9, FL 1710, South Africa

H. F. Babamale
Department of Industrial Chemistry, University of Ilorin, PMB 1515, Ilorin, Nigeria

School of Chemical Sciences, Univesiti Sains Malaysia, 11800 Gelugor, Penang, Malaysia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_19

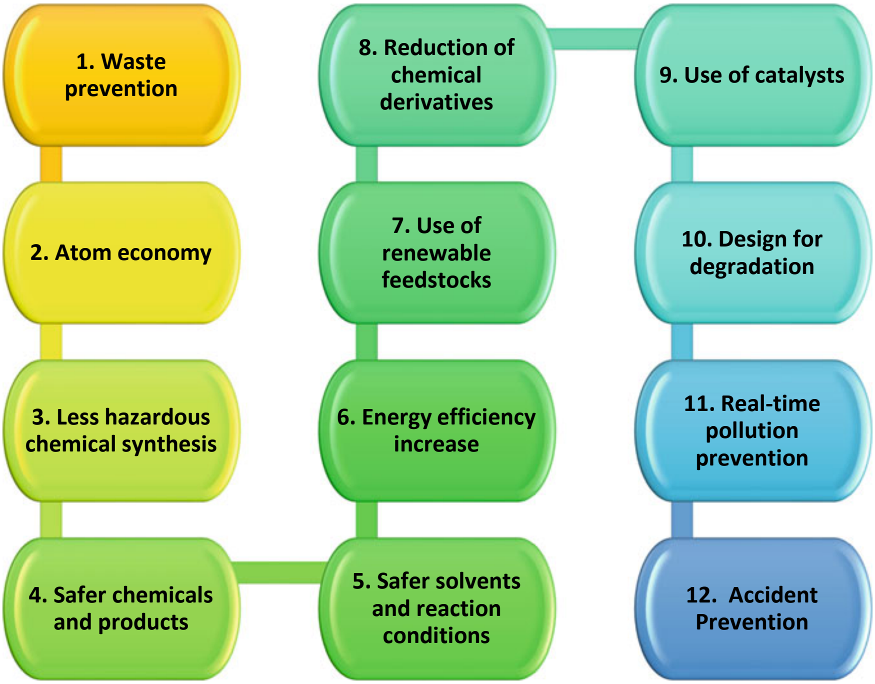


Fig. 1 The 12 principles governing green chemistry as coined by Anastas and Warner [1]

chemical yield, the cost of feedstocks, safety in managing chemical substances, energy profile, ease of product workup and purification, among others. This has also seen several agencies, countries and institutions showing commitments to the goals of green chemistry such as the US Environmental Protection Agency (EPA) that is fostered with the responsibilities of pollution control for sustainable development. Others include the University of New York which founded Green Chemistry Network in conjunction with the Royal Society Chemistry and established of Journal of Green Chemistry; and we also have National Cleaner production Centre in South Africa (NCPC-SA) that plays a key position in the African Roundtable on Sustainable Production and Consumption (ARSCP), among others [4–6].

Different materials have revolutionized the concept of green, and this includes an indispensable vegetable fiber [7]. The roles played by vegetable fibers in green chemistry and sustainable development cannot be overemphasized. Each year, many synthetic fibers are being substituted and high energy consuming products are also being swapped with vegetable fibers and their composites. The reasons for this are not farfetched; it is because of their numerous environmental and economic benefits which include renewability, recyclability, and low consumption of resources in the production processes, among others [8–10]. They have also been influencing many applications as green, economic, and biodegradable plastic composites [11].

2 Vegetable Fibres

Natural fibres, which can also be regarded as vegetable fibers, encircle all forms of fibres extracted from different parts of plants. They are basically grouped into primary and secondary based on their utilization. While those fibers that are produced for their fiber compositions are referred to as primary fibers, the secondary fibers are those obtained from some other preliminary usage as a by-product. Examples of primary fibers include, but not limited to kenaf, jute, sisal, hemp, cotton, while secondary fibers include coir, pineapple, stalks, agave, cereal, oil palm, among others [12]. They may also be classified as leaf, bast, seed, wood, stalk, fruit and grass according to their sources [13]. Vegetable fibres consists of hemicellulose, cellulose, lignin, pectin, waxes and water-soluble compounds, with the exception of cotton fibres containing about 90 wt% cellulose, 5.7 wt% hemicellulose, 1 wt% pectin and 0.6 wt% waxes [14].

2.1 Bast Fibres

Bast fibers consist of bundles of fibers in the inner bark of stems of dicotyledonous plants, enclosed by a stem supplying the plant stem with structural stiffness and strength [12, 15]. The bundles have up to 25 basic units of fibers between 22 and 5 mm length and a diameter found with the range of 10–50 μm arranged laterally in a 3D network. Basic fibrils and bundles are reinforced by intercellular components of lignin and pectin, which must be got rid of during the extraction process [16, 17]. In terms of applications, bast fibers are used not only in the textile industry but also to fabricate green composites for applications in constructiton industries, building materials, nanomedicine, cosmetics, biopolymers etc. [16]. Examples of bast fibre include flax, jute, ramie, hemp, kenaf, among others [12, 15].

2.1.1 Flax

Flax fibres are obtained from the stems of the plant *Linum usitatissimum.* Flax is popular for its diverse applicability because of its intriguing properties including high thermal and mechanical resistant properties. It is a cellulosic fibre like cotton, although it is harder and tougher to handle due to its higher crystallinity [18]. Its applications cut across textile markets, and in the fabrication of thermoplastic matrix composite for automobile components [19–21]. The flax fibres have a smooth handle and look very lustrous. Fibre lengths range from 6 to 65 mm, but they are around 20 mm long on average. Their diameter is approximately 20 μm. It is produced in temperate regions and is one of the world's oldest fiber crops [16, 18].

2.1.2 Jute

Jute is a bast fiber, typically obtained from the bark of the white jute plant, Corchorus capsularis or tossa jute (*Corchorus olitorius*) [17] from the genus Corchorus. It is a long, smooth, shiny and cheap fiber with the highest output volume that can be spun into rough, solid threads [16, 18]. It is also the most flexible fibre available, eco-friendly, natural, robust and antistatic [16]. The fibers contain 61–71% cellulose, 14–20% hemicellulose, lignin (12–13%) and pectin (0.2%) [19]. The best conditions for the growth of jute are provided by Bangladesh, India, and China. Jute is an annual plant that thrives in monsoon climates and grows up to to 2.5–4.5 m [18]. In addition to being used as carpet backing, jute scrims, tarpaulins, canvas, tar felts, and soil savers, jute and jute-like mesta fibres are historically used for packing as sacking, hessian bags and soil savers. Jute is also used as technical textiles, geotextiles, agro-textiles, handicrafts [22] and as thermoplastic composites for the automotive door panel industry [23].

2.1.3 Hemp

Hemp is another prominent fiber belonging to the Cannabis family. It is an annual herbaceous plant native to Central Asia and is known to have been cultivated more than 4500 years ago in China. It grows easily to a height of 4 m without additional chemicals and consumes large quantities of carbon. True hemp is a fine, light-colored, lustrous and strong fiber obtained by retting [16, 24]. Chemically, hemp is composed of cellulose (77%), pectin (1.4%) and waxes (1.4%). In the middle lamellae, pectin is found and glues the elementary fibres to form bundles. The fibre is an embedding part of lignin (1.7%). It encrusts cellulose and contributes to the fiber's hardness and strength. It is found in the primary cell wall of the middle lamella and fibre. Other components of hemp fibres are tannin, resins, fats, proteins etc. In hemp, the content of such components is much higher than in cotton [16]. Hemp is historically used in textile manufacturing, but due to interest in alternative renewable resources, its use has gained relevance in many industries in recent years. Applications have been reported in the manufacture of composites, special cellulose materials (papers), as well as technical textiles, geotextiles and agricultural textiles [25]. Its use has also been well documented in the automotive sector [24].

2.1.4 Ramie

Ramie originally belonged to the Urticaceae family and is native to Eastern Asia. Ramie fibres are extracted from the nettle family's stem of the plant Boehmeria nivea. In fiber bundles, individual fibre cells in stems are connected together by hard-to-remove waxes, hemicelluloses, lignin and pectins. The efficiency of the retting method traditionally used for the extraction of hemp fibers, for example, can therefore not be sufficient to extract ramie fibers from stems. A hybrid microbial and chemical treatment is, however, very efficient and cost-effective. The chemical composition of ramie fiber is as follows: cellulose (91–93%), hemicellulose (2.5%), pectin (0.63%) and lignin (0.65%). Ramie fibers have excellent mechanical properties, i.e. the strongest in the bast fiber category (45–88 cN/tex) and, like most natural cellulose fibers, when fibers are wet, the strength increases by 25%. The ultimate fiber length is between 120–150 mm and 40–60 μm fiber diameter. Fibres are robust and have strong resistance to attacking bacteria, mildew and insects. Its poor elasticity (elongation at break is 3–7%) is the key drawback of ramie, which means it is rigid and brittle [19]. The fibres are oval to cylindrical in shape and are white and highly lustrous in color. The surface of the fibres is rough and marked by small ridges, striations and deep fissures. By its coarse, thick cell wall, absence of twist, and surface characteristics, ramie fibre can be easily identified [26]. Of all the vegetable fibers, ramie is the strongest and therefore has great potential for advanced applications. It is used for fabrics, ropes and for producing blanks of currency paper [22].

2.1.5 Kenaf

Kenaf belongs to the Hibiscus family and is obtained from Hibiscus cannabinus by its fibres. It is a new generation in the USA and demonstrates strong potential for use in composite goods as a raw material. In India and Bengal, it is known as mesta, in South Africa as stock root, in Indonesia as java jute, and in Taiwan as ambari [18, 23, 27]. There are two types of fibers in Kenaf: long bast fibre bundles in the cortical layer and short bast fibers in the ligneous region. The elementary fibres are small, with a fibre length varying from 3 to 7 mm and a diameter of 21 μm on average. With rounded edges, the cross-sections are polygonal and the lumens are mainly wide and oval to circular in shape [26]. Kenaf has a high rate of growth, growing in about 4–5 months to heights of 4 to 6 m. There is great interest in this plant in Malaysia as it grows rapidly and can produce two crops per year in the local climate [23, 27]. Kenaf fibres contain about 45–57% of cellulose, 21.5% hemicelluloses, 8–13% lignin and 3–5% pectin. Kenaf fibres are coarse, brittle and difficult to process. Their breaking strength is similar to that of low-grade jute and is weakened only slightly when wet. There are many potential specific utilization possibilities for kenaf whole stalk and outer bast fibres, including paper products, textiles, composites, building materials, absorbents, etc. [17].

2.2 Leaf Fibres

Leaf fibers are sometimes referred to as stiff or cordage fibers found in the leaf fibrovascular systems of perennial, monocotyledonous plants cultivated in the Philippines, Central America, East Africa, Indonesia and Mexico [28]. They have restricted commercial value, primarily because they are stiffer and coarser than the bast fibers in general texture. By mechanically scraping away the non-fibrous material, the fibres are normally collected from the leaves The fibres of the leaves are primarily used for the manufacture of cordage and ropes. Sisal, abaca henequen [16] and pineapple are the most important fibres of this group.

2.2.1 Sisal (*Agave sisalana)*

Sisal fibre is a hard fibre derived from the fresh leaves of the Agave sisalana sisal plant. It is normally obtained by a method of decortication, in which the leaf is smashed between rollers and then scraped mechanically. The length of the sisal fibre spans between 0.6 and 1.5 m and ranges from 100 to 300 μm in diameter [17]. The content of cellulose in sisal fibres is around 70%. The fiber consists of multiple elongated fiber cells narrowed to both ends.. Middle lamellae, consisting of hemicelluloses, lignin and pectin, bind fibre cells together. A cross-sectional sisal fibre is composed of around 100 fibre cells. The dimension of the cross-section of sisal fibres is neither circular nor reasonably uniform. The size of the lumen varies, but it is generally well defined. The longitudinal form is roughly cylindrical. It is fairly coarse and rigid with sisal fibre. The tensile properties of the sisal fibres along its length are not uniform. The fibres extracted from the root or lower parts of the leaf have a lower tensile strength and modulus. There is a lower tensile strength and modulus in the fibres derived from the root or lower sections of the leaf. The fibers at the midspan become stronger and stiffer, and the fibers extracted from the tip have mild properties. Because of its high cellulose and hemicellulose content, the lower grade fibre is processed by the paper industry. In the cordage industry, medium grade fibre is used for the manufacture of cords, balers and twine binders. After preparation, the higher quality fibre is processed into yarn and used by the carpet industry [16].

2.2.2 Abaca (Manila Hemp)

Abaca or Manila hemp is harvested around the trunk of the abaca plant from the leaf sheath (Musa textilis). In the form of strands, commercial fibers are used, and the strands are made of bundles of individual fibers in turn. Individual fibres are smooth and fairly uniform in diameter when separated from the strands by boiling in an alkali solution. In relation to wall thickness, the lumens are high. Cross-marking is unusual, with pointed and sometimes flat and ribbon-like fibre ends. The technical fibres have a length of 2–4 m. The single fibers have narrow pointed ends and are relatively smooth and straight. Individual fiber diameters vary from 14 to 50 μm and from 2.5 to 13 mm in length [26]. Chemically, abaca contains 76.6% of cellulose, 14.6% of hemicellulose, 8.4% of lignin, 0.3% of pectin, 0.1% of wax and fat. As one of the strongest of all natural fibres, Abaca is known to be three times stronger than cotton and half that of sisal, and is much more resistant than other vegetable fibres to saltwater decomposition. Abaca is a lustrous, yellowish white fibre. Abaca fibres are primarily used for the development of ropes and handicraft goods [25].

2.2.3 Henequen

A close relative of the sisal plant is the Henequen (Agave fourcroydes) plant of the agave family. The henequen plant is native to Mexico, where since pre-olumbian times it has been a source of textile fibre. Many variables may affect the properties of the fibre, including climatic conditions, plant age, soil type, method of extraction, etc. Approximately 77% of cellulose, 4–8% of hemicellulose, 13% of lignin and up to 6% of pectin and waxes are composed of Henequen fibre [25, 29]. Thses fibres have adjustable diameters, which are bigger at the tail end and smaller at the end of the fiber. The diameter is often related to the origin of the fibre; fibres produced at different spots have different diameters. The cross-section of the fiber varies from a bean-like shape at the end of the tail to a rounded shape at the end of the fiber. Henequen fibres, like sisal, are smooth, straight, yellow and easy to degrade in salt water. Henequen has low break elongation and low modulus compared to other leaf fibres, but a relatively high tenacity, which makes it ideal as a polymer reinforcement [25].

2.2.4 Pineapple Leaf Fibre

Pineapple leaf fibre is collected by mechanical or retting methods from the leaves of pineapple. Pineapple leaf fiber is a natural fiber option that is more compatible and has a strong chemical composition [30]. It composed of high quantity of cellulose (81.27%), low contents of hemicelluloses (12.31%) and lignin (3.46%) [31]. Its higher cellulosic content is comparable to that of stem fibers of oil palm, coir and banana [32]. In producing threads for textile fabrics, sporting equipment, baggage, cars, cabinets, and mats, pineapple leaf fibre is used [30]. It is also used in cosmetics, medicine, chemical-coating biopolymers [33, 34] and in the manufacture of paper in Malaysia [35].

2.3 Seed-Hair Fibres

The seed-hair fibres are manufactured from the plant's seed or fruit [36]. They are cellulosic fibers that are often bound or encapsulated in husk to hairs or fibres that may be fibrous and commercially relevant. These include kapok, cotton, coir, etc.

