Green Energy and Technology

Mohammad Jawaid
Mohd Sapuan Salit
Othman Y. Alothman *Editors*

Green Biocomposites

Design and Applications

Springer

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To my lovely daughter "Ayesha Jawaid"
(Mohammad Jawaid)

Preface

Green biocomposites have received attention from researchers and industries to develop biodegradable and sustainable products by using natural fibres, which possess outstanding degradable and sustainable properties. Green biocomposites-versatile materials are useful in future to help researchers, scientists and industries to understand the need of green biocomposites for utilization in development of different biodegradable and eco-friendly products. The design of biocomposites plays a crucial role to find its potentiality in different real-world applications. This book will elaborate the design of biocomposites and prospective applications with real examples. This sustainable material penetrates into the market segment and has significant potential in automotive, marine, aerospace, construction and building, wind energy and consumer goods, etc. The book contains extensive examples and real-world products that will be suitable for commercial market.

This book covered versatile topics such as details about green composites and cellulosic biocomposites as future material for versatile applications, design and fabrication of green biocomposites, conceptual design of biocomposites, green biocomposites, and polylactic acid green nanocomposites for automotive components, design of prosthetic leg socket from kenaf fibre based composites, green biocomposites for structural applications, biocomposites for packaging applications, biocomposite applications in acoustical comfort and noise control, bamboo, okra, and jute fibres for different applications.

We are very thankful to all authors who contributed book chapters and provided 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 green composites and biocomposites and finally complete this venture in a fruitful way. We greatly appreciate contributors' commitment and their support to compile our ideas in reality.

We are very thankful to Springer UK team for their generous cooperation at every stage of the book production.

Serdang, Malaysia	Mohammad Jawaid
Serdang, Malaysia	Mohd Sapuan Salit
Riyadh, Saudi Arabia	Othman Y. Alothman

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About the Editors

Dr. Mohammad Jawaid is currently working as Fellow Researcher (Associate Professor), at Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, Serdang, Selangor, Malaysia and also Visiting Professor at Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia since June 2013. He is also Visiting Scientist to TEMAG Laboratory, Faculty of Textile Technologies and Design at Istanbul Technical University, Turkey. Previously he worked as Visiting Lecturer, Faculty of Chemical Engineering, Universiti Teknologi Malaysia (UTM) and also worked as Expatriate Lecturer under UNDP project with Ministry of Education of Ethiopia at Adama University, Ethiopia. He received his Ph.D. from Universiti Sains Malaysia, Malaysia. He has more than 10 years of experience in teaching, research, and industries. His area of research interests includes hybrid reinforced/filled polymer composites, advance materials: graphene/nanoclay/fire retardant, lignocellulosic reinforced/filled polymer composites, modification and treatment of lignocellulosic fibres and solid wood, nanocomposites and nanocellulose fibres, and polymer blends. So far he has published 8 books, 17 book chapters, and more than 150 international journal papers and 5 published review papers under Top 25 hot articles in science directly during 2013–2015. He is also the Deputy Editor-in-Chief of Malaysian Polymer Journal, Guest Editor of Special Issue-Current Organic Synthesis & Current analytical chemistry, Bentham Publishers, Guest Editor, International Journal of Polymer Science, UK and Editorial board member-Journal of Asian Science Technology & Innovation. Besides he is also reviewer of several high-impact ISI journals of Elsevier, Springer, Wiley, Saga, etc. Presently he is supervising 20 Ph.D. students and 10 master's students in the field of hybrid composites, green composites, nanocomposites, natural fibre reinforced composites, etc; and 4 Ph.D. and 3 master's students graduated under his supervision during 2014–2016. He has several research grants at university and national level on polymer composites of around

RM 700,000 (USD 175,000). Recently he received Newton-Ungku Omar (NUOF) fund, a research fund created by the British and Malaysian governments as Malaysian Project Head. He has also delivered plenary and invited talks in international conferences related to composites in India, Turkey, Malaysia, Thailand, and China. Besides he is also member of technical committee of several national and international conference on composites and materials science.

Prof. Mohd Sapuan Salit, Ph.D., is a senior Professor of Composite Materials at Department of Mechanical and Manufacturing Engineering, Universiti Putra Malaysia (UPM). He is currently head of Laboratory of Biocomposite Technology, INTROP, UPM, and also head of composites Technology Research Program at UPM. He is the vice president and honorary member of Asian Polymer Association; Fellow of Institute of Materials, Malaysia, Plastic and Rubber Institute, Malaysia, Malaysian Scientific Association and Society of Automotive Engineers International, USA. His research interests include natural fibre composites, composite materials selection and concurrent engineering for composites. Professor Mohd Sapuan Salit has published more than 450 journal papers and 400 conference papers. He has authored and edited 15 books in engineering. He has guided more than 40 Ph.D. students and 40 M.Sc. students. He is the recipient of various awards such as ISESCO Science Prize, Alumni Award, University of Newcastle, Australia, Rotary Research Award, Khwarizmi International Award, Plastic and Rubber Institute Malaysia Fellowship Award and Vice Chancellor Fellowship Prize, UPM.

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Green Biocomposites for Structural Applications

N. Saba, Mohammad Jawaid, M.T.H. Sultan and Othman Y. Alothman

Abstract The quest for the development of innovative materials having zero impact with high performance at affordable costs to meet the basic human and society demands results a dynamic composite materials. Green or biocomposites regarded as a high-performance or 'advanced' fourth generation engineered composite materials that are comparatively better and attractive in terms of environmentally friendly, composability and complete degradability of end use products. The reinforcement of renewable and environment-friendly plant based 'lignocellulosic' fibers with bio-based polymeric matrix (plastics) is the only ways to fabricate the green composites or to make them fully greener materials. Green composites offer a significant environmental key for both food and non-food market including the aerospace, automotive, decking and for others variety of structural applications over the past decades because of their relatively higher specific modulus and strength compared to metals. Developed bio-material undoubtedly delivers greater impact on the world economy by developing energy saving products for the improvement of life quality. Present study is designed to deliver an outline of the comprehensive recent research studies and works reported on sustainable "green" friendly biocomposites, focusing the concern on biopolymers, natural fibers, composite processing and their diverse structural applications.

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Currently, green composites considered as one of the emerging innovative products in materials and polymer composite science to expand the commercial application in the sectors ranging from packaging to the constructional industry.

Keywords Natural fibers · Polymer · Biopolymer · Green composites · Applications

1 Introduction

Recently, higher motivation, efforts and consideration has been given by the materials scientists and politicians in the composite fields towards the utilization of renewable bio-based and biodegradable materials due to persistent discussions on the climate changes and growing regulatory demands underlining the need for cleaner and safer environment globally. Green composite materials are refers to those materials which are completely ‘biodegradable or renewable’ and can address the twin issues of ‘sustainability’ and ‘zero environmental impact’.

The chemical, physical and biological degradation of composite materials having time resistant polymeric matrix, poses serious concerns, when used in certain human related areas such as surgery, pharmacology, agriculture and the environment. Such biodegradable materials have become invaluable gifts to the society through the modern science and technology as they are preferred in products having single use, short-life, and easy disposability. Besides this, they have controlled-life and hence used in applications such as packaging, consumer products (disposable plastics, agricultural films) and marine disposables components (Satyanarayana 2015).

2 Bio or Green Composites

The ecological concerns and issues such as recycling and environmental care are increasingly important to handle the present situation. As a consequence of growing environmental awareness surrounding society a great interest in the research on more environmentally friendly materials that are derived from non-renewable resources are gaining attention (García-García et al. 2015). Green composites classified as particular type of biocomposite materials comprising both reinforced and polymer matrix phase(s) derived from a biological origin or from renewable sources (Terzopoulou et al. 2015; Cheung et al. 2009; John and Thomas 2008; Zini and Scandola 2011; Signori et al. 2012). The most general fabrication scheme of green composite is shown in Fig. 1.

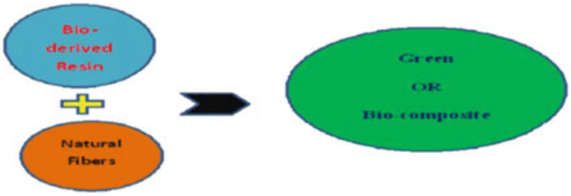

Fig. 1 General scheme for the fabrication of green composite (Color figure online)

In green composites the reinforcing fibers possess a high tensile strength and stiffness, while the embedding or reinforcing agent (matrix) offers the shape of the composite structure and transmits the applied shear forces between the fibers and also protects them against destructive and radiation source (Nickel and Riedel 2003). The developed products are called green composites, principally due to their sustainable and degradable properties, without impairing the surrounding environment. As non-biodegradability results many serious environmental problems such as unsightly litter, eutrophication and polluted marine waters.

Currently, green composites material become extremely valuable not only in the scientific world but also in the commercial daily applications with their marked futures (Niaounakis 2014). Meanwhile biocomposites have properties similar to well-established glass fiber composites, along with additional eco-friendly recovery options (Nickel and Riedel 2003). Green composites are quite durable and hence are used to increase the life cycle of short life end products. However, the only challenge is to procured 'green' polymers to be used as polymer matrices required during the fabrication of green composites.

3 Reinforcement/Filler

Reinforcement in green composites include materials from renewable source consisting of cellulose and chitin such as plant fibers (bast, leaf, core fibers), fibers from recycled wood or waste paper, regenerated cellulose fibers (viscose/rayon), by-products from food crops, bio-agricultural wastes. To the present, significant research efforts were made in developing a new class of fully biodegradable 'green' composites by combining natural fibers with biodegradable resins (Netravali and Chabba 2003). Natural fibers are the sub divisions of fiber and are subdivided into vegetable, animal and mineral fibers shown in Fig. 2 (Saba et al. 2014). Currently, natural fibers are acquiring increasing importance as reinforcing materials in composites due to their significant advantages of low cost, low density, minimal toxicity, balanced mechanical properties along with relatively lower environmental impact (García-García et al. 2015; Taşdemır et al. 2009; Saenghirunwattana et al. 2014; Džalto et al. 2014; Le Duigou et al. 2010). The main problem related to the use of natural fibers is their low compatibility and lower wetting properties with most polymer matrices (García-García et al. 2015). In the composites, reinforced

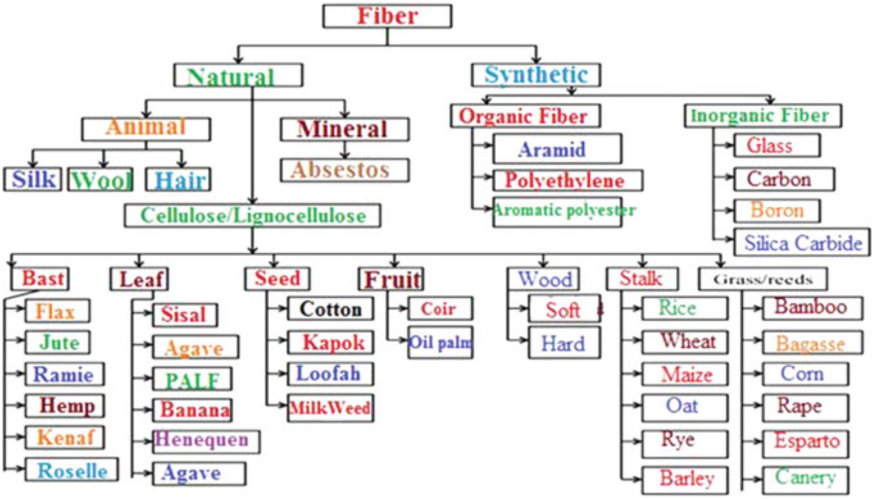

Fig. 2 Broad classifications of fibers (Saba et al. 2014)

fibers provide stiffness,sufficient strength and governed the inherent properties of the final material.