2.3.1 Cotton Fibre

The fiber of cotton is derived from seeds of the plant species Gossypium, belonging to the genus Malvaceae. It's a shrub native to the world's tropical and subtropical regions. It could rise to 0.5 ± 1.5 m in height. In the United States, nearly all commercial cotton is the species Gossypium hirsutum (upland cotton) and G. Barbadense

Barbadense (Egyptian cotton). There are two types of cotton fibers: longer fibers known as lint, and shorter fibers recognized as linters. Although linter fibers are shorter (2 ± 7 mm) and more cylindrical, lint fibers are smooth and twisted and have thicker cell walls than lint fibers. Upland cotton has a length of 15 ± 30 mm of medium fiber and a width of around 20 m (12 ± 38 m) of fiber. Egyptian cotton has a length of 20 ± 40 mm of medium fiber and a width of 22 m (15 ± 40 m) Cotton fibres constitute of 80–90% of cellulose, 6–8% of water, 0.5–1% of waxes and fats, 0–1.5% of protein, 4–6% of hemicellulose and pectin, and 1–1.8% of ash [37].

Cotton is hydrophilic, and in water, the fibres swell greatly. In water, fibres are flexible and their wet tenacity is up to 20% higher than their dry tenacity (25–40 cN/tex). Compared to hemp fibres, the strength and initial cotton modulus are lower, although its elongation at break (5–10%) and its elastic recovery are higher. The fibres are alkali-resistant but acid-degraded. Cotton has low microbial resistance, burns rapidly and effortlessly, can be boiled and sterilized, and does not lead to inflammation or other allergies [37, 38]. Cotton seed fiber, as well as cellulosic textile fiber, is the world's most important natural textile fiber for the manufacture of garments, household goods and industrial products[39].

2.3.2 Coir

Coir is the fiber of seed hair collected from the coconut husk and is a major agricultural waste in Malaysia [40]. Coir is a natural fiber that has a high proportion of lignin. This high proportion of lignin makes the fiber of the coir very resistant to bio-degradation. Coir fibre is commercially used to produce brushes, rugs, sacks, doormats, insulation panels, mattresses and packaging materials [41]. Coir is also used for soil erosion and prevention of sedimentation [42].

2.3.3 Kapok Seed Fibres

Kapok (Ceiba pentandra) contains 35–50% of cellulose, 22–45% of hemicelluloses, 15–22% of lignin and 2–3% of waxes, and is a highly lignified organic seed fiber. It also contains smaller starch amounts, around 2.1% of proteins, and iron (1.3–2.5%) inorganic substances. Kapok contains 70–80% air and offers outstanding thermal and acoustic insulation [16]. Kapok is a cylindrically shaped, smooth, unicellular, twistless fabric. With characteristic air bubbles in the lumen, kapok fibers are transparent by microscope inspection. The wall structure of the kapok cell varies from other natural cellulosic fibres. The primary cell wall, directly connected to the superficial properties of the fibers, consists of short microfibrils, rectangularly oriented to the fibre surface. Microfibrils in the secondary cell wall run almost parallel to the axis of the fibre [26, 43–46]. Given the alpha-cellulose material, kapok is more like wood than flax and other plant fibres. The average polymerisation degree is 6600 [44]. Kapok fibres, with a diameter of 20–43 µm, are 10–35 mm long. The thickness of the cell wall is around 1–3 µm. 0.84 cN/dtex (93.3 MPa), Young's module 4

GPa, and 1.2 percent breaking elongation are the tensile strength [36]. Kapok has an outstanding capacity for liquid retention due to its large lumen. Its outstanding insulating thermal and acoustic properties, high buoyancy and strong absorption of oil and other non-polar liquids distinguish kapok from other cellulosic fibers. Kapok is primarily used in stuffing and nonwovens; it is seldom used in yarns, mainly because of its fibers' poor cohesiveness and durability, brittleness and low strength. In the field of technical textiles, yachts and furnishing of vessels, insulating materials in cooling systems, sound insulation, industrial filtration of wastewater, elimination of spilled oil from water surfaces and reinforcement components in polymer composites, kapok has new potential [43]. A photograph of some extracted vegetable fibres is shown in Fig. 2.

3 Roles of Vegetable Fibers in Green Chemistry

Vegetable fibers which are a class of natural fibers have received a huge attention from researchers across the globe due to their intriguing characteristics such low density, biodegradability, ease of recyclability, and low price [47]. Additionally, vegetable fibers are renewable and have a CO_2-neutral life cycle, especially when compared with their synthetic components (such as glass and carbon) [48]. The use, reuse and recycling of vegetable fibers subside environmental hitches, and subsequently make them highly influential in green chemistry. Many countries have abundance of vegetable fibers in their unprocessed forms which can serve as a continuous source of renewable materials that require less amount of energy and less difficulty to process [49].

Vegetable fibers, which may also be referred to as lignocelluosic fibers, contain majorly cellulose and have found limited applications when they are present in their raw forms [50]. However, they can be refined or chemically modified to afford distinct properties that are useful in sustainable and green technology. One of such modifications is the transformation of vegetable fibers to produce biocomposite materials because of their cost effectiveness, recyclability, and ability to compete favorably with respect to strength per weight of material. The vegetable fibers-derived materials are versatile and valuable resources with several benefits. Their eco-friendliness, low density and availability have endeared them to several applications in textile industry, paper making, construction, automotive industry, among others. Apart from the polymers, several other synthetic materials have been functionalized with vegetable fibers hybrid composites containing vegetable fibers and filler materials [51].

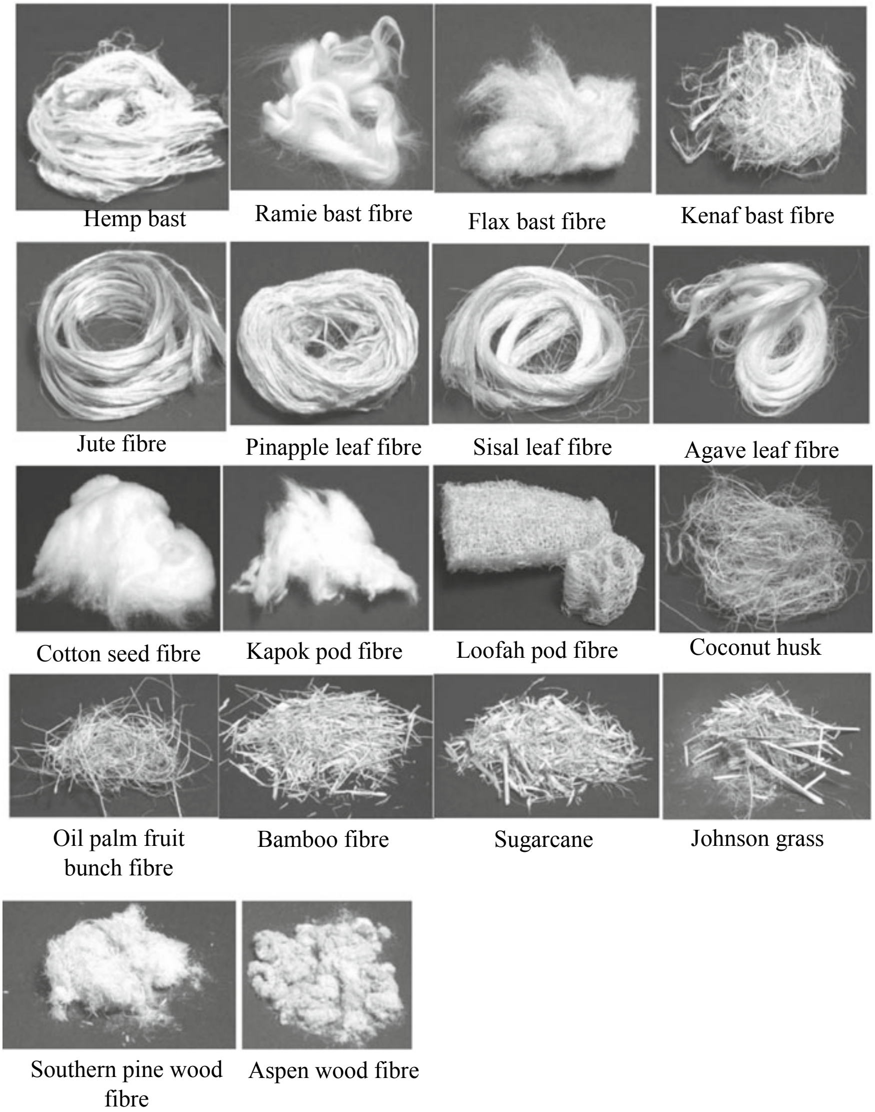

Hemp bast
Ramie bast fibre
Flax bast fibre
Kenaf bast fibre
Jute fibre
Pinapple leaf fibre
Sisal leaf fibre
Agave leaf fibre
Cotton seed fibre
Kapok pod fibre
Loofah pod fibre
Coconut husk
Oil palm fruit bunch fibre
Bamboo fibre
Sugarcane
Johnson grass
Southern pine wood fibre
Aspen wood fibre

Fig. 2 Photographs of some vegetable fibres [12]

3.1 *Green and Sustainable Paths Towards Vegetable Fiber Composites*

As mentioned earlier, for vegetable fibers to have much pronounced roles in green technology, they must be functionalized with other materials to produce composites with proven applications in different fields. These composites need to either be 100%

green or partially green for sustainability as depicted in Fig. 3. By green composites, we mean those composites whose compositions are all sourced from renewable resources and which can mitigate emission of CO_2 and lessen over-reliance on petroleum products. In contrast, the partly green composites are those in which one of their components is not derived from renewable resources. Some of the petroleum-derived polymers that can be used to reinforce vegetable fibers include polyethylene, polypropylene, epoxy, unsaturated piolyester, vinyl ester, among others. They can be processed by several techniques that include compression molding, extrusion, injection molding, sheet molding compound, etc. [52]. The resultant properties of the bio-based composites produced depends on intrinsic properties of the constituents that make up the composites, the processing techniques adopted, compatibility and interfacial adhesion between the polymer and the fiber [53].

Meanwhile, the scourge of global warming and other related environmental challenges have given rise to the more sustainable use of vegetable fibers as composite materials. Benefiting from the intriguing properties of vegetable fibers, the composites derived from vegetable fibers exhibit substantial toughness, flexibility, ease of processing, availability, low cost, and minimal environmental risks. However, the formation of these composites my suffer from some challenges such as lack of interfacial adhesion emanating from lack of compatibility between the hydrophilic vegetable fibers and hydrophobic host matrices [54]. Several approaches have been deployed to overcome this challenge which include but not limited to chemical methods or grafting hydrophilic fibers with hydrophilic chemical species [55]. Although the use of toxic chemicals is not sustainable and can limit the greenness of the vegetable fibers from which the composite was derived.

Alternatively, finding sustainable solutions that combine environmentally benign methodologies while preserving the goals of enhancing interfacial adhesion between matrix and filler is only the way to go as far as green chemistry is concerned. In the light of this, scientists have found, for instance, biobased matrices as appropriate and renewable hosts for interaction with the hydrophilic groups of the vegetable fibers

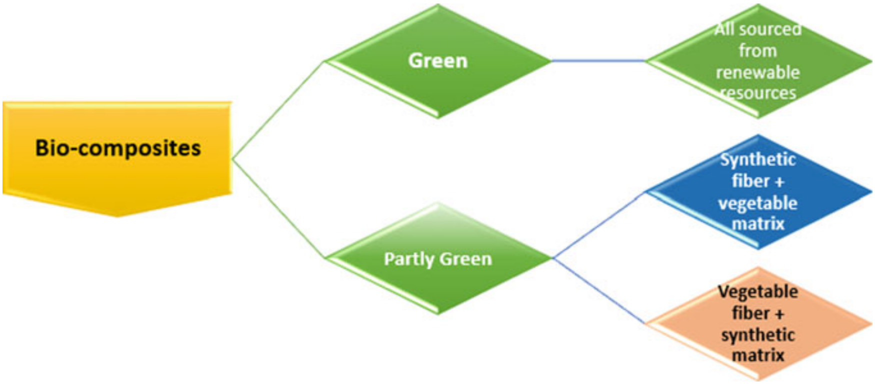


Fig. 3 Classification of biocomposites into green and partly composites (Adapted from [56])

[57]. Examples of this could be seen in several studies involving the use of soybean as host to synthesize vegetable fibre-derived composites with outstanding interfacial adhesion [58–61]. Moreover, another sustainable approach is the fabrication of all cellulose composites in which both the matrix and reinforcement contained entirely cellulose, thus enhancing the interfacial adhesion to produce composites with excellent properties [62]. Evidently, green biocomposites are, without an iota of doubt, the solution not only to the ever-increasing environmental threat but in overcoming the obstacles associated with petroleum products and their supply. Because of the high demand of vegetable fibers globally, the market size of composites of natural fibers is expected to hit 6.5 billion USD by 2021, with about 11.7% compound annual growth.

Recently, Guigo et al. prepared all green composites that comprise flax fibers and resins of humins. It was shown that humins offer good adhesion between the fiber and the matrix, which formed a good interface and enhanced their tensile properties. In this study, the use of humins for functionalizing vegetable fibers is attractive because both are green and can effectively solve the problems related to compatibility of the host and substrate [63].

Overall, as much as it is highly important to use vegetable fibers to make up for the drawbacks of synthetic fibers, it is equally critical to employ treatment methods that will not defeat the main objectives of green chemistry.

4 Vegetable Fibers and Composites for Different Green Applications

Recently, focus has been shifted to vegetable fibers to make up for the drawbacks experienced in using synthetic reinforcement to fabricate polymeric matrix composites employed for various applications in building, textile, and automotive industries, among others For instance, materials made from vegetable fibers are well known and have been increasingly used to make building materials especially in developing countries because of the inherent advantages [64]. In Europe, hemp and flax are cheaply available and are regarded as captivating vegetable fibers to replace glass fibers in composites. However, design of sustainable green composites with enhanced properties that can withstand not only high-performance lightweight demands but also the strict environmental conditions is quite challenging. Reinforcement of two or more vegetable fibers is one of the techniques that combine the advantages of the two materials and exhibit superior mechanical performance and environmental impacts, leading to excellent sustainability [65]. Herein, we will discuss ways in which vegetable fibers have contributed to the green and sustainable developments in different applications.

4.1 Green Automobiles

Vegetable fibers such as flax, hemp, jute or kenaf have been largely used in automotive industry to make different materials. For vegetable fibers and their composites to offer green solutions in automotive sector, they must possess desirable qualities in addition to their eco-friendliness. The use of biocomposites in this industry is not only environmentally benign but also reduce weight via replacement of high-density synthetic fibers with low-density vegetable fibers [66]. Interestingly, lightweight vehicles minimize cost with respect to cost of production and fuel consumption, which will subsequently lessen the release of CO_2 to the atmosphere. For instance, in 2012, Yang and coworkers reported that when the weight of a vehicle is reduced by 25%, there was an equivalent decrease in the consumption of crude oil by 250 million barrels, and this corresponded to a total reduction in CO_2 emission to the tune of 220 billion pounds per annum [67].

Furthermore, Alves et al. [68] replaced glass fiber, a synthetic fiber with jute fiber (vegetable fibers) to fabricate structural frontal bonnet for a vehicle. It is noteworthy to mention here that the jute fiber did not only reinforce the bonnet but also enhanced the environmental activity of the whole vehicle, simply because of the lower weight of the vegetable fibers when compared with the conventional ones, even though Witik et al. were of the contrary opinion that weight reduction of automobile parts does not always lead to enhanced environmental performance [69].