Different types of natural fibers and their properties have been studied which can as a potential replacement of synthetic fibers like glass and carbon fiber. Individual properties of each types fibers have significant importance to generate new applications and opportunities for biocomposite for the 21st century "green" materials environment (Gurunathan et al. 2015). Some of the most common natural fibers used as reinforcement in polymer industries especially for biopolymer are displayed in Fig. 3. Fibers having higher degree of polymerization, cellulose content and a lower microfibrillar angle exhibits higher tensile modulus and strength, required for the selection of fibers in the green biocomposites fabrication (Gurunathan et al. 2015; Yu et al. 2014; Wu and Liao 2014). However, the quest for the entrance of biocomposites into commercial markets to stimulate the increasing demand of non-food crops ensuring suitable fiber selection relative to the bio-polymer would led to future novel innovations.

4 Bio-Based Polymeric Matrix

The growing desire to mitigate climate change due to greenhouse gas emissions, biodegradable resins or bio-resins are explored as the best potential alternatives of petroleum/fossil based traditional polymers for composites in a wide range of applications (Rwawiire et al. 2015). The bio-based matrix similar like other polymer matrix binds the fibers together, transfers the applied shear loads to fibers and protects them from physical and mechanical damage in a green composites.

Fig. 3 Different types of natural fibers used as reinforcement in polymer composites

Table 1 Classification of biopolymers http://www.biocom.iastate.edu

Biodegradable polymers	
Natural	Synthetic
1. Polysaccharides • **Starch** • **Cellulose** • Chitin • Pullulan • Levan • Konjac • Elsinan **2. Proteins** • Collagen/gelatin • Casein, albumin, fibrogen, silks, elastins • **Protein from grains** **3. Polyesters** • Polyhdroxyalkanoates **4. Other Polymers** • Lignin • Shellac • Natural Rubber	**1. Poly(amides)** **2. Poly(anhydrides)** **3. Poly(amide-enamines)** **4. Poly(vinyl alcohol)** **5. Poly(ethylene-co-vinyl alcohol)** **6. Poly(vinyl acetate)** **7. Polyesters** • Poly(glycolic acid) • Poly(lactic acid) • Poly(caprolactone) • Poly(ortho esters) **8. Poly(ethylene oxide)** **9. Some Poly(urethanes)** **10. Poly(phosphazines)** **11. Poly(imino carbomates)** **12. Some Poly(acrylates)**

The classification of biodegradable polymers or biopolymers in natural and synthetic bio-polymers is shown in Table 1.

The first families of natural bio-polymers are agro-polymers (e.g. polysaccharides, proteins) obtained from biomass by fractionation. The second families are polyesters obtained respectively by fermentation from biomass or from genetically modified plants such as polyhydroxyalkanoates (PHA). The others family polyesters are totally synthesized by the petrochemical process such as polyester-amide (PEA), polycaprolactone (PCL), aliphatic or aromatic copolyesters (Avérous 2004) are commercially available.

Bio-polymers that are obtained by chemical synthesis involves PCL, PEA are quite common. PLA one of the most attractive, established versatile thermoplastics material for the development of green composites, among bio-polymeric materials (Satyanarayana 2015), synthesized from renewable resources through biotechnology. Its ease of availability from renewable agricultural sources along with inherent and comparable properties such as high mechanical strength, tensile modulus, biodegradability and biocompatibility are quite comparable with those of polystyrene and polyethylene. The summarized mechanical properties of some important bio polymer used in green composites with their comparison to commercial polyolefins polymer are shown in Table 2 (Koronis et al. 2013; Gurunathan et al. 2015). Chemically bio-based polymer matrixes are aliphatic polyesters and comparatively hold more favorable life-cycle profile than petrochemical-based traditional thermosets and thermoplastics. Biodegradable plastics or polymers can be fully degraded in composters or sewage treatment plants and in landfills merely by the action of naturally occurring micro-organisms (Mooney 2009), or through enzymatic reactions such as esterases, when exposed to a compost environment, however some of them also degrade in moist/wet outdoor environments through similar microbial/bacterial attack (Netravali and Chabba 2003). The green composites demands the polymer ideally derived from natural renewable resources, such as cellulose and starch including sweet potatoes, sugarcane, starches (corn and cassava), castor oil cake, pie, potato, rice, wheat and vegetable oils. (Saenghirunwattana et al. 2014; Reddy et al. 2013; Mooney 2009). Among vegetable oils epoxidized vegetable oils form the basis of the nascent thermosetting biopolymer industry. Plant oil based matrices such as soya oil and mango puree-based edible films have also been used in the fabrication of nanobiocomposites (Satyanarayana 2015; Xie et al. 2010). Currently, the green composites are commercially produced, with the aliphatic polyesters which can be degraded from enzymes like esterases. The conversion of corn and soybean products into the monomers currently offers the most cost-effective way (http://www.compositesworld.com). Presently, research investigations has been carried out concerning the production and utilization of bio-polymers covering many aspects such as their availability, synthesis, structure properties, mechanism of degradation and their potential applications. Research studies elaborated that biodegradable aliphatic polyesters including polycaprolactone (PCL), poly (3-hydroxybutyrate) (PHB), polyhydroxyvalerate (PHV), and their copolymers, polylactide (PLA), polyglycolate (PGA), poly(butylene succinate) (PBSu), poly (propylene adipate) (PPAd) and their copolymers with different monomer ratios, poly(ethylene succinate) (PESu), etc., are effectively used in various applications, such as bottles, packaging materials, fibers, mulch films and implants (Terzopoulou et al. 2015). The epoxidized vegetable oils and their combination with polycarboxylic acid anhydrides, isocyanates (Ortega et al. 2011) and acrylate (Scala and Wool 2005) exclusively commercialized for thermosetting and industrial