In another study, Luz et al. examined the environmental implications of substituting talc with sugarcane bagasse fiber to reinforce composites that make up automotive parts [70]. It was concluded from their study that bagasse carbon absorption was observed during cultivation, which ultimately mitigates greenhouse gas emissions and ensures cleaner production processes.

In summary, it is obvious that the advances in green chemistry via the use of vegetable fibers are not only useful for weight reduction of automobile parts and clean environmental but also beneficial for renewable and sustainable development. Additionally, vegetable fibers can be modified to generate biocomposites which can serve as good substitutes or even perform better than the synthetic polymer-fiber composites. As a result of this, they can proffer solution to waste disposal challenges of synthetic polymer-based composites.

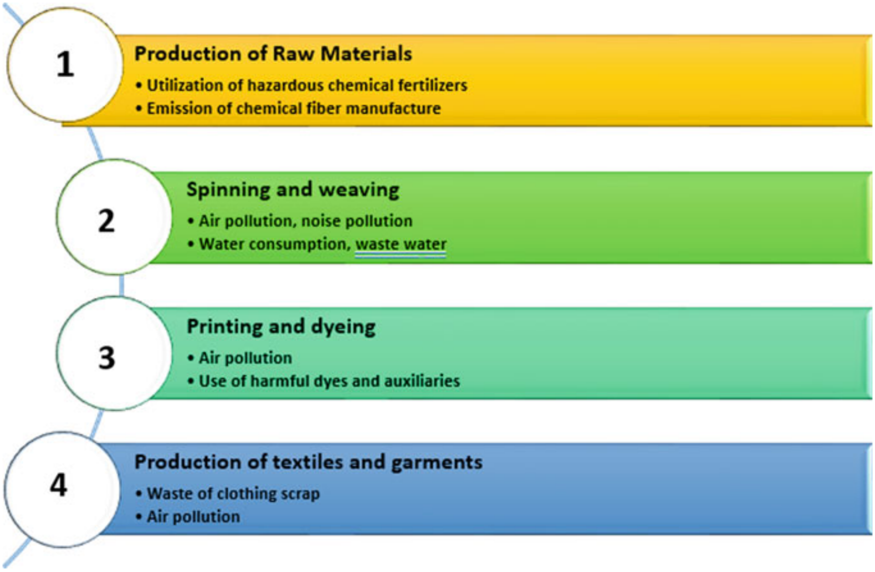
4.2 Green Building Technology

Vegetable fibers represent a promising solution to optimize environmental sustainability in construction companies. Unlike synthetic fibers, vegetable fibers have widened the field of applications in construction sectors because of their excellent hygrothermal and sound insulation characteristics. Additionally, these materials also allow good storage of carbon because of the sequestration of CO_2 during agricultural activities. Of course, the trees do not only absorb CO_2 as they grow, but also requires less energy to process them into construction materials [71].

Furthermore, for a material to be useful in green building technology, they must possess characteristics such as ease of recyclability, renewability, and minimal consumption of resources during production chains. Interestingly, vegetable fibers match perfectly all these requirements and can sometimes exist in form of fiber mats with credible sustainability features, by being biodegradable and retrievable [72]. Moreover, these fibers can be reinforced with cement, sand, and other materials to improve their properties. Based on this, it is reasonable to replace petroleum-based composites with biocomposites to reduce their rate of impacts on human health and environment. In summary, to foster the growth of sustainable construction materials, the use of vegetable and green materials has to be prioritized to minimize the risks associated with climate change and other health risks.

4.3 Green Textile Industry

One of the goals of textile manufacturers is to find sustainable and biodegradable materials for their products to get rid of the negative impacts of man-made fibers (acrylic, polyester, nylon, etc.) [73]. This is because all the processes involved in textile production have impacts on the environment and human health in one way or the other. These effects are shown in Fig. 4.



1 **Production of Raw Materials**
- Utilization of hazardous chemical fertilizers
- Emission of chemical fiber manufacture

2 **Spinning and weaving**
- Air pollution, noise pollution
- Water consumption, waste water

3 **Printing and dyeing**
- Air pollution
- Use of harmful dyes and auxiliaries

4 **Production of textiles and garments**
- Waste of clothing scrap
- Air pollution

Fig. 4 Processes involved in textile making and associated effects on environment and human health

Table 1 Applications of vegetable fibers for green applications

S/N	Application	Example	References
1	Storage devices	Supercapacitors, lithium ion batteries	[76]
2	Electronic gadgets	Cable wires, optical fibers	[77]
3	Housing	Door panels, upholstery, interior designs, carpet, mats	[78]
4	Sport equipment	Ball, tennis racket	[79]
5	Transportation	Railway interior design, bonnet, vehicle doors, etc	[80]

However, vegetable fibers are biodegradable and can satisfy the demands of these manufacturers. Cotton is a renowned natural fiber with a big market share in textile industry, although its cultivation involved widespread use of toxic chemicals and large amount of water which calls for economical and environmental concerns [74]. As a result of this, other sources of natural fibers including hemp, flax, banana, sisal, bamboo and organic cotton, can be used as ecofriendly and energy-efficient bioresources in textile industry Of all these, organic cotton can serve as a sustainable replacement for the conventional cotton. Another vegetable fiber on the list is the bamboo that is 100% biodegradable and naturally regenerative [75]. It has shown good promise in the textile industry due to its exceptional sustainable properties that can help satisfy human needs and at the same time helps keep our environment green. The widespread use of green chemistry, balanced by economic and market realities in the textile industry, would obviously pave the way for a future of cleaner and more environmentally sustainable goods. Other potential applications of green fibers are summarized in Table 1.

5 Challenges of Vegetable Fibers in Green Chemistry

Despite the successes recorded by vegetable fibers in green technology, they do experience some drawbacks which may limit their practical green applications. These include:

1. Vegetable fibers incorporating polymeric composites have some disadvantages that include lack of compatibility between hydrophilic fibers and hydrophobic matrices. As such, this requires adequate use of physical and chemical pretreatment processes for the adhesion of the vegetable fiber and host matrix.
2. Vegetable fibers are prone to biodegradation; hence composites derived from them are at higher risk of degradation under applications when compared with the synthetic fibers.
3. Vegetable fibers have sometimes; low mechanical properties and poor moisture resistance and this may limit their applications to interior and non-structural applications.

6 Conclusions

In recent times, rapid economic boom coupled with technological advancement have generated significant advancement in human endeavors, while at the same time, led to environmental pollution and destruction of natural resources around the world. In light of this, global attention is being paid to the new paradigm and innovations based on renewability and sustainable development where the terms such as ‘green’, “ecofriendly”, atom economy, atom efficiency, environmentally benign, etc. are the order of the day. In this chapter, we have summarized the properties vegetable fibres, discussed their roles in green chemistry and highlighted the challenges that limit their applications in different fields. Vegetable fibers represent one of the largest renewable resources known. They are excellent candidates that can replace synthetic fibers such as glass and carbon fibers in composite applications. When vegetable fibers are used as precursors in fabricating composite materials, they bring both economic and environmental benefits, and subsequently advance the course of green chemistry. Consequently, they have a role to play in the fight against global warming and other environmental challenges. In addition, because they are biodegradable, they can be employed as thermal energy at the end of their life cycle, hence not contributing to the landfill crisis. However, their applications in green chemistry can be limited by factors that include lack of compatibility between hydrophilic fibers and hydrophobic matrices in the course of transforming them to composites for enhanced applications in building, textile, automotive, paper making, among others.

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Tribological Behavior of Glass/Sisal Fiber Reinforced Polyester Composites

M. Ramesh, D. Balaji, L. Rajeshkumar, V. Bhuvaneswari, R. Saravanakumar, Anish Khan, and Abdullah M. Asiri

1 Introduction

It is a usual practice these days to reinforce artificial fibers like carbon, aramid and glass in polymer matrix composites and the common matrix materials used includes either thermosets or thermoplastic materials like polyester, polyurethane, polypropylene, phenolic material and epoxy [1, 2]. In general, glass fibers are usually hybridized with other natural fibers and are employed in various applications due to their appreciable properties [3]. Commonly, synthetic fibers are having limited use owing to their non-renewability and non-biodegradability which gave rise to more environmental friendly fiber materials called natural fibers. In contrast with synthetic fibers, all natural fibers are biodegradable, renewable, sustainable and eco-friendly which could be potential candidate materials for numerous applications in the field of engineering and technology [2, 4–7]. Recent day researches emphasize much towards the hybridization of natural fibers with glass fibers [8]. Yet, it was proven in many stages that natural fibers could act as potential substitutes for synthetic fibers only by partial amount even though they are characterized with merits like surplus

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

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

R. Saravanakumar
Department of Mechanical Engineering, VSB College of Engineering Technical Campus, Coimbatore, Tamil Nadu, India

A. Khan · A. M. Asiri
Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_20

availability, low cost, non-corrosive, non-abrasive and non-toxic nature [9–11]. It was estimated that by 2020, natural fibers can capture the market of fiber reinforced composites by 28% by acting as a significant category of reinforcement in many fiber reinforced plastics materials [12–14].

Sisal fibers (SF) (*Agave sisalana*) is a commonly used natural fiber extracted from the leaves of the plant which has been in the interest of researchers lately because of their appreciable tensile properties, high abrasion resistance and toughness and cheap in cost [4, 8, 11]. Many experiments were conducted previously to determine the mechanical properties of the SF reinforced composites. Few experimenters used randomly oriented SF in epoxy matrix with a weight fraction of 30% and evaluated various mechanical properties of the composites. It was observed from the results that if the length of SF was about 20 mm, it renders maximum impact strength and at the same time SF of length 15 mm rendered maximum tensile and flexural strength [15]. Many researches focused in determining the effects of SF content upon the mechanical properties of fabricated composites and came up with the result that increase in the content of SF led to enhanced mechanical properties with the maximum volume of SF being 40%. Researches for determining the tribological behavior of natural fiber composites, including their coefficient of friction and rate of wear, were very minimum [11, 16–19]. When compared with the tribological studies on individual natural fiber reinforced composites, studies on hybrid composites were still minimum [19].

Experiments were carried out to evaluate the tribological behavior of SF reinforced epoxy composites with various fiber orientations. Results showcased that the wear rate of the parallel SF oriented composites were higher than pure epoxy composites while the lowest wear rate was achieved for the composites with SF oriented in normal direction to the counter facing disc [16]. Tribological behavior of silane treated SF polyester composites and the fiber volume fraction of SF upon the wear behavior of composites ere experimentally analyzed. Two different composition of SF by weight fraction such as 10 and 27% of both silane treated and untreated fibers were used to make the polyester composites. Results exhibited that the influence of the content of SF was not independent and in turn depended on the applied load and a maximum wear rate was obtained for the untreated SF reinforced composites with higher content of SF. Yet, the wear rate of silane treated SF composites were lower and their coefficient friction was also higher which could be attributed to the better interfacial adhesion between the matrix and treated fibers [17]. Xin et al. [18] were the forerunners in experimenting the SF reinforced composites for automobile brake pad applications and evaluated their wear behavior. Authors used NaOH-NH_3 treated SF to fabricate the composites which enhanced the bonding between fiber and matrix. It was reported in the results that SF possessed appreciable wear and friction behavior and could be readily substituted in place of asbestos brake pads [18]. Figure 1 represents various applications of tribo-components in industry.

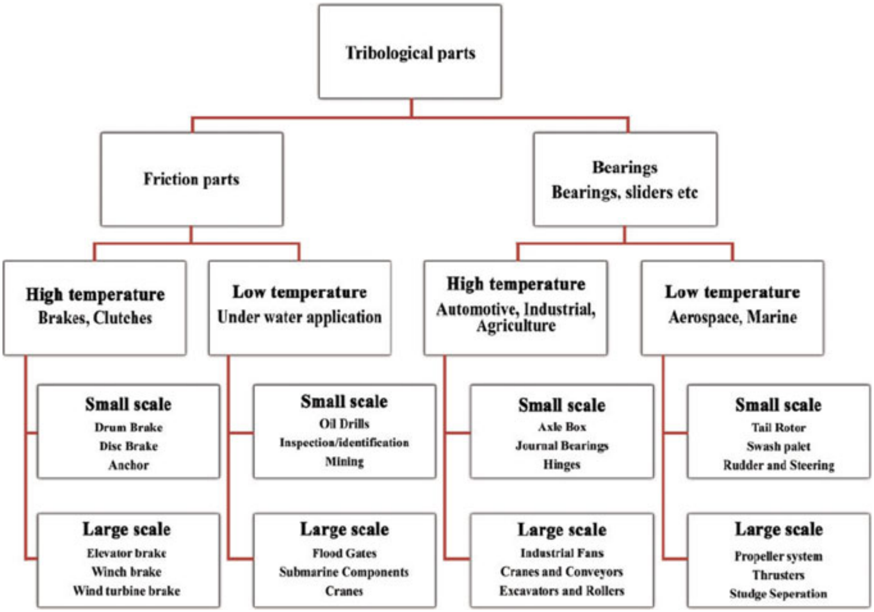

Fig. 1 Various applications of tribology in industries [1]

2 Tribology of Natural Fiber Composites

Tribology is the branch of science that deals with friction and wear behavior of the materials along with the lubrication. Generally, many fiber reinforced composites are fabricated using hand lay-up or compression moulding method and are made to undergo tribological tests of various kinds. Tribological behavior of polymer composites is assessed by two body abrasive wear principle and either pin-on-disc or ball-on-disc equipment is used to carry out the experiments. ASTM G99 standard specify the condition and specimen dimension for wear tests in case of a metal or polymer composite specimen. In most of the cases, the pin material that undergoes wear tests are of dimensions 10 mm × 10 mm × 30 mm in length, breadth and height. Parameters for the wear tests are usually maintained as 20 N applied load for various sliding distances from 25 m to 100 m in intervals of 25 m. Before subjecting to wear tests, the counter facing disc will be polished by 300 grit emery paper to make them devoid of dirt or foreign particles and the flat specimen surface is fixed against the disc. Counter facing disc should be polished with emery paper after each experiment to enhance the accuracy of the reading. Usually, for a two body abrasive wear test, sliding speed, applied load, sliding distance, weight fraction of the reinforcement and disc rotating speed are the parameters influencing the wear behavior of the specimen [19].

2.1 Wear Loss

Wear loss in terms of volume or weight was represented by means of a graphical representation by many researchers for better interpretation of results and the interdependency between the process parameters. Few experiments were conducted in determining the tribological behavior of glass-sisal hybrid composites filled with abrasive SiC powder with epoxy as matrix. An applied load of 20 N and a counter facing disc of steel were used for the test. Evaluation of wear volume loss was determined with sliding distance and applied load as process parameters for both SiC filled and unfilled composites. Results depicted that wear volume loss of the composite material increased with increase in the sliding distance. It was also observed during the experimentation that, the counter facing disc contains the worn-out layer debris of the fibers, matrix and disintegrated powder filler. This prolonged to happen during every test and the debris remained over the counter facing disc until the completion of the experiment. It was also noted from the experiments that as the content of SiC increases the wear resistance of the material also increases due to the wear resistance nature of the powder filler. For a content of 10 wt% of SiC powder within the composites, wear resistance was higher than all other combinations. For the composite containing G-SF-E-10 wt% SiC when subjected to 20 N applied load, 25 m sliding distance and 500 rpm counter facing disc speed, the wear volume loss was noted to be very minimum. Results portray that this combination is the hardest of all combinations as their wear resistance is higher while the unfilled G-SF-E composite experienced lowest wear resistance and hence it was considered to the smoothest of all material combinations [20].