Table 2 Compiled mechanical properties of bio-based polymers

Polymer	Density (g/cm^3)	Melting point Tm °C	Glass transition T g °C	Tensile strength (MPa)	Young modulus (GPa)	Elongation at brake (%)
Thermoplastic starch	1–1.39	110–115	–	35–80	0.125–0.85	31–44
PLA	1.21–1.25	150–162	45–60	21–60	0.35–3.5	2.5–6
PLLA	1.25–1.29	170–190	55	15.5–65.5	0.83–2.7	3–4
PHB	1.18–1.26	168–182	5–15	24–40	3.5–4	5–8
PHBV	1.23–1.25	144–172	−1	20–25	0.5–1.5	17.5–25
DL-PLA	1.25	–	50	27.6	1	2
PGA	1.5	220–233	35–40	60–99.7	6–7	1.5–20
DL-PLA/PGA50/50	1.30–1.40	–	40–50	41.4–55.2	1–4.34	2–10
DL-PLA/PGA75/25	1.3		50–55	41.4–55.2	0.21–0.44	2.5–10
PCL	1.11–1.146	58–65	−60 to −65	20.7–42	0.21–0.44	300–1000
PP	0.9–1.16	161–170	−10 to −23	30–40	1.1–1.6	20–400
PS	1.04–1.09	110–135	100	30–60	4–5	1–2.5

Source Koronis et al. (2013), Gurunathan et al. 2015

Notes: Poly (hydroxyalkanoate) (PHA), Poly(3-hydroxybutyrate) (PHB), Poly(3-hydroxybutyrate-co-3-hy droxyvalerate (PHBV), Poly(lactic acid) (PLA), Poly(propylene) (PP), Poly(styrene)(PS), Poly (D-lactic acid) (PDLA), Poly (L-lactic acid) (PLLA), poly(e-caprolactone) (PCL) coating applications (Fowler et al. 2006). Moreover, the recent work on biocomposites reveals that in most of the cases specific mechanical properties of biocomposites are comparable to widely used glass fiber reinforced plastic (Satyanarayana 2015).

5 Factors Influencing the Performance of Green or Biocomposites

The properties of green composites depend on the type of selected bio-matrix, incorporated reinforced fiber/filler (type and aspect ratio), plasticizer used (type and amount) and processing technique for the fabrication of composites (Satyanarayana 2015). The selection of suitable fibers is critically determined by the required tensile strength, thermal stability and stiffness of the fabricated composites (Nickel and Riedel 2003). Besides these factors certain issues based on natural fibers (shown in Fig. 4), such as fibers alignment, elongation at break, interfacial adhesion between fibers and matrix are of prime concern (Nickel and Riedel 2003).

To increase the compatibility between fibers and bio-polymers, many efforts and approaches were explored and reported, including the introduction of compatibilising agents during processing and chemical modification of the fibers prior to fabrication of composites (Fowler et al. 2006). Green composites shows effective applications and can efficiently compete with non-biodegradable polymers in different industrial applications such as mass-produced consumer products with (1–2 years) short life cycles (nondurable) or products intended for one-time or short-term (few times) use before disposal as well as for long-term indoor applications of several years life just like wood (Ghaffarianhoseini et al. 2013; Netravali and Chabba 2003). They can be easily composted/disposed or completely assimilated without destroying the environment at the end of their life.

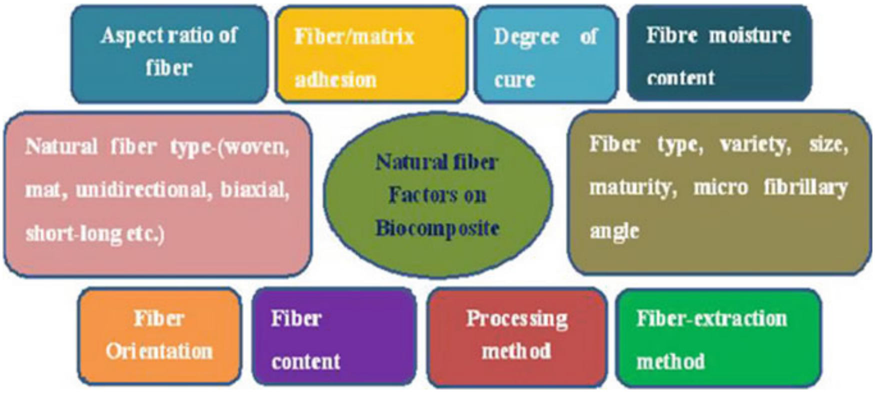

Fig. 4 Factors governing the properties of green composites (Color figure online)

6 Green Composites Manufacturing

Exclusively same techniques based on existing techniques for conventional processing of plastics or composite materials are designed to manufacture/fabricate green composites. These include open mould (hand lay-up and spray-up), and closed mould techniques such as pultrusion, extrusion, direct long-fiber thermoplastic (D-LFT), vacuum infusion, injection moulding, filament winding, resin transfer moulding, compression moulding and sheet mould compounding (Fowler et al. 2006).

The processing conditions and appropriate processing methods have substantial effect on the parameters such as dispersion, aspect ratio, orientation and moderate temperatures (below 200 °C), that govern the mechanical properties of a developed green composites (Sallih et al. 2014). Fiber drying before processing is crucial as the presence of moisture on the fiber surface acts as a debonding agent at the fiber–matrix interface. Additionally, evaporation of water during the reaction generates voids within the matrix. Both the aspects lead to a significant decrease in the mechanical properties of green composites (Gurunathan et al. 2015). However manufacturers believe that the major challenge to fabricate green composites basically involves the contest to procure the bio-polymers from natural resources as matrices.

7 Applications

7.1 *Applications of Biodegradable or Bio-Polymers*

- Biodegradable polymer for vascular, skin adhesive, tissue engineering, orthopedic, ocular and surgical glues.
- Polymer system for gene therapy.
- Bio-polymeric materials are used to improve soil aeration and to promote plant growth
- Biodegradable drug system for therapeutic agents such as antipsychotic agent, anti-tumor and anti-inflammatory agent.
- Bio-materials particularly blood vessels and heart valve replacements are made of polymers like Teflon, dacron and polyurethane (www.slideshare.net) (http://www.materialstoday.com).

7.2 *Applications of Green Composites*

The persistent and growing problems associated with waste disposal or its management, depletion of petroleum fuel sources at high rate and striking oil prices

Table 3 Green composite aspects and its features in corresponding applications

Material attributes	Application attributes
Excellent weight specific stiffness, good weight specific strength	Weight critical vehicles/products (transport, mobile electronics, sport equipment
Variable fiber properties	Non-safety critical/low required reliability applications
Renewable resource, low embodied energy Biodegradable	Short life-span product (disposable and high obsolescence rate products)
Non-toxic	Children's toys, consumer handled items, hobbyist built items
Biocompatible	Medical devices and implants
Low cost	Competitive consumer products
High water absorption	Dry use products
Poor durability	Short life-span products, limited exposure to harsh environments

Source Dicker et al. (2014)

triggered the global environmental awareness and regulations program with the concepts of sustainability and complete assimilation of end products among manufacturers and consumers throughout the world. All these leads to inclination towards the processing of green materials and bio-based 'green' products, which are compatible with the environment to alleviate fast raising problems for diverse applications, including packaging, secondary and tertiary structures and consumer products for casing (Mülhaupt 2013; Harmsen et al. 2012). Green composites have the unique features combination involving environmentally sustainable, compatible and fully biodegradable which perfectly widened its applications to play a significant role in the management of huge volumes of wastes (Gejo et al. 2010; Gurunathan et al. 2015) and greening the future commercial products (Wu et al. 2014). Researchers in their study reported the green composites aspects and its features in complementary applications, (Table 3) (Dicker et al. 2014).

However it also reflects some constraints, which can be managed by pre considering its limitation before applying in specific applications. Although, in order to explore its commercial markets, such as construction and consumer goods for external applications it required favorable high-quality performance, durability, long life with reliable rules or standards (Gurunathan et al. 2015).

7.3 Commercial Applications of Green Composites

Many developing countries are compelled to stimulate green chemistry and green products development, that are derived solely from nature. The green composites are currently getting targeted towards the automotive (such as panels separating the engine and passenger compartments), sporting goods, electrical/electronic

Table 4 Possible extension of green composites application

Industries	Appliances
• Product casings and packaging	Telephones and cell phones, computers, printers, monitors (other consumer items)
• Microelectronics	Chip packaging, circuit boards
• Housing and transportation (auto) panels	–
• Mass-volume disposable commodities	–
• Non-invasive medical applications and casts etc.	–
• Secondary load-bearing structures	–

Source http://www.biocom.iastate.edu

components, construction (such as door/ceiling panels), furniture, food packaging, energy industry and various appliances based industries as an excellent alternative feedstock sources (Dicker et al. 2014; Koronis et al. 2013). Nowadays green composites also being extended to redefine its applications in the advanced and hi-tech applications (Table 4) (http://www.biocom.iastate.edu).

7.3.1 Domestic/Households Applications

El Capitan guitar from Blackbird Guitar (San Francisco, Calif.) appear with the wistful appeal of a vintage instrument. Company claims that it is made from Ekoa-brand high-performance, eco-friendly green composite materials having the same stability to that of carbon fiber composites with the feel, look and sound same like wood.

Recently, Ayers cork furniture developed by the Portuguese designer Albertina Oliveira consisting of the tabletop and luminaire, crafted from a composite of cork and basalt fibers (corkbalt) are quite strong but light in weight (http://blog.gessato.com). Applications of green composites are expanding to skateboards, skis, surfboards, furniture, boat paddles and auto interiors are generally processed via compression molding, resin transfer molding, resin infusion and hand lay-up (www.compositesworld.com). The beautiful electronic guitar and Ayers cork furniture are shown in Fig. 5a, b.

Greenline Jakob Winter (Germany) based company produces laptop cover from organic bio plastics, industrial cases and special brief-cases made from retainable natural fibers reinforced plastics (www.naturfaserverbundwerkstoffe.de). Additionally, Sam Whitten’s company prepared flax fibers and hemp based eye wear. ‘Hemp eyewear’, sunglasses made from a hemp fibers composites by compression moulding under heat, impregnated with an eco-friendly binder. The sunglasses are also coated with an eco-friendly bioresin to add extra waterproof and strength properties (http://

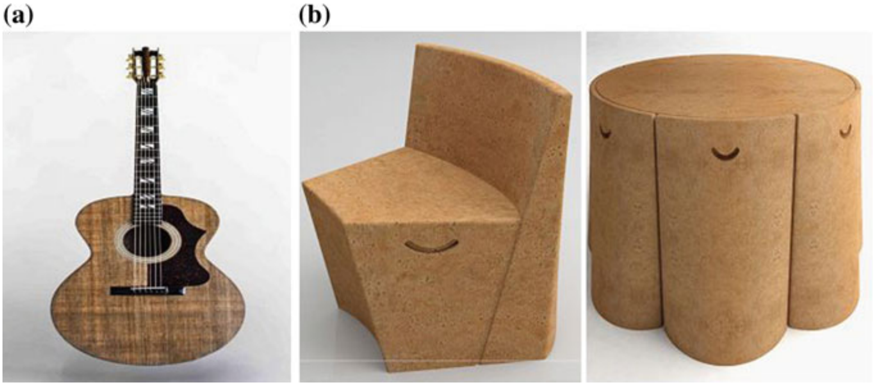

Fig. 5 El Capitan guitar (**a**) and Ayers cork furniture (**b**). **a** www.compositesworld.com, **b** http://blog.gessato.com

Fig. 6 Special suitcases (**a**) and hemp eyewear (**b**). **a** www.naturfaserverbundwerkstoffe.de, **b** www.hempeyewear.com

www.hempeyewear.com) and (http://www.naturalfibersforauto motive.com). The organic bio-plastics based suitcases and hemp eye-wear sunglasses are shown in Fig. 6a, b.