2.2 Specific Wear Rate

Specific wear rate is generally calculated based on the surface area undergoing wear. Interpretation of specific wear could be made by using graphical plot of parameters taken for analysis of wear rate. Experiments on unfilled and filled SF-G-E composites were carried out to evaluate their specific wear rate under an applied load of 20 N and four sliding distances such as 25 m, 50 m, 75 m and 100 m. It was observed from the results that the specific wear rate and the wear loss decreased with the increase in sliding distance. It was also noticed that if the sliding distance increased further, the specific wear rate decreased but at a slower pace and the decrease of specific wear rate from 50 m to 100 m decreased linearly. Authors stated that the above behavior was due to exposure of the composite specimen directly to the counter facing disc at the earlier stage of experiment and the abrasion of smooth epoxy resin was higher at this stage. This phenomenon arises since the SiC fillers were less in quantity and got abraded at the earlier stage of experiments which exposed the fibers and matrix to the counter facing disc. This was evidently observed from the worn-out glass and SF fibers. Epoxy matrix which is of smooth nature abrades at a rapid rate

Table 1 Tribological analysis of various fibers

S. No.	Natural fiber for tribological analysis	Matrix material	References
1	Betelnut fiber	Polyester	[21–23]
2	Sisal with	Polypropylene	[24]
3	Oil palm fiber	Polyester	[25]
4	Coir	Polyester	[26]
5	Kenaf	Epoxy	[27]
6	Cotton	Polyester	[28, 29]
7	Sisal	Phenolic resin	[30]
8	Sugarcane	Polyester	[31]

initially during the experiments and forms a debris layer over the counter facing disc and the fiber layers trail the epoxy layers which constitutes the stronger part of the composites. It could be stated from the above process that the wear resistance of the hybrid fibers were greater than the resistance offered by the epoxy materials against wear. This could be attributed to the requirement of more energy required to disintegrate the fibers than the matrix and hence the wear of fibers slowed down which in turn reduced the rate of specific wear of the material. Similar results were observed by various authors when such hybrid composites were subjected to wear tests [19, 20]. This renders an inference that when thermoset matrix material was used it was concluded from the experiments that the specific wear rate relies on the material composition, counter facing disc hardness and the sliding distance. SiC filled composites exhibited lower specific wear when compared with the unfilled composites. Table 1 enlists various natural fibers and matrix materials used to form composite materials that were subjected to tribological analysis.

2.3 Tribological Analysis of Sisal/Glass Fiber Composites

Many tribological applications are currently available for the composite materials made of natural fibers and the components fabricated with natural fiber as constituents undergo wear in many situations [32–35]. Current focus has been majorly given for determining the wear and friction properties of natural fiber reinforced composites. It was assessed by the earlier studies that 90% of the components failure subjected to wear would be because of loading conditions and hence the studies upon the wear and friction behavior of the natural fiber composite materials [36]. Enhancement or decline of wear properties of the composite depends on the nature of the reinforcement added [37, 21]. Few experiments deals with the determination of tribological behavior of sisal/glass fibers reinforced hybrid composites (Fiber volume fraction of 50:50) and individual fiber reinforced composites. Overall volume of fibers were maintained as 20 and 40% and the friction and wear behavior of composites containing fibers in above volume fraction was determined with the aid of SAE1020 steel as counter facing disc and the influence of fiber volume fraction on the wear behavior was evaluated. ASTM G99 standard was adopted for performing the tribology tests. Experiments were conducted with composites fabricated using E-glass fiber (density: 2.54 g/cc) and sisal fiber (density: 1.13 g/cc) while 40 mm fiber length was adopted. It was reported in the work that the critical fiber length either shorter or longer than that influenced the wear and friction behavior of the composites [20]. The following equation was used to calculate the critical fiber length of the fibers:

$$L_c = (D \times \sigma_f)/\tau \tag{1}$$

where D = diameter of the fiber in mm) σ_f = tensile strength of the fiber in MPa and τ = matrix material shear stress in N/mm^2. Comparison of length of the fibers used and the critical length has to be made and the cut fibers were categorized as long and short fibers if the critical length is more or less than the cut length respectively [36].

Majorly the volume fraction of fibers used in case of sisal (S) and glass (G) were 20% and 40% by volume with four different specimens such as S20, S40, SG20 and SG40 and all the fiber length were long. In Eq. 1, the shear strength of the matrix was determined following ASTM D2344 standards through short beam tests and was found to vary in between 4 MPa and 8 MPa. Similarly, the value of tensile strength was substituted as 600 MPa and the average diameter of the fiber was taken as 0.2 mm. Initially the SF were cleansed and rinsed in distilled water to make them devoid of dirt and contaminants and were dried in oven at 60 °C for a time of 3 h with free air circulation. At the time of fabrication, fibers were oriented randomly and homogenously in different compositions. Content of the fibers used were specified in terms of volume fraction, which in turn is calculated by using the ratio of mass to the density of the fiber. Hydrophilic nature of the natural fibers may render poor mechanical properties due to lower bonding between fiber and matrix at the interface. In order to enhance the interfacial adhesion between the matrix and fiber, sisal and glass fiber mats were dried in oven at 105 °C for a time of 30 min as the sisal fibers were hydrophilic and the moisture content has to be removed. Compression moulding method was adopted to fabricate the composite plate and the mould size was maintained as 15 × 15 cm^2. Contents of the composite were transferred to a hydraulic mould of capacity 6 tons to reduce the volume and the polyester resin of density 1.16 g/cc along with methyl ethyl ketone peroxide initiator was used. Temperature of hot compression was maintained as 80 °C and the holding time was 70 min per specimen and a plate of 3 mm thickness would be obtained. Composites were then post-cured for a period of 4 h at 60 °C in a hot air oven. Table 2 specifies the various fiber volume fractions and their designations used in the current work along with their density values obtained after the plate fabrication [37].

Few experiments were carried out on the sisal/glass fiber reinforced polyester composites to determine their tribological behavior. Specimens were cut from the fabricated composites in circular shape with 18 mm diameter and they were affixed

Table 2 Composition of SF-GF composites [31]

Specimen designation	Overall fiber volume fraction (in %)	Vol. fraction of SF (in % volume)	Vol. fraction of GF (in % volume)	Density of the composite plate
S-20	20	100	0	1.14
S-G-20	20	50	50	1.28
G-20	20	0	100	1.45
S-40	40	100	0	1.12
S-G-40	40	50	50	1.37
G-40	40	0	100	1.70

on the pin-on-disc tribometer with glue in order to perform the wear test. Figure 2 shows the glass, sisal and hybrid composite specimens mounted on the specimen holder of the tribometer against a counter facing disc of SAE1020 steel which is a commonly used engineering material for the disc. Usually, the counter facing disc would possess 12 mm thickness and 160 mm diameter. At the time of wear tests, the counter facing disc was polished with series of sand papers such as 240, 300, 400, 500, 600 and 1200 grit emery in order so as to obtain the surface roughness of the disc as 12 μm (with standard deviation of 1.2 μm) for all the experiments. It was also assumed that, due to low variations in standard deviation the disc would be assumed to have similar during all the experiments. Variation in temperature of the disc and the specimen was tracked and recorded by a k-type thermocouple which was mounted at a distance of 1 mm from the counter facing disc. Figure 3 denotes the pin-on-disc tribometer test setup for performing the tribology tests on composite material from which the friction and wear behavior of the specimen could be evaluated. Test setup possess a range temperature of up to 600 °C, normal force in between 0 and 2500 N and sliding velocity between 1.8 and 16,000 mm/s. Tests setup which renders the tribological characteristics of S-G-E composites had a repeatability of ±0.013 specifically for the coefficient of friction [38].

From the above experiment, coefficient of friction could be calculated through indirect measurement by using the following Eq. 2.

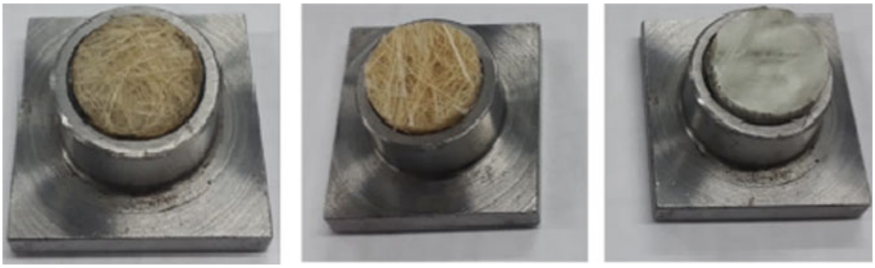

Fig. 2 Wear tests setup of composite specimens against counter facing disc [38]

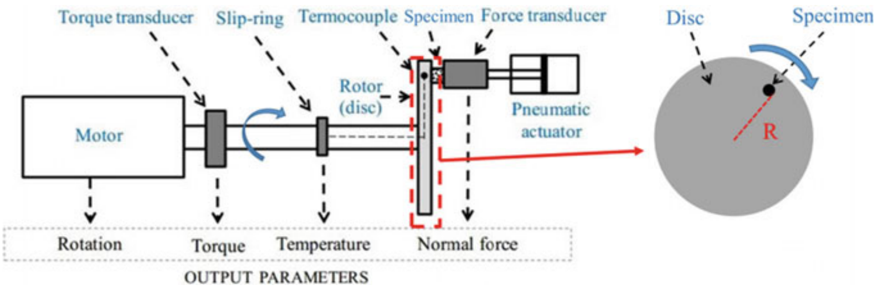

Fig. 3 Tribometer for wear test [38]

$$\mu = T/F_N R \tag{2}$$

Wear tests were usually carried out by the sliding action of the wear pin (specimen) against the counter facing disc made of steel material [39]. Parameters like normal force and sliding velocity were maintained at the same values throughout the experiments. In the above described experiments, a total of four specimens in each composition of S-G-E composites were used and a total of 12 trial runs were made for each specimen. As the adverse effect of thermal degradation of polyester composites had to be dodged during the wear test, all the process parameters such as applied load, sliding velocity, normal force and duration of wear were maintained at certain levels such that the highest value of temperature did not exceed 100 °C. Additionally, a 200 Hz of sampling frequency was set for all the data acquisitions. On the whole, a sliding radius of 40 mm, sliding distance of 900 m, normal force of 150 N, pressure of 590 kPa, speed of rotation of disc as 718 rpm, sliding velocity of 3 m/s and test duration of 300 s were maintained as the process parameters in order to satisfy all the above conditions. Difference between the mass of all the composite specimen were measured before and after the wear tests and the wear rate was determined by means of mass loss in each specimen. For this purpose of measuring the specimen mass, an electronic weighing balance of accuracy ±0.1 mg was utilized. Rate of wear of each specimen based on the wear volume loss using the Eq. 3.

$$\Delta V = (1000 \times \Delta m)/D \tag{3}$$

where ΔV = volume loss of the specimen before and after wear in mm^3, Δm = mass loss of the specimen before and after wear in g, D = density of the composite material taken for analysis which is displayed in Table 2 in g/cc. In the above experiment, it was observed that the counter facing disc had not undergone sufficient wear and hence the influence of counter facing disc material loss was not taken into account for analysis. From the scanning electron microscopic images of worn specimen, it was noted that the no tribofilm was formed over the disc and the mechanism of wear was also discussed. In addition to this, the scanning electron microscope (Model:

Zeiss Axio Lab A1 microscope) was also used to visualize the surface condition of the wear pin before and after test at a macroscopic scale.

2.4 Interrelationship Between Thermal and Tribological Properties

The thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) plot for the composite material comprising of a fiber content of 40 vol. % were analyzed experimentally. It was observed that with the value of 180 °C weight loss of pure glass composite is very less. It was also observed that temperature of the composite compare with wear tests, attained a high value at 110 °C, the weight loss is: for S40 it was 2.96%, for SG40 it was 1.84% and for G40 it was 0.17%. The reason behind this is the emitting hold as a thin film on the outside surface of water at the temperature range of 40–110 °C for both S40 and SG40 containing the SF which was observed from the outcomes of the experiments [40, 41]. Glass fibers started to decompose at temperatures more than 250 °C and for natural composites reinforced with lingo cellulosic fibers, such as sisal, the safe operating temperature was noted to be 250 °C [42, 43]. Compared with S40 and SG40, G40 had shown a dissimilar performance in TGA. For glass composite one high intensity peak and for sisal and hybrid composites two high intensity peaks were derived as a curve through derivative thermogravimetric analysis (DTG). For both composites S40 and SG40 the initial peak curve value was obtained within the range of 200–400 °C. Usual result of natural fiber like decomposing of cellulose, lignin and hemicellulose was the reason behind this. It was observed that initial peak started at the temperature of 200 °C and fiber decomposition occurred at 361 °C for S40 fiber and for SG40 at the temperature of 371 °C. But unlike the first peak, second peak occurred for both fibers at a temperature of 500 °C. The reason behind this was the generation of tar due to the decomposition of char. For pure glass composite, a single peak generated at a temperature of 381 °C due to the decomposition of polyester resin. 33% Weight sustainability of a glass fiber occurred after this peak because of high thermal resistance of it. There was no important thermal decomposition was suspected for polymer or fiber matrix composites since the temperature of the tribo-tests never exceeded 100 °C.

The average outcome was suitable for wear, coefficient of friction (CoF) and disc temperature generated for all materials. By natural lubrication action of water existing in natural fibers like sisal, CoF of composite material containing sisal fiber as reinforcements was noted to be low. Water absorption of composites occurred after removal of moisture content during its manufacturing process by two ways: either through the pores of the composites or by the exposure of maximum surface area of the fiber reinforcement to the atmosphere at the time of wear test. For individual SF composites, water absorption by those above mentioned method behaved as an oil medium of during wear test. In case of friction value, there was no important variation for both individual glass fibers of SF-GF hybrid composites. Increase in CoF value was noticed as the fiber content increased for all the composite specimens. If sisal bundle was more, then the maximum amount of cavities identified which resulted in discontinuous phases. This is the case in both pure sisal and hybrid composites. CoF is high if intervals or gaps among the composite particles are more. As it was mentioned earlier, CoF was directly proportional to discontinuous phases. Robust abrasive method created by the higher substance of abrasive particles of glass fibers was the major reason for the increment of CoF values of the composites. Wear resistance of raw sisal composites was more amidst the previously studied materials. SF had not undergone much damage during the completion of the tribological tests. This illustrated that the sisal fibers are characterized with a heavy load bearing ability purely because of the thin layer of tribo-film generation upon the surface of the individual SF composites at the time of wear tests.

Wear rate of the composites were decreased through tribo-film which lubricated and protected the surface of the composite material [44]. Further investigation showed that natural fibers reinforced composites resulted with good increment of wear resistance in which tribo-film was present [45]. Tribo-film plays a major role in composites and in individual SF composites it was homogenously dispersed over the composite surface whereas in both individual GF reinforced and SF-GF hybrid composites, no or ultrathin tribo-film on their damaged surface of the components was observed. Perfect resistance to wear of the individual SF reinforced composites was elucidated from the observation temperature readings of S20 and S40 specimens. Surface contact between the specimen and counter face of the polymer matrix is enhanced because of its softening during very high temperature. This also enhanced the actual contact area and generated more frictional force. Few authors investigated that increment in wear rate is directly proportional to energy and friction force. By adding pure sisal as a strengthening agent with composites results in reduction of high temperature, force and effort. This is shown evidently in S20 and S40 specimens in which very low wear occurs on these specimens compare to other composites [46]. The SEM micrographs of the tribo-film in S-20 and S-40 specimen are depicted in Fig. 4.

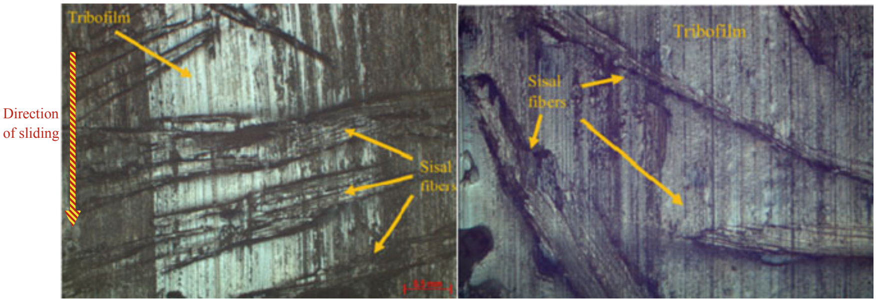

Fig. 4 SEM micrographs depicting the tribo-film in S-20 and S-40 specimen [38]

In previous literatures, effective and proper wear resistance of sisal fiber explained in a sufficient and effective manner. Many experimenters investigated the wear, corrosion and coefficient of friction of composites strengthened by sisal fiber and done the comparison with remaining actual fibers like Bhimal (grewiaoptiva) and Urtica dioica (nettle). Experiments on sisal fibers proved that braking material composites strengthened by sisal fibers can be compared with glass or steel/mineral fibers for wear rate property. At the same time, G20 and G40 composites strengthened by glass results in maximum amount of wear. Special characteristics of glass fiber was found to be split into minute rough particles which is not available in long fibers before investigation [47]. As discussed in previous cases, glass fibers had brittle characteristics that break into very small pieces while making a contact in opposition to the metal counter face which is an anticipated attitude of it. As per previous literature, composite matrix expresses the glass fibers and support for their crack at a temperature of 70 °C. It was remarkable to note that, in natural sisal composites breakage of fibers was not found. That means actual fibers used to get strengthen subsequent to experiment [48]. Scattered pieces of wear debris on the substrate of G20 and G40 specimen create the significant effect of a flexible matrix by scratching the specimens. It is due to the hardness test which ensures the specimen to be hard.

As per the statement of few authors, creation of tribo-film was avoided by this scratching action. By comparing individual SF and GF reinforced composite materials, amalgamation of composites having an intermittent state of wear. The reason behind this is the scratching behavior of the tough GF was incompletely reduced forcibly by lengthy SF which was holding the delaminated portions of GF thereby safeguarding their convenient motion on the composite surface. Glass scattered pieces of rubbish (Glass debris) effect was found in both mixture composite. It cannot behave like an abrasive particle while in contact. It was found that, initiation of tribo-film is high in hybrid composite than in pure glass. But in pure sisal it is more than hybrid composites. Say for example, in SG20, incomplete tribo-film layer could be observed on the composites surface. Main function of creation of abrasive glass debris found in hybrid composite was incomplete formation of tribo-film layer which is used in strengthening the composites. Influence of fiber volume fraction upon the wear was calculated and analyzed by using Analysis of variance (ANOVA), with significance level $\alpha = 0.05$. For both individual GF reinforced and SF-GF hybrid composites, even by adding the volume fraction from 20 to 40 vol. % there was no important or special variation in wear property. Considerable amount of wear is enhanced in raw sisal composites by adding sisal fibers [49].

Many other experimenters stated that there was no considerable amount of wear by increasing the sisal fibers. Many researchers investigated and reported the wear behavior of composites in terms of fiber mixture even it was not sufficient to render the clarification wear and frictional behavior of natural fiber composites [50]. Few researchers done the investigation on wear behavior based on various load applied on the composites. It was done for either glass reinforced or hybrid sisal composites. A high amount of wear rate was observed in sisal fiber-reinforced polyester composite with a sliding velocity of 1–3 m/s and a low amount of wear rate was observed in glass fiber composite with a sliding velocity of 2–3 m/s. Filler content also plays a role in wear rate and it is indirectly proportional to it. As mentioned, the wear rate of the sisal fiber-reinforced polyester composite is maximum of 20% filler content. But for 30% filler content, wear rate is minimum at 3 m/s. Design of experiments (DOE) has been introduced to evaluate which parameter in mostly impacting for wear rate. Most influencing parameters for wear rate was finalized and as follows: sliding speed, filler content and fiber, in that order [51–53]. By varying the silicon carbide filler was examined to two body abrasive wear test for following composites were conducted by using pin-on-disc equipment, those are Fabricated Glass –Sisal-Epoxy, Glass-Jute-Epoxy and Glass-Rubber-Epoxy composites. Different sliding distance (25 m, 50 m, 75 m, and 100 m) for different weight percentage of filler content (0, 5, and 10 wt%)of composites were tested for 20 N load in wear test. It was observed that filler polymer composites produce less wear than the unfilled polymer composites [54].

3 Conclusion

The major conclusions of this chapter could be consolidated that: From thermo gravimetric (TGA) analysis all the wear tests were experimented less than 100 °C temperature. Mass transfer or loss was not credited to changes to the molecular weight (thermal degradation). With less CoF, better wear resistance was achieved by adding individual sisal fibers into the composites materials. Major contribution was by the formation of a thin tribo-layer that enacted as a shielding layer for composites and the secondary contribution was by the water lubrication resulted due to presence of moisture content in natural fibers through absorption from the surroundings. Less wear rate of the composite was found which was strengthened by pure glass fibers. The reason behind this is brittle nature of the hard glass fiber debris present over the worn surface of the composite. Intermittent or biased wear resistance identified in either hybrid sisal or glass composites. Sisal fibers used to save the glass fibers from its free movement into the matrix which reduce the strong abrasive effect of the artificial fibers. Fiber content is a major element to enhance the CoF in all composite specimens. Value of friction is increased by increasing the sisal bundle which creates heavy discontinuous phases into the fiber matrix. While comparing G40 with G20 composite, CoF of fiber was anticipated by reminding robust scratch effect which was created by huge amount of glass fibers. There is not much important in variation of wear by adding 20–40 vol. % of fiber content.

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From the Understanding of Fluorination Process to Hydrophobic Natural Fibers

Olivier Teraube, Jean-Charles Agopian, Martial Pouzet, Karine Charlet, and Marc Dubois

1 Introduction

Vegetal fibers and other lignocellulosic materials are ones of the main renewable materials, used for numerous end products such as pulp and paper, furniture, wooden frames, wooden panels, rope, etc. However, for several decades these compounds were increasingly used to substitute glass fibers for polymer strengthening to make eco-composites [1–7]. Indeed, in addition to the fact that vegetal fibers and glass fibers present equivalent specific properties, the use of the former allows to valorize bio-based and local resources while lightening the overall weight and reducing the cost of composites. Therefore, all these advantages provide them to be more and more used in the transport industry (aeronautics, automotive, etc.) [1, 4, 8], and this is expected to increase in light of current environmental issues and the emerging context of the bio-economy aimed at continuing economic growth while preserving the environment and earth resources [9, 10]

However, lignocellulosic materials are hygroscopic, especially sensitive to ambient humidity and temperature. Swelling and shrinkage, caused by water absorption and desorption, lead to deformation of these compounds which is a real issue when natural fibers reinforce polymers [11–13]. Indeed, in case of contact with water, fibers will swell, generating cracks in the composite structure (as exemplified in Fig. 1) [14]. In addition, another issue of natural fibers/polymer composites manufacturing, is the lack of compatibility between the matrix and lignocellulosic materials

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O. Teraube (✉) · J.-C. Agopian · M. Pouzet · M. Dubois
Université Clermont Auvergne, Clermont Auvergne INP, ICCF, BP 10448, 63000 Clermont-Ferrand, France
e-mail: olivier.teraube@uca.fr

O. Teraube · J.-C. Agopian · M. Pouzet · K. Charlet
Université Clermont Auvergne, Clermont Auvergne INP, Institut Pascal, BP 10448, 63000 Clermont-Ferrand, France

M. Jawaid and A. Khan (eds.), *Vegetable Fiber Composites and their Technological Applications*, Composites Science and Technology,
https://doi.org/10.1007/978-981-16-1854-3_21

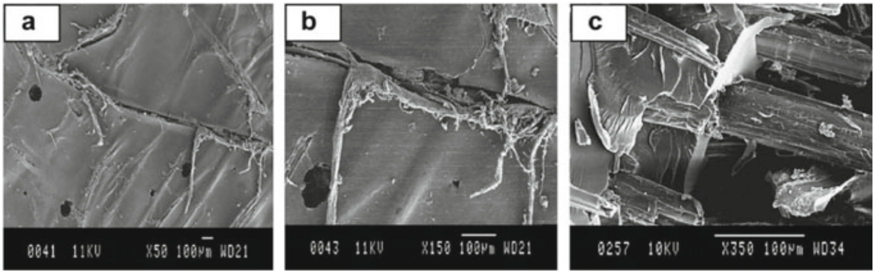

Fig. 1 Failure showing **a** matrix cracking, **b** fracture running along the interface, and **c** fiber–matrix debonding due to interaction with water molecules on a hemp fiber reinforced unsaturated polyester composites. Reprinted from [14], Copyright 2007, with permission from Elsevier

[15–17]. Indeed, the former is usually hydrophobic while the latter is hydrophilic. Thereby, when both are combined to form the composite, this chemical incompatibility lead to a poor ability to transfer load at the interface, because of the poor adhesion between both component results in poor filler/matrix adhesion, reducing the global mechanical performance of the composite and consequently the interest of natural fibers polymer composite [14, 18–20].

Reducing lignocellulosic material hydrophilic character has therefore been the subject of different studies and thereby, several treatments were developed with this aim, e.g. thermal treatment [21, 22], electric discharge [23, 24] or chemical treatment [25–31]. Nevertheless, these processes present different disadvantage. First of all, most of them are expensive, long, energy consuming and with a low yield. In addition, some of them generate degradation onto fibers surface and consequently reduce the mechanical performance of it [32]. Finally, those processes may be harmful to the environment and people by using toxic solvents.

Recently, researchers have developed novel treatments to make vegetal fibers compatible with hydrophobic polymers by reducing the surface tension of the fillers [33–36]. However, if these approaches work on a laboratory scale, however their scale-up to industry is difficult.

In contrast, fluorination is an industrial treatment used to modify the surface of the polymers to make them hydrophobic, reduce their permeability to hydrocarbons and other compounds, enhance their friction properties, and improve their chemical resistance [37–39]. Finally, fluorination is performed without using toxic solvent (as a gas/solid reaction) and then with a very low environmental footprint; such a treatment allows fibers to be changed without any human contact with the reactant (fluorinating agent and polymer being contained in a sealed reactor). Thereby, this treatment would be very convenient and secure to modify the surface properties of vegetal fibers for reinforcement of hydrophobic polymers.

Therefore, the present chapter summarizes the recent works about the direct fluorination of lignocellulosic materials in order to improve their hydrophobic character and therefore, expand both the mechanical properties and the water-resistance of composite materials by compatibilizing the filler and the polymer matrix.

2 Fluorination of Lignocellulosic Materials

Fluorination is a chemical reaction which leads to the covalent grafting of fluorine atom(s) on the surface of different substrates (materials, molecules, etc.). Under normal conditions of temperature and pressure, fluorine is a diatomic gas F_2, which is extremely reactive because of its low dissociation energy (155 kJ mol^{-1} [40]). Its high electronegativity (the highest of the periodic chart (3,98 on Pauling scale [41]), its small size allows fluorine to form a very stable bond with carbon ($\Delta H =$ 490 kJ mol^{-1}). However, if these characteristics are an asset for fluorination, toxicity and corrosivity of fluorine coupled with its high reactivity make this reaction tricky, and oblige to operate with caution.

The first fluorination of a lignocellulosic materials has been archived in an aqueous solution by Polčín in 1955 [42]. To carry out this reaction, a chlorinated lignin (18–20% chlorine content) has been used in a solution of ethanol, toluene and xylene, in the presence of sodium, potassium and silver fluoride, and antimony trifluoride at 80–150 °C. However, only 2% of fluorine have been incorporated into the lignin molecules [42]. If this work marks the beginning of fundamental research of lignocellulosic product fluorination, it was not until 1990 that applicative work on this field has been achieved, in order to prepare waterproof Kraft paper [43]. Later, CF_4 radio-frequency plasma technique has been performed to fluorinate the surface of paper sheet [44]. Results of both studies on papers showed an increase of the water contact angle of paper after fluorination, demonstrating a lower affinity of paper with this liquid.

However, during many years, fluorination of lignocellulosic materials was mainly archived using a fluorine-containing compound in an organic solvent. If these methods are still in use today, the use of organic solvents and catalysts to modify a natural product is harmful for the environment, and consequently not in accordance with the environmental issue of the twenty-first century, and the “eco-composite” concept. In addition, the use of a liquid phase may damage the lignocellulosic material, because of its hygroscopic properties. Thereby, the use of a dry process fluorination (e.g. plasma fluorination or direct fluorination with F_2 gas) appears as much more appropriate in order to develop eco-composites.

2.1 Plasma Fluorination

Plasma treatment is a useful technique, frequently used in order to modify the surface properties of different substrates (notably natural products) without modifying bulk properties of the latter. Method is based on the use of a plasma, i.e. an ionized gas, electrically neutral which is form when at least one electron is no longer bond with an atom or a molecule because of thermal condition [45]. Even if the use of plasma is common to treat polymer surface in order to change its surface properties (hydrophobicity, adhesion, friction, bio-compatibilization, etc.) [46], this method is also applied with the aim of improving the properties of the filler/polymer interface of eco-composites, since the 1960s [47–51]. Thereby, Lee et al. [48] have evidenced a decrease in the amount of -OH on flax fibers surface treated with an ethylene plasma (C_2H_4). This increased the hydrophobicity of these fibers without loss of mechanical properties. Alternatively, Sun and Stylios [52], have increased the wetting properties of cotton fibers by applying a dioxygen plasma treatment. Consequently, depending on operating conditions (and particularly on which gas is chosen), results could be diametrically opposite. However, generally speaking, plasmas which generate polar oxygenated groups (C=O and COOH) tend to increase wetting properties towards water [53]. On the contrary, treatments that increase the surface hydrophobicity, generally decrease the amount of hydrophilic groups (COOH, OH, etc.) on the material surface [54].

Along with chemical modification provided by plasma treatment, topological changes are also observed. Here too, treatment effect depends on the experimental conditions. Thereby, some authors have observed an increase in roughness of their materials [50, 54, 55], when others have noted the opposite [48, 53].

Fluorine containing plasma

Fluorine plasmas have been first developed for micro-electronic etching. Nowadays, in addition of this use, they are also applied to carry out surface treatments aimed at modifying the reflectance or the wettability of some materials [56]. Typical fluorinating agents are SF_6, NF_3, CF_4, CHF_3, C_2F_6, C_3F_6 and C_4F_8 gases [45, 57].

For lignocellulosic material treatment, four predominant reaction mechanisms may take place (Fig. 2), depending on the treatment duration, the gas pressure and the applied power [58]:

- surface functionalization with fluorine atoms, i.e. fluorination via reaction of these latter on hydroxyl groups at the surface;
- deposition of fluorinated groups on the material surface (CF_x, SF_x, etc.);
- surface roughness changes;
- minimization of the surface energy by rearrangement reactions of excited molecules ($AB + CD \rightarrow AC + BD$ [59]), including those on the surface of fibers.