The biopolymers and biocomposites research team are excitingly involved in developing biodegradable and bio-renewable plant containers for the specialty crop industry. Bio-based plant containers are produced from carbohydrates, oils, natural proteins with relatively cheaper low-cost natural fibers. The developed bio-based plant containers (made from soy and corn proteins polymers) deliver a sustainable alternative for petroleum-based pots as it degrade completely in the end of its life cycle during plant culture, providing fertilizer for growing plants (http://www.biocom.iastate.edu). Kitchen trays made using starch-polyvinyl acetate (PVA) based biodegradable polymers are also quite attractive product. The phenix-biocomposites also designed green biocomposites for architecture indoor

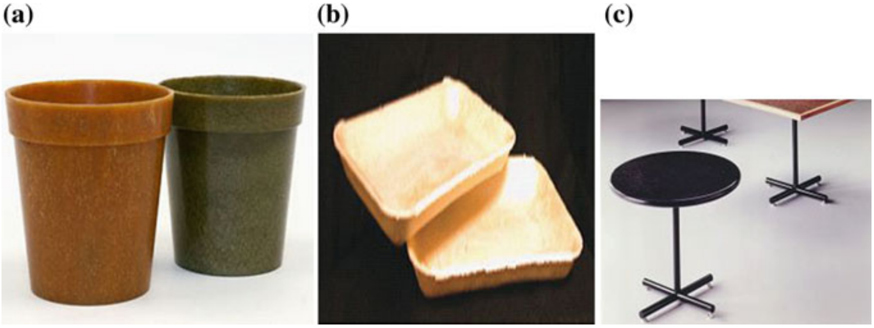

Fig. 7 Bio-based plant containers (**a**), kitchen trays (**b**) and green composites based tables (**c**) (Phenix-Biocomposites)

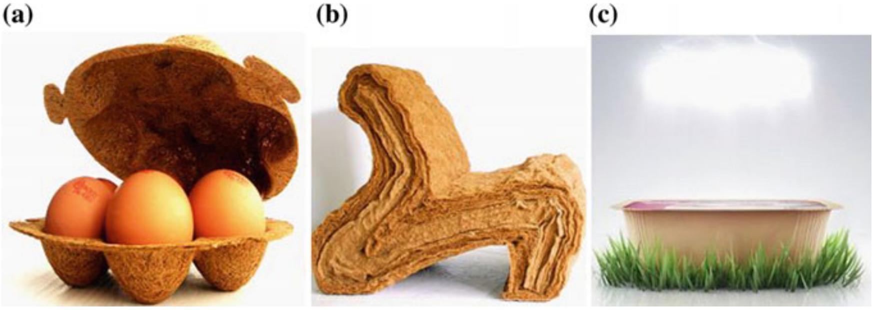

Fig. 8 Egg shelves (**a**), layered chair (**b**) and multi-purpose packaging material (**c**). **a** http://hellomaterialsblog.com, **b** http://flavorwire.com **c** http://www.ahlstrom.com

items such as different shapes of chairs and tables. The bio-based plant containers, kitchen trays and different green composites tables are presented in Fig. 7a–c. Ahlstroms high performance fiber-based materials company offering products for clean and healthy environment, recently develop compostable, biodegradable, multipurpose packaging and molding material, NatureMold™, having a wide range of features to benefit both brand owners and food processors. NatureMold™ found suitable for both microwave to table and freezers to oven as it is quite safer to freeze and to be heated to 220 °C (428 °F) in the oven (http://www.ahlstrom.com).

Inspired by Cocolok®, which is a resilient material based on natural coconut fibers bonded with 100% natural latex, developed by Enkev, designed layer chair and egg shelves (http://hellomaterialsblog.com). The egg shelves, multilayered chair and multi-purpose packing material are displayed in Fig. 8a–c.

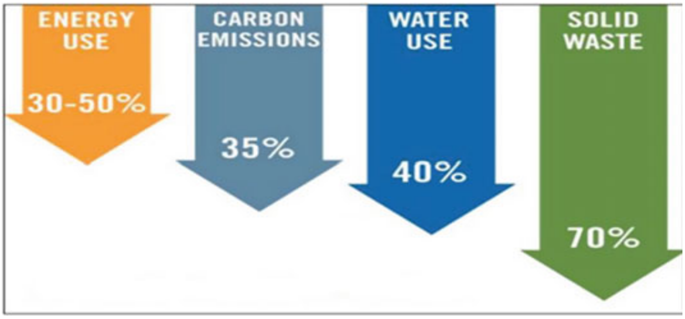

Fig. 9 Average savings of green buildings greenblueprint.com (Color figure online)

7.3.2 Architectural Applications

Eco-design and energy-efficiency are urgent concepts that express the need of environmental friendly new building solutions for the reduction of materials and energy consumption (La Rosa et al. 2014). Currently, the development of green building received higher attention to conserve and to minimized the impact of buildings made on the environment through reducing the energy, fuel and emission of toxic gases especially (COx) (as shown in Fig. 9).

Green and sustainable buildings design usually show the replacement of cement, steel and other heavy constructional materials by green composites round the globe. Green composites architecture and constructional applications offers several advantages and benefits such as recycled content, rapidly renewable materials, regional materials, building and material re-use (Yudelson 2010), summarized in Fig. 10.

Green biocomposites are extensively used in roof panels, street furniture, curtain walls, lineals for windows/doors (Yudelson 2010). Use of green composite bars in buildings to replace conventional steel rebars are already been reported to make the structures more earthquake resistant. Additionally the growing society demands for greener buildings and LEED certified (Leadership in Energy and Environmental Design), from the architects, designers and engineers for primary structural as well

Fig. 10 Benefits of green sustainable buildings http://www.ashland.com (Color figure online)

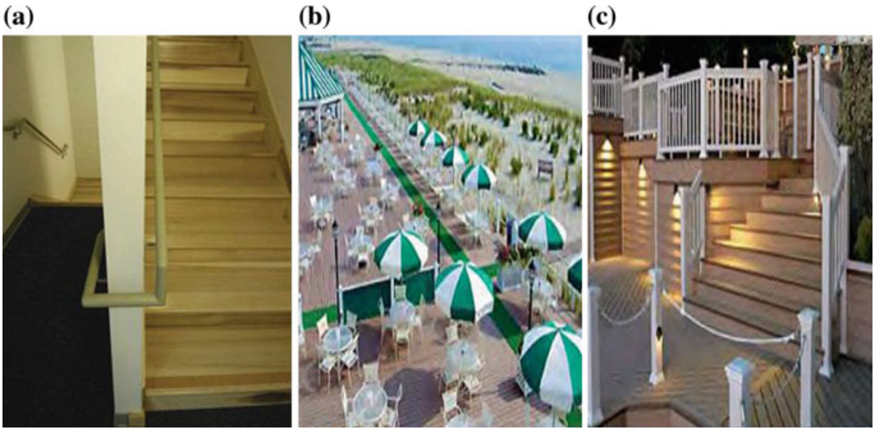

Fig. 11 Staircases (**a**), decks (**b**) and elevator panels (**c**). (**a**) http://www.ahlstrom.com, (**b**, **c**) http://www.biocom.iastate.edu

as secondary components. Some of the secondary structural components for sustainable buildings are:

- **Elevator panels**—Building elevator sidings bio-fiber wheat composite panels from wheat straw, a byproduct of wheat harvesting had been developed by Phenix biocomposites (www.phenixbiocomposites.com).
- **Stairways**—Stairways throughout the building made from poplar, a fast-growing, widely available, abundant wood composite by the tailor stair company certified by the Forest Stewardship Council (FSC) (www.taylorstair.com).

Green composites based staircases, decks and elevator panels are shown in Fig. 11a–c.

- **Green Fiber Cabin**—Green fiber cabin also been produced by using soy protein based resin, and natural fiber (sisal, kenaf, jute, hemp, etc.) mats of desired shape depending on green fibers cabin design through hot press, signifies a new greener approach. A green fiber cabin construction incorporates medium strength molded green composites for walls, roofing and advanced green composites for structural elements. The fabrication process of the manufacturing of green fiber cabin is shown in Fig. 12. Figure perfectly illustrates the incorporation of natural fibers such as hemp mat in biopolymer, with the water and soy protein as a binder agent, followed by putting the mold in the hot press for a definite time and then left to cure for final biocomposites product.

Recently, BioBuild, a European Commission funded project coordinated by net composites are launched to reduce the embodied energy in construction materials with comparatively minimal increase in cost, at “Architects’ Day” at Advanced Composites in Construction 2013. The biobuild projects highlights the high

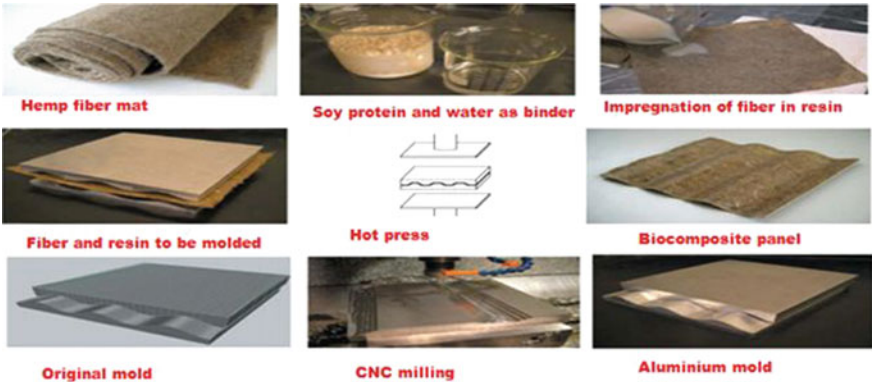

Fig. 12 Composite fabrication process using soy protein based resin and natural fibers

performance, economical and sustainable biocomposite building materials. The laminates, partitions, panels, shutters, door frames and roofing have been designed as an promising substitute to prevailing woody materials (Cheung et al. 2009; Gurunathan et al. 2015). Green composites also cover applications which include bridge decks and structures, external cladding, structural repair, refurbishment and modular buildings. A Dutch architecture created the world's first "bio façade" commissioned by the horticultural development company. The bio-façade is a natural gas transfer station, comprising of small building clad with composite panels exclusively made from locally sourced hemp fibers reinforced bio-resin that are collectively derived from soy beans, linseed oil or even waste from biodiesel production (http://www.globalconstructionreview.com). Moreover, in 2011, U.S. Green Building Council's prepared the solid surface sink from unsaturated polyester developed from AOC's Eco-Tek line of bio-resins (http://www.compositesworld.com). The bio-façade and solid surface sink are shown in Fig. 13a, b.

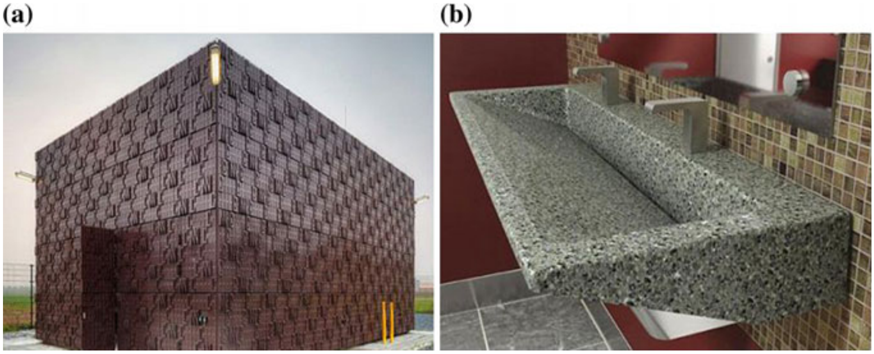

Fig. 13 The bio façade (**a**) solid surface sink (**b**). **a** www.globalconstructionreview.com, **b** www.compositesworld.com