To change the surface tension of lignocellulosic materials, the aim is to jointly form a fluorocarbon layer onto their surface and increase the roughness of the substrate. This two modifications allow the hydrophobicity of the samples to be chemically and physically increased [56, 60]. Thereby, treatments of cotton fabric, performed with CF_4 or C_3F_6 plasma, achieved water contact angles from 30° up to 150° (depending on the experimental conditions) [61, 62]. Still with the aim of manufacturing hydrophobic lignocellulosic materials, some researchers were interested by a combination of an O_2 plasma etching and a CF_4 plasma deposition. Thanks to this treatment, Sapieha et al. [43] have succeeded to obtain cellulose fibers which do not absorb water drop anymore, for a CF_4:O_2 ratio greater than 50% in CF_4. By using the same gas mixture, Xie et al. [63] have presented a superhydrophobic wood,

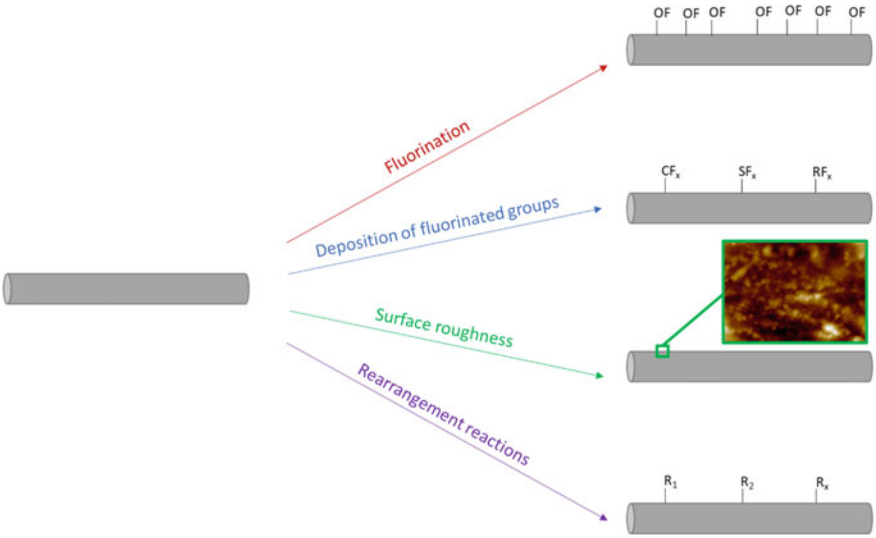

Fig. 2 Reactional mechanisms of plasma fluorination vegetal fibers

with a contact angle water up to 161°. Both studies evidenced that plasma treatment allowed significant enhancement of vegetal material hydrophobicity. In addition, some other works dealing with fluorine plasma treatments have also succeed to increase the hydrophobic character of lignocellulosic materials, e.g. wool and cotton fabrics treated with hexafluoroethane [64], wood fibers modified with CF_4 and SF_6 plasma [58], chemithermomechanical pulp (CTMP) sisal paper treated with fluorotrimethylsilane (CH_3SiF) [65].

2.2 Direct Fluorination (F_2)

Although the chemical reaction was studied for the first time in 1890 by Moissan (who have isolated fluorine four years earlier, in 1886), technique named «La-Mar direct fluorination process» has been reported only in 1974 that allowed to control this reaction [66, 67] and then to consider further works on this process.

Generally speaking, direct fluorination refers to a solid–gas reaction, where molecular fluorine F_2 (potentially diluted with an inert gas such as N_2 or Ar) reacts with a substrate, in order to covalently graft fluorine at its outmost surface [39, 68–70]. The process is based on the high reactivity of F_2 molecules which first dissociate itself on the surface and combine with the surface in a second time.

Overall, the reaction occurs as following (1):

$$M(\mathrm{s}) + \frac{x}{2}F_2(\mathrm{g}) \rightarrow MF_x(\mathrm{s}) \qquad (1)$$

In addition, direct fluorination is exothermic, that facilitates operation at room temperature for most of the commercial polymers (and even below, at liquid nitrogen temperature). Fluorination occurs first at the outmost surface of the material, thanks to a formation/growth process. Thereby, if correctly controlled, fluorination allows to modify the surface properties of a material without change bulk properties. However, direct fluorination using F_2 generates co-products such as CF_4, C_2F_6 or HF, which must be trapped or neutralized to avoid any risk or alteration of desired properties (HF may form hydrogen bonding with water molecules and then mask the hydrophobicity).

With the aim of surface treatment direct fluorination was mainly used to treat commercial polymers [38, 39, 71–73]. This treatment allows a thin fluorinated layer to be generated on the polymer surface; the superficial properties of a fluoropolymer is then added while reducing cost in comparison with the use of fluorinated monomers to polymerize polytetrafluoroethylene PTFE or polyvinylidene fluoride PVDF. Nowadays, the most known application of fluorination is the treatment of the interior of polyethylene-HD fuel tank and pipes used between reservoirs and pumps at gasoline stations. For the latter, fluorination allows to reduce the loss of petrol (petrol grade = 93 octane high altitude) by a factor of 80 [39]. Some other well-known applications of fluorination are reduction of the friction coefficient (e.g. PE-HD ski coating), increase of chemical resistance, obtaining anti-UV properties, etc. [39, 72]

However, one of the novel applications of fluorination is compatibilization of fillers with polymer matrix, to increase the transfer load at the interface with hydrophobic polymer (e.g. polypropylene, polyethylene, …). Indeed, to achieve good filler/matrix interfacial properties, both materials must have close polar and dispersive components of surface tension. Thereby, fluorination allows PTFE structure to be generated on substrate surface, giving it a surface tension close to the PTFE one ($\gamma_s = 20.1$ mN/m, $\gamma_s{}^d = 20.1$ mN/m, $\gamma_s{}^p = 0.0$ mN/m [74]). Consequently, fillers become compatible with hydrophobic polymer (Polyethylene: $\gamma_s = 35.3$–35.7 mN/m, $\gamma_s{}^d = 35.3$–35.7 mN/m, $\gamma_s{}^p = 0.0$ mN/m; Polypropylene: $\gamma_s = 30.1$ mN/m, $\gamma_s{}^d = 30.1$ mN/m, $\gamma_s{}^p = 0.0$ mN/m [75]). Direct fluorination of different fillers has thus been carried out on with synthetic fibers, such as aramid fibers [76–78], ultra-high molecular weight PE (UHMWPE) fibers [68], carbon fibers [72, 79–81], Poly(p-phenylene benzobisoxazole) (PBO) fibers [69], or fiber sizing [82, 83], evidencing a clear increase of the fiber hydrophobicity, consequently the interfacial adhesion of filler with polymer matrix is improved.

Therefore, this treatment applied to vegetal fiber fillers appeared as promising in order to prepare eco-composites.

3 Direct Fluorination of Lignocellulosic Material

The first reported work about direct fluorination to vegetal product dates from 1960, when Friedrich Brauns and Dorothy Brauns considered direct fluorination possibilities with lignin [42]. However, it is only in 2013 that the first direct fluorination of a lignocellulosic material: wood flour, has been realized by Saulnier et al. [84], and completed by Pouzet et al. with works on direct fluorination of wood and derived [70, 85, 86]. Finally, Belov et al.[87] have recently realized the direct fluorination of acetyl and ethyl celluloses (in perfluordecalin medium). These works laid the foundations of actual knowledge of direct fluorination of vegetal materials and allow to identify the impact of this treatment on lignocellulosic material.

Materials and methods

In order to perform fluorination of vegetal products, Pouzet et al. [86] have selected seven lignocellulosic compounds: pure cellulose, pure lignin, cotton fibers, flax fibers, Silver fir, Douglas and a mixture of spruce and Douglas, previously outgassed during at least 1 h at 90 °C and under primary vacuum (at 10^{-3} mbar). These lignocellulosic species were fluorinated using 20 mbar of pure fluorine F_2 gas, in static condition, i.e. inside a closed passivated nickel reactor (covered with NiF_2).

Covalent grafting of fluorine atoms

The characterization performed on treated products allows to evidence the covalent grafting of fluorine atom on the lignocellulosic material surface. Indeed, Fig. 3 shows FT-IR spectra of raw and treated samples. The emergence of vibration bands at 1080, 1160, 1200 and 1280 cm^{-1} (shaded curves on Fig. 3) after fluorination demonstrated the formation of fluorine-carbon bonds (C–F). It was also noted that the contribution of –OH groups between 3500 and 3000 cm^{-1} decreased with treatment. This proved that fluorination treatment consists in the substitution of C–OH groups by C–F groups during the fluorination. Furthermore, knowing that these hydroxyl groups are responsible for the affinity of lignocellulosic materials with water, via the formation of hydrogen bonds, lower interaction between vegetal fibers and water is expected after fluorination through their replacement by hydrophobic C–F bonds.

In order to identify the different fluorinated species that have formed as a result of the fluorination treatment (–CHF, $-CF_2$ and $-CF_3$), ^{19}F solid state NMR experiments were carried out (Fig. 4). According to [88], three environments of fluorine atom have been identified:

- –CHF groups (from −180 to −220 ppm);
- $-CF_2$ groups (from −100 to −160 ppm), related to a perfluorination mechanism;
- $-CF_3$ groups (from −70 to −90 ppm), related to cleavage in the main carbon chain.

Thereby, covalent grafting of fluorine atoms onto fiber surface has been proved by both solid state NMR and FT-IR.

Increase hydrophobicity

As explained previously, fluorination allows the surface tension of the substrate to be decreased, thanks to the decrease of the polar component of surface tension [82, 83]. In addition, it has been proved by Maity et al., that fluorination of filler allows to improve the adhesion between aramid fibers and PE [76], and between UHMWPE fibers and LD PE [68]. Indeed, this type of filler modification by fluorination increases

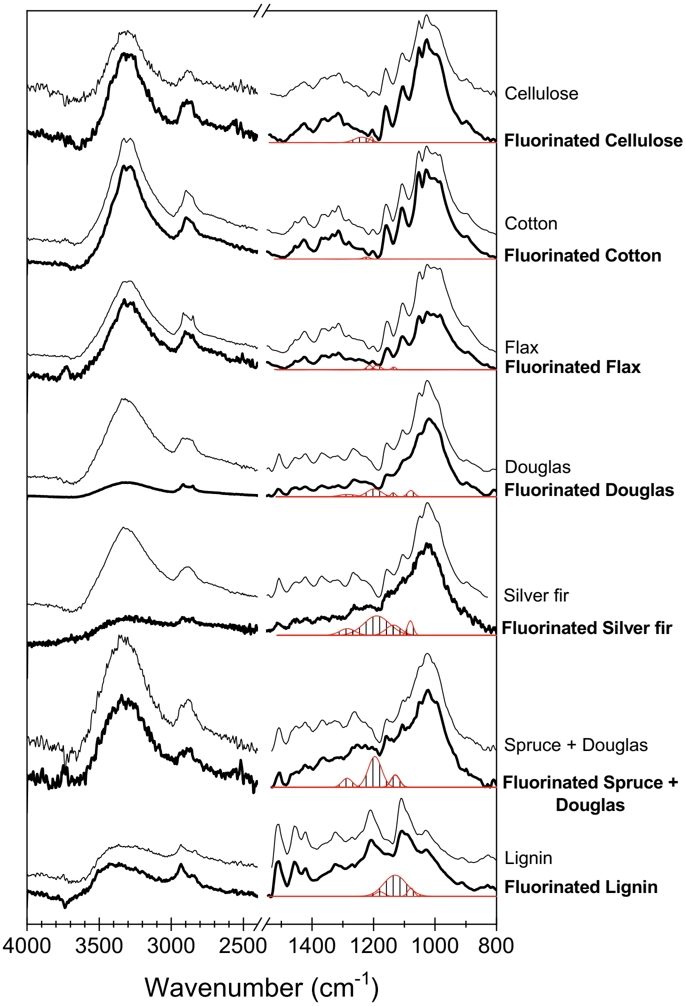

Fig. 3 FT-IR spectra of untreated (grey line) and fluorinated (dark lines) fibers. Reprinted from [89], Copyright 2017, with permission from Elsevier

load transfer between the filler and the hydrophobic in the composite (resulting in better mechanical properties) as well as improving its thermal stability and wetting properties. Thereby, same results have been expected with fluorinated natural fibers.

In order to evidence that fact on fluorinated vegetal materials, water contact angle measurements have been carried out. The hydrophilic character is related to strong interaction with water and related to a small angle. Results (Table 1) demonstrate that fluorination significantly increases the hydrophobic character of lignocellulosic materials. However, this phenomenon is not observed on cellulosic compounds i.e. cellulose and cotton.

Fig. 4 ^{19}F NMR Magic Angle Spinning MAS 30 kHz spectra of fluorinated fibers.; Reprinted from [89], Copyright 2017, with permission from Elsevier

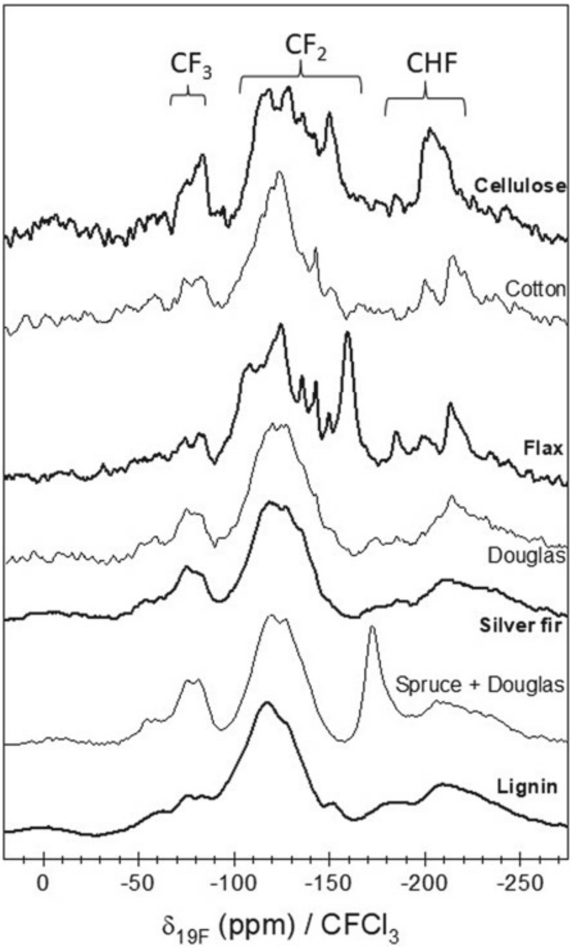

Table 1 Water contact angle of different lignocellulosic materials

Sample	Untreated	Fluorinated
Cellulose	28°	30°
Cotton	NM[a]	20°
Douglas	70°	85°
Silver fir	51°	98°
Wood flour (spruce + Douglas)	80°	95°
Lignin	48°	77°

[a] Non-measurable because of spontaneous absorption of the water drop

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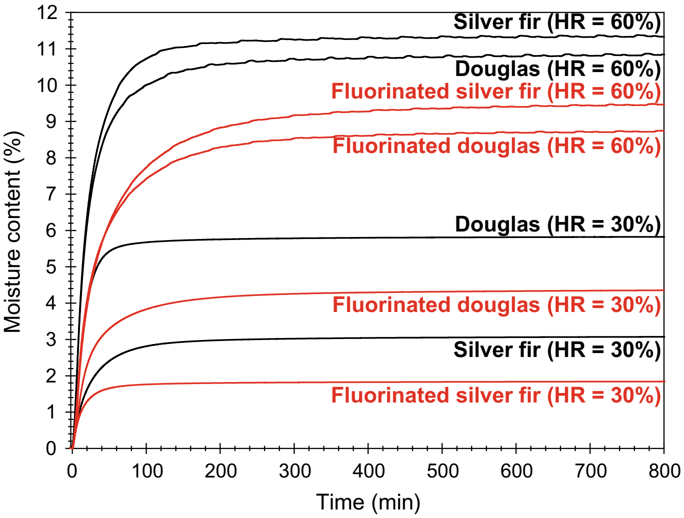

Fig. 5 Water absorption rate of raw and fluorinated woods. Reprinted from [90], Copyright 2019, with permission from Elsevier

In addition to contact angles, fluorinated and raw wood samples were placed during 800 min at 30 and 60% of relative humidity (at 20 °C). Data (Fig. 5) evidenced that fluorinated samples exhibited a significant lower water content compared to the raw ones, demonstrating once again the hydrophobic character provided by the fluorination treatment.

Lignin, a key factor

As discussed previously, fluorination does not provide a significant hydrophobic character to cellulosic materials. This point has been investigated evidencing that lignocellulosic materials do not have the same reactivity towards direct fluorination with molecular fluorine F_2. The differences were explained by the chemical composition of plants, and more particularly, related to the lignin and the cellulose contents.

Indeed, static direct fluorination treatment (in a closed reactor) showed that fluorine consumption (related to the pressure decrease in the oven, because reaction was carried out in a closed reactor) differs, depending on the material. However, fluorine consumption and that way, Fig. 6 underlines a decrease of pressure inside the reactor after the fluorine gas injection which is directly related to reactivity of samples towards F_2. Therefore, the reactivity of these materials follows the order:

Lignin > wood flour > Silver fir > Douglas > Flax > Cotton > Cellulose.

However, Table 2 summarizes the chemical composition of the lignocellulosic materials treated by direct fluorination and ordered by reactivity, from the less reactive (pure cellulose) to the highly reactive (pure lignin). It appears that there is a correlation between direct fluorination reactivity and the cellulose/lignin content. Indeed, the higher the lignin content, the greater the reactivity of the substrate. On

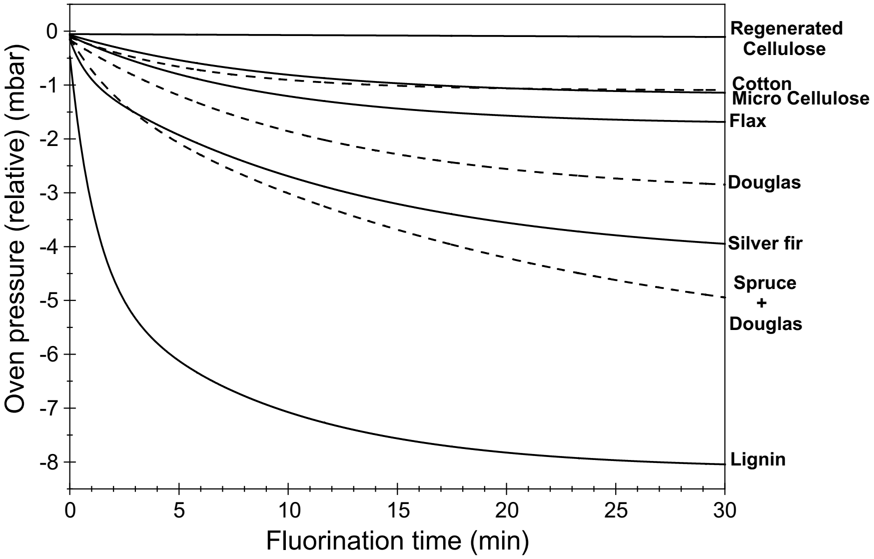

Fig. 6 Evolution of pressure in the reactor during fluorination; Reprinted from [89], Copyright 2017, with permission from Elsevier

Table 2 Cellulose, lignin and hemicellulose contents of the studied lignocellulosic materials

Sample	Cellulose	Lignin	Hemicellulose	Other
Cellulose	100	/	/	/
Cotton	90–93	0–2	1–5	2–3
Flax	64–72	16–21	2–4	4–6
Douglas	45–56	23–29	13–21	2–7
Silver fir	42–52	29–31	/	1–3
Wood mix	39–45	32–35	15–24	3–4
Lignin	100	/	/	/

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the contrary, cellulose seems to inhibit the reaction [89]. This phenomenon appears also regarding the FT-IR spectra (Fig. 3). Indeed, reduction of the –OH band and consequently substitution of hydroxyl groups during the treatment is more important with lignocellulosic fibers than with cellulosic fibers.

In addition, Belov et al. [87] have realized the direct fluorination (in perfluordecalin medium) of two modified celluloses, namely acetyl and ethyl cellulose (structures illustrated on Fig. 7). ^{13}C NMR spectrum exhibited practically no difference with fluorinated celluloses. However, narrowed spectral lines that correspond to carbon atoms in the methyl groups were observed in fluorinated samples. This may indicate that the glycopyranosyl rings of cellulose have not reacted with fluorine. ^{19}F

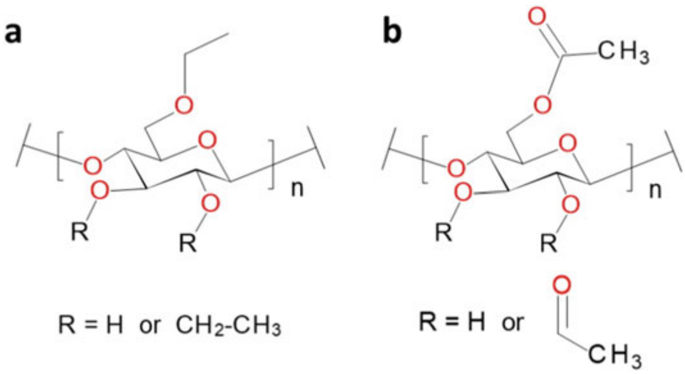

Fig. 7 Chemical structure of ethyl-cellulose (**a**), and acetyl cellulose (**b**), Inspired by [87]

NMR spectrum also confirmed that fact, demonstrating once again the resistance of cellulose to fluorination.

Starting from this statement, Pouzet et al. [89] proved that the reactivities of lignocellulosic material and lignin or cellulose content are correlated following a linear law (Fig. 8). Thereby, Table 3 presents the average chemical composition of some lignocellulosic fibers. By using these compositions and the two proportionality relations, it is possible to predict the reactivity of these compounds as presented on Fig. 9. Thereby, all these fibers have different reactivity to molecular fluorine. However, for each one, covalent grafting may be expected.

A treatment localized on the surface

As discussed previously, direct fluorination mainly converts C–OH groups into C–F ones, generating a hydrophobic character of the fiber surface without modify bulk properties of these materials. It has been reported that this phenomenon is directly related to plant microstructure.

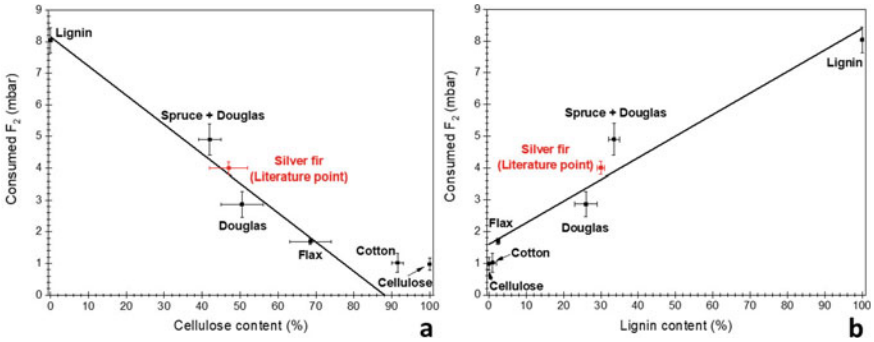

Fig. 8 Correlation between fluorine consumption and **a** cellulose content, **b** lignin content. Reprinted from [89], Copyright 2013, with permission from Elsevier

Table 3 Average chemical composition of some lignocellulosic materials

	Cellulose	Hemicellulose	Lignin	Other	References
Banana	66	14	9	11	[91, 92]
Bamboo	35	25	28	12	[91, 93]
Coir	42	1	45	12	[91, 94]
Cotton	86	4	1	9	[91, 94]
Flax	68	19	3	10	[2, 91, 95]
Hemp	69	19	9	3	[91, 95]
Jute	58	17	18	7	[91, 95]
Kenaf	48	20	16	16	[91, 95]
Ramie	80	11	1	8	[91, 96]
Sisal	69	11	8	12	[91, 94]

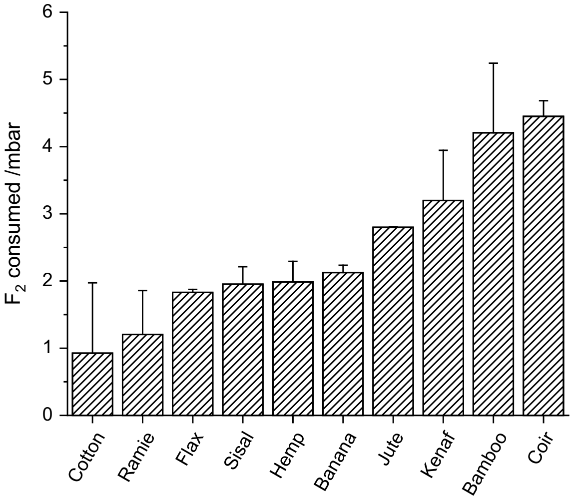

Fig. 9 Expected F_2 consumption of natural fiber, related to their reactivity towards direct fluorination at 20 mbar of F_2

Indeed, wood and plant fibers are made up of "plant cells" whose diameter is in between 10 and 100 μm. This cell is itself composed of different sub-layers (Fig. 10). From the outside of the cell, the medium lamella (ML) makes the junction between all the cells; the primary wall (P) delimits the cell and is mainly composed of cellulose microfibrils arranged in a spiral within an amorphous matrix of lignin. Lastly, the secondary wall (S) is present and is itself sub-divided into 3 sub-areas (S1, S2 and S3), which are mainly composed of cellulose. Those latter sub-areas give to cell its mechanical properties. Also, as shown in the Fig. 10, the relative contents of cellulose, hemicellulose and lignin depend on the considered component, i.e. middle lamella, primary or secondary wall [70, 97].

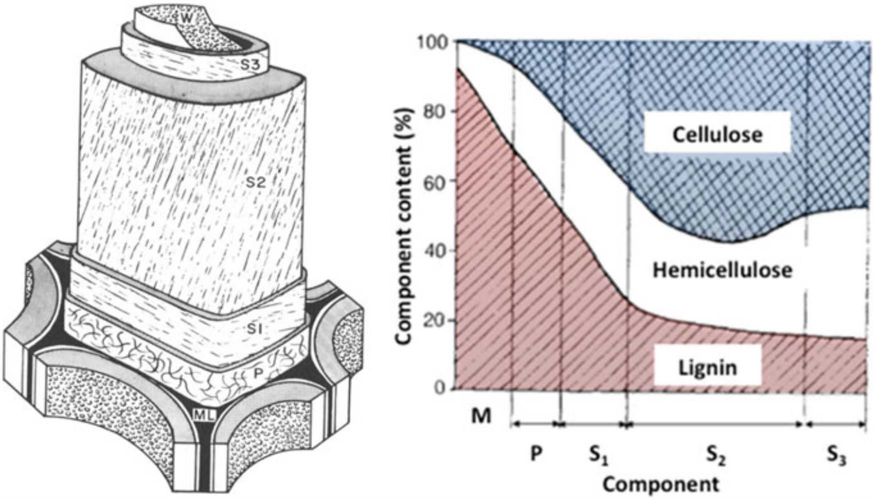

Fig. 10 Components and composition of cell plant; Left image reprinted from [98], Copyright 1993, with permission from Elsevier; Right image from [99]

Pouzet et al. [89] underlined that the reactivity of plants is proportional to their chemical composition. Indeed, the higher the relative content of lignin, the higher the reactivity; the opposite behavior is found with the cellulose content.

Thereby, for the same species, lignin-rich areas (i.e. middle lamella and primary cell) (Fig. 10) are the most reactive to fluorination, and it is in these zones that fluorine atoms will be preferentially grafted. Consequently, when the process is controlled, CHF, CF_2 and CF_3 are mainly formed in the external parts of the cell maintaining the bulk non-modified.

Without degradation

Thereby, no bulk modification takes place in the material's structure. This fact allows to maintain the mechanical properties of treated materials (Table 4), contrary to the torrefaction which provides hydrophobic properties on the one hand, but deteriorating the mechanical performance of the treated compounds on the other hand [22].

In addition, it is known that prolonged fluorination of biomass generates deterioration of the carbon skeleton of bio-molecules [85]. This phenomenon is highlight by the presence of CF_3 groups on chain ends [37, 82, 100]. However, on Pouzet's works, ^{19}F solid-state NMR (Fig. 4) did not show the presence of a significant quantity of CF_3 groups and SEM images (Fig. 11) did not evidence any presence of degradation (after a 3 h treatment at room temperature). This demonstrating that it is possible, by controlling the reaction, to avoid degradation of the substrate.

Therefore, fluorination of lignocellulosic materials allows the hydrophobic character of these compounds to be improved. This may increase the composite adhesion between fiber and hydrophobic polymer matrix, as already observed with other fluorinated fibers [68, 76]. Finally, these modifications do not impact the material bulk

Table 4 Mechanical properties of raw and fluorinated woods (data from [86])

Sample		Silver fir		Douglas	
		Raw	Fluorinated (5 min, T_0)	Raw	Fluorinated (5 min, T_0)
Tensile test	Young modulus (MPa)	699 ± 276	599 ± 214	348 ± 66	381 ± 129
	Ultimate tensile strength (MPa)	3.5 ± 0.9	3.6 ± 0.5	3.4 ± 0.4	3.5 ± 0.6
Flexural test	Young modulus (MPa)	332 ± 106	342 ± 94	338 ± 46	328 ± 38
	Ultimate tensile strength (MPa)	6.2 ± 1.0	6.6 ± 1.0	8.8 ± 1.3	8.4 ± 1.1

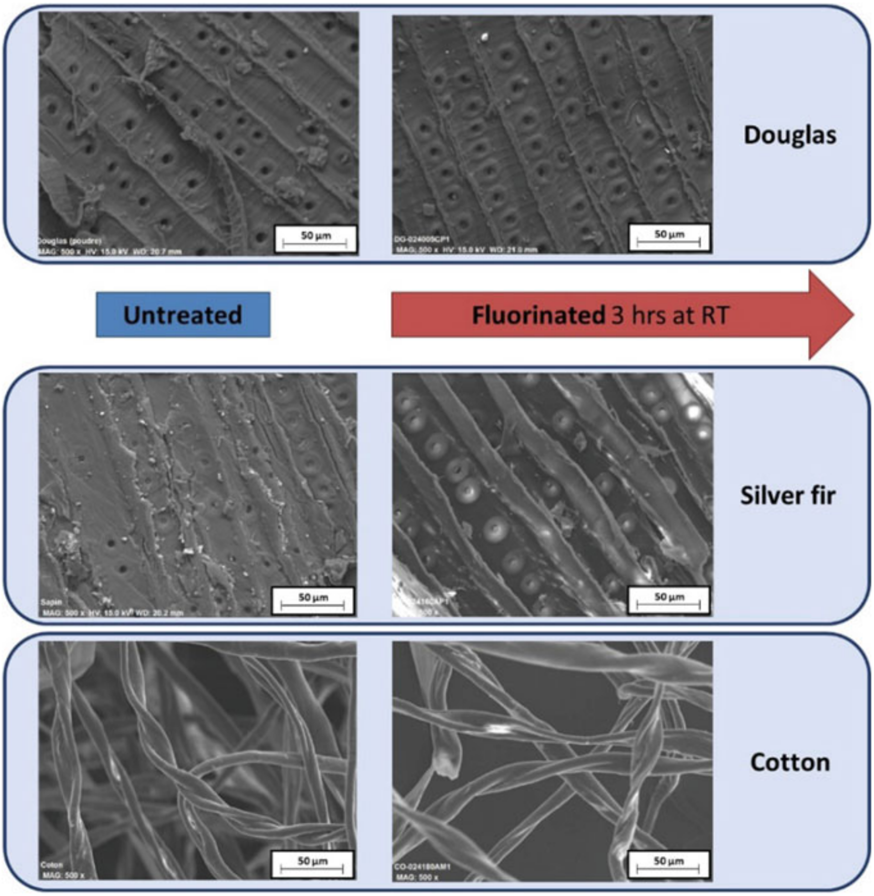

Fig. 11 Scanning electron micrographs of pristine and fluorinated vegetal materials [86]

and consequently, do not degrade the other characteristic of the treated material, especially the mechanical properties.

4 Fluorinated Lignocellulosic Materials Eco-composite

In order to evaluate the impact of fluorination on lignocellulosic materials for reinforcement of hydrophobic polymers, Saulnier et al. [84] have applied dynamic fluorination to wood flour and prepared a wood–polymer composites using this fluorinated wood flour as filler and unsaturated polyester as matrix.

Materials and methods

The wood flour under study was a mix of spruce and Douglas species obtained from sawmill co-products in Auvergne, France, with a diameter smaller than 250 μm. Wood flour (~5 g) was fluorinated under static condition in a passivated nickel reactor. Sample was first outgases under vacuum (−960 mbar) at 150 °C for 2 h. Then, fluorination reaction was performed:

- 20 mbar of pure fluorine (purchased from Solvay Fluor, 99.9% purity (V)) was insert first.
- 80 mbar of pure Nitrogen (99.999 purity) was then added, in order to reach 1 atm.

Reaction was performed during 3 h at 3 different temperatures according to the location in the owen (respectively 42 °C, 55 °C and 70 °C, from the left to the right of the reactor) as presented Fig. 12, to avoid or at least limit inhomogeneity in the treatment. After the treatment with F_2, pure nitrogen gas is insert inside the reactor during 2 h at 150 °C to stop the reaction. Finally, after 11 h of cooling, wood flour was thermally treat again for 1 h at 150 °C under Nitrogen to eliminate traces of adsorbed reactive gas F_2 or side-products, HF, CF_4, and C_2F_6.

Both wood flour and polyester (Norsodyne G703) were mix together to prepare the composites, with a weight fraction of fillers equal to 45% (100 mm × 100 mm × 2 mm) were formed at 80 °C, by hot compression molding under 60 kN of pressure during 2 h. Covalent grafting of fluorine in wood flour structure was proved by ^{19}F

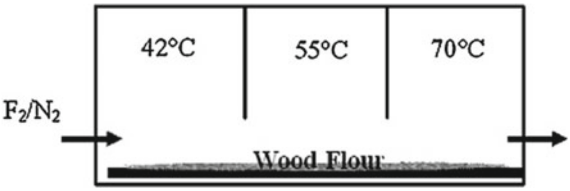

Fig. 12 Direct fluorination system of wood flour Reprinted from [84], Copyright 2013, with permission from Elsevier

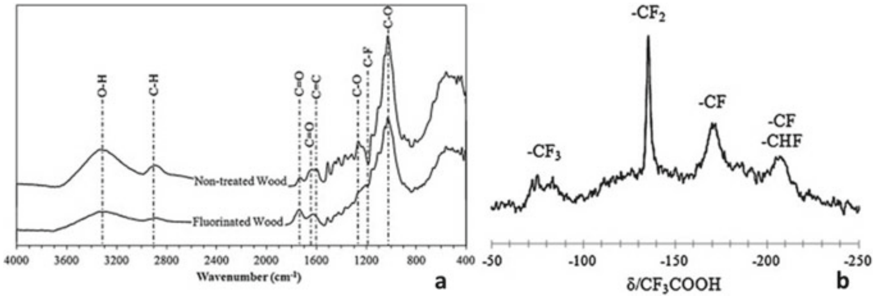

Fig. 13 **a** FT-IR, and **b** 19F NMR spectra of fluorinated wood flour. Reprinted from [84], Copyright 2013, with permission from Elsevier

NMR and FT-IR experiment (Fig. 13). The assignments of both FT-IR and ^{19}F NMR spectra are rigorously similar to the case of natural fibers.

Decrease of composite's porosity

Once prepared, composites were analyzed by X-ray tomography in order to visualize the porosity. Indeed, wood and polyester presenting a similar density (~1.4 and ~1.2 respectively), it is not possible to distinguish them. Thereby, only air bubbles formed during the manufacture of composites present a sufficient difference in density, and therefore allows to underline porosity in the bulk (Fig. 4). Data evidenced a clear difference between the two composites: Non treated wood flour composite (Fig. 14a) exhibited much more porosities than the one made from fluorinated wood flour (Fig. 14b). Thereby, by the fact that both composites have been prepared according to the same protocol, the decrease of porosity could only be assigned to the presence of F atoms onto the filler surface. Indeed, enhancement of the compatibility between polyester and wood particles allows to decrease porosity resulting from the lack of filler/polymer compatibility. In addition, thermogravimetric analysis (TGA) analysis

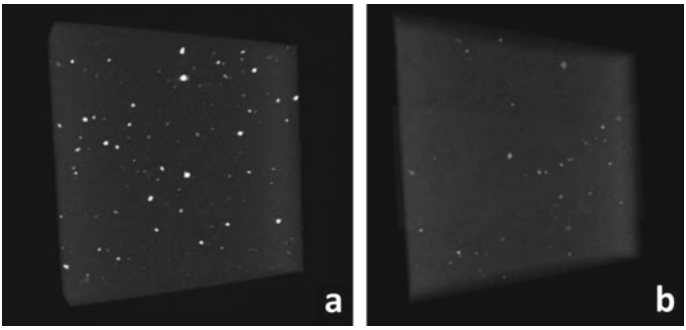

Fig. 14 X-ray 3D reconstruction of composites with non-treated **a** or fluorinated, **b** wood flour (size of the samples: 10 mm× 10 mm × 1.76 mm). Reprinted from [85], Copyright 2015, with permission from Elsevier

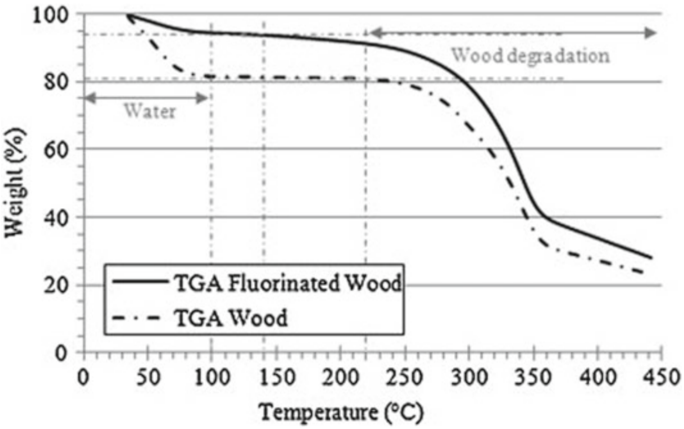

Fig. 15 TGA curves of raw wood flour (W) and fluorinated wood flour (FW); Reprinted by permission from Springer Nature: Springer Nature, Natural Fibres: Advances in Science and Technology Towards Industrial Applications [101], Copyright (2016)

(Fig. 15) underlined that fluorinated wood flour contained much less water. Because of the temperature of the composite shaping process (80 °C), a part of this water will be vaporized during the process, creating additional porosity. Consequently, fluorinated wood flour generates less porosity due to less absorbed water.

This tends to prove that the composite health was improved by the fluorination pre-treatment of the wood. Indeed, composite porosities are privilege places of rupture and birthplace of cracks. Thereby, better properties were expected from the fluorinated wood composite.

Improvement of the composite mechanical performances

In order to prove that fact, tensile tests and flexural tests have been carried out [101]. Results (Table 5) show an increase of the composite stiffness (related to the Young modulus increase) and of the mean tensile strength with the direct fluorination of the reinforcements. However, the elongation at break remains constant after the treatment. Thereby, because of the enhancement of the tensile properties, it can be concluded that the fluorinated filler/matrix interface is of better quality than the raw filler one. In other words, the compatibilization between the wood flour reinforcements and the polyester resin is achieved. This generating a better load transfer between both components.

The authors report that the magnitude of these increases are similar to those observed by Garcia R.A. [102] after a maleic anhydride treatment or by Nachtigall et al. [103] after a silane treatment. This point evidences the efficiency of the direct fluorination treatment for eco-composite application.

Reducing the composite hygroscopic character

In addition, water contact angles θ_c measurement were performed on composites (Fig. 16). The composites made from fluorinated wood flour exhibit a greater

Table 5 Tensile and flexural properties of the composites with non-treated or fluorinated wood flour (data from [101])

Sample	Tensile properties		Flexural properties	
	Untreated wood/UP	Fluorinated wood/UP	Untreated wood/UP	Fluorinated wood/UP
Young modulus (MPa)	4.4 ± 0.2	4.8 ± 0.2	4.5 ± 0.3	5.6 ± 0.6
Mean tensile strength (MPa)	32.4 ± 1.5	41.7 ± 2.4	50.1 ± 1.8	63.8 ± 5.7
Elongation at break (%)	1.4 ± 0.3	1.3 ± 0.1	1.4 ± 0.1	1.3 ± 0.1

contact angle ($\theta_c = 101°$) than its counterpart made from raw filler ($\theta_c = 78°$). This phenomenon can be explained by the fact that fluorinated particles emerge on the composite surface, bringing their hydrophobic character to the composite (Fig. 17). Fluorination always competes with decomposition of the surface, i.e. etching with release of CF_4, C_2F_6, … gases. The decomposition explained the emergence of fluorinated fillers (see scheme in Fig. 17).

Moreover, the absorption time measurement of a water drop was also carried out. The water drop was absorbed in 42 s into the composite containing untreated wood, while it took more than 50 min for the composite made with fluorinated flour. Thereby, water diffusion into the composite has been reduce by the fluorination

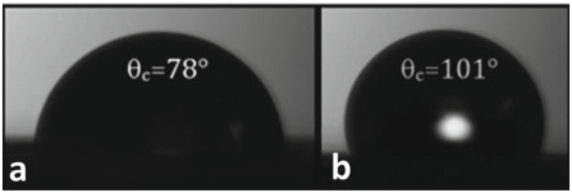

Fig. 16 Water contact angle contact of composite made from **a** raw wood flour, and **b** fluorinated wood flour. Reprinted from [85], Copyright 2015, with permission from Elsevier

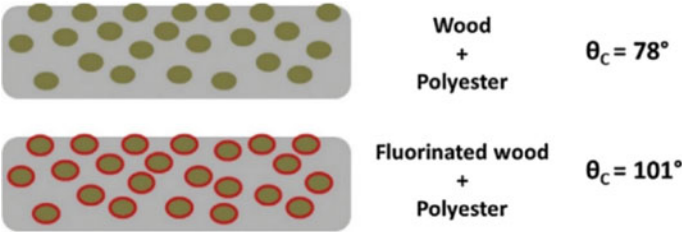

Fig. 17 How fluorination of the filler makes composites hydrophobic. Reprinted from [85], Copyright 2015, with permission from Elsevier

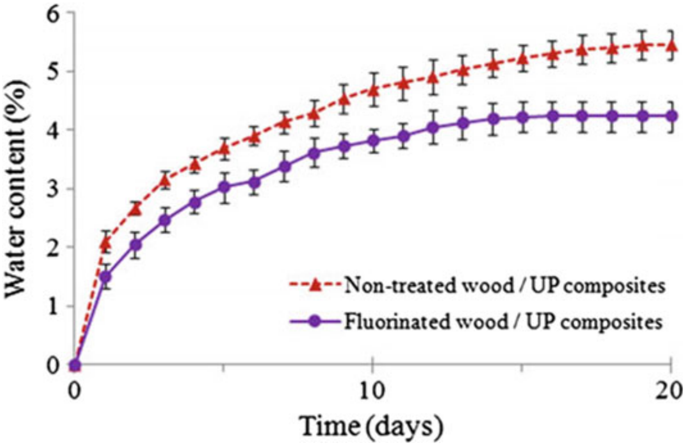

Fig. 18 Evolution of the water content of fluorinated or non-treated wood composites. Reprinted by permission from Springer Nature: Springer Nature, Natural Fibres: Advances in Science and Technology Towards Industrial Applications [101], Copyright (2016)

treatment. This phenomenon is directly related to the enhanced compatibility between wood particles and polyester, proved by X-ray tomography. Indeed, because of the enhanced compatibility between filler and polymer, space between both components was reduced, decreasing the possibility for water to penetrate it, thus increasing the composite resistance to degradation due to water absorption.

Protection against water uptake behavior

To go further, composites were store during 20 days at 80% of relative humidity (at 20 °C). Figure 18 displays the increase of the water content in the samples. Data underline that fluorinated wood flour composites exhibited a significant lower water content compared to the untreated one.

After 20 days spent at 80% of RH, flexural tests was undergone (in the same conditions than previously described), and results are presented in Table 6. These samples exhibit an increase of the moduli compared to those that did not undergo ageing in a humid environment. It has been noticed by Charlet et al. [101] this may be related by the fact that the composites have not been cured after their fabrication. Thereby, humidity would have made it possible to complete the reticulation of the polysester matrix as already observed in some works on thermoset resins [104, 105]. However, it is clear that fluorinated samples exhibit better mechanical properties (Young modulus and mean tensile strength) after 20 days spend at 80% of relative humidity than the untreated ones.

Thereby, the use of fluorinated lignocellulosic materials to reinforced hydrophobic polymer allows filler to be compatibilized with the polymer matrix and therefore increases the transfer load at the interface. In addition, this compatibilization consequently reduces the porosity of the composite, reinforcing the composite health, its

Table 6 Flexural properties of the composites stored 20 days under a relative humidity of 80% (data from [101])

Sample	Tensile properties	
	Untreated wood/UP	Fluorinated wood/UP
Young modulus (MPa)	5.8 ± 0.5	7.8 ± 0.4
Mean tensile strength (MPa)	50.6 ± 0.4	59.2 ± 3.4
Elongation at break (%)	1.0 ± 0.1	0.8 ± 0.1

mechanical performance, and protect it against water uptake, which is a real problem for vegetal fiber composites [14].

5 Conclusion

Direct fluorination with F_2 gas is an efficient technique studied and employed for many years in order to modify the surface properties of different substrates. This method, performed at the industrial scale, allows the hydrophobicity of the treated materials to be increased by generating the PTFE-like layer on substrate surface. Works archived on lignocellulosic materials have demonstrated that direct fluorination of these products may be controlled to significantly increase the hydrophobicity of samples. Spectroscopic analysis (^{19}F NMR and FT-IR) evidences the covalent grafting of fluorine atoms on the outmost surface of the substrate. By decreasing the polar component of surface tension, a compatibilization of vegetal products with hydrophobic polymers (e.g. polyethylene, polyethylene, polyester, etc.) is achieved. The composite health is significantly enhanced by reducing porosity in the composite, as well as its mechanical properties (because of the better transfer load at the filler/matrix interface). In addition, as a treatment localized at the surface, fluorination does not affect the mechanical properties of the treated material.

Thereby, vegetal fiber fluorination is a promising process, which has already proved its efficiency on fluorinated wood flour for reinforcement of hydrophobic polymer in eco-composites. The next step will be the application of this promising treatment on long fibers; works are currently under progress.

Acknowledgements The authors express their acknowledgments to Région Auvergne-Rhône-Alpes for funding this work through the FLUONAT Project. We also express our gratitude to Solvay Group to encourage this project.

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