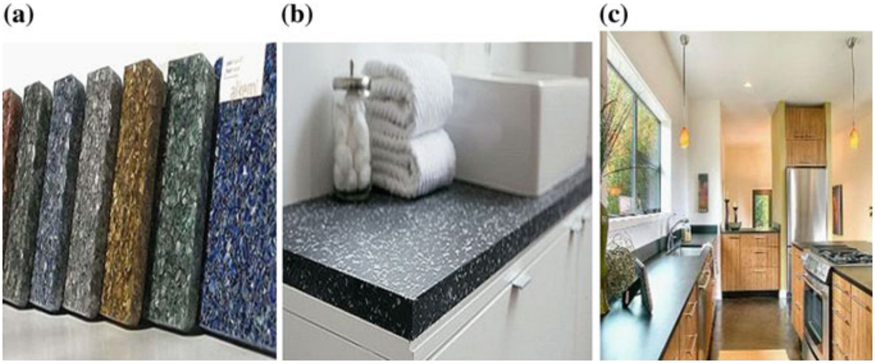

Fig. 14 Composites floor (**a**), bathroom products (**b**) and interior furniture's (**c**) http://meganbarkerdesign.blogspot.my

7.3.3 Interior Decorative Buildings Components

The green composite correspondingly reflects a revolutionary trend in the interior of the buildings components. Recently the manufacturers used green materials in designing extremely environmental solid surfacing materials such as buildings floor, bathroom products (caroma toilets) and other indoor furniture's for greener and sustainable LEED green school (http://meganbarkerdesign.blogspot.my). The green composites floor, bathroom products and interior furniture's of LEED green school are displayed in Fig. 14a–c.

Ahlstrom partnering with leading businesses around the world is a fiber-based materials company developing high performance composites materials. Some of the buildings and decorative panels made by Ahlstrom are shown in Fig. 15.

A wide variety of 100% sustainable green products materials belonging to daily applications such as medical fabrics, filters, food packaging, wallcoverings, decorative floor/surfaces, building/construction as well as life science/diagnostics are being manufactured for healthy and safer environment (La Rosa et al. 2014;

Fig. 15 Constructional panels made by green composites http://www.ahlstrom.com (Color figure online)

Fig. 16 Decorative surfaces from genuine vegetable parchment http://www.ahlstrom.com

Fig. 17 Most luxurious elevations (**a**), decks (**b**) and outdoor railings (**c**) by Trex. http://www.trex.com

Gurunathan et al. 2015). Figure 16 illustrates some decorative surfaces (floorings) from genuine bio-source (vegetable) parchments. The world's largest manufacturer of wood-alternative decking products based company Trex-USA , is currently preparing high performances green composite deck, from an innovative blend of 95% recycled wood and plastic film. Besides this it also involved in making greener, durable and highly luxurious elevations, docks and marinas, outdoor railing, outdoor deck fencing and outdoor furniture through green biomaterials. The beautiful elevations, decks and outdoor railings are displayed in Fig. 17a–c made from green biocomposites.

7.3.4 Transportation

The persisting issues of synthetic polymers price, high rate of oil depletion and greenhouse gases drive the concerns to explore an innovate materials products having potential tendency to replace the existing traditional materials finished from petroleum-based resins, synthetic fibers (such as carbon, glass, aramid) as reinforcements, iron bars and stainless-steel (http://www.materialstoday.com).

From past few decades, the application of natural fiber composites and green composites to niche markets marked a new revolution, especially in the automotive sector to minimize the use of nonrenewable and expensive materials (Koronis et al. 2013). Green composites provides lower energy consumption along with vibration damping benefit in transportation and automotive sectors, owing to lighter in weight as compared to steel and iron components for automotive industry, shipbuilding and in huge mass transit. The composites structural parts are fuel-efficient, environment-friendly (emits less carbon dioxide) and are relatively more flexible than metal thus can be molded and designed into various shapes.

The water absorption properties is the only factor which exclude them from being used in the vast array of wet glass fiber reinforced polymer (GFRP) applications such as in kayaks, piping, tanks and boats (Dicker et al. 2014).

Extensive research work has been reported by many companies and research institutes regarding the innovative applications of bio-composites involving natural fiber fabrics and bio-polymers. A grit container from CEMO, an interior panel from the CAYLEY project, electric car charging station from car parts design (CPD) and e-scooter are the best attractive applications of green bio composites (http://www.materialstoday.com). Recently, the first biocomposites, two-wheeled light electric vehicle (**e**-scooter) called Be.e electric scooter has been reported. It is consists of an extremely sustainable, lightweight and strong material, as its monocoque body made of hemp, dutch-flax and biologically derived resin. Figure 18a, b shows the e-scooter and electric charging station for the cars. The windscreen is nano-coated with a hydrophobic layer that deflects water droplets and dirt particles. The unique construction design of e-hemp scooter is exclusively based on state of the art propulsion systems with well proven drive train components. This design remarkably justify that supporting structures in high-impact transportation vehicles, exclusively made with iron and steel can be replaced with more sustainable natural fibres and bio resin combinations, without losing mechanical strength or performance (www.dezeen.com). Thus the object's external skin supports the load, similar to an eggshell, eliminating the need for a frame and the usual numerous plastic panels. The batteries of hemp scooter can be charged with a 600 W charger, allowing users to fully re-charge in under 3 h, and to allows to drive about 2 h at 60 km in the worst of conditions (www.designboom.com).

Moreover, Hemp Earth, a company designed a four seater hemp plane made up of 75% industrial grade hemp with a more special future to run on hemp-based biofuel (http://gearheads.org). In other side, Lotus company has developed composite hemp panels to replace more traditional glass fibers in the development of their Lotus Elise Eco Concept Car (http://gearheads.org).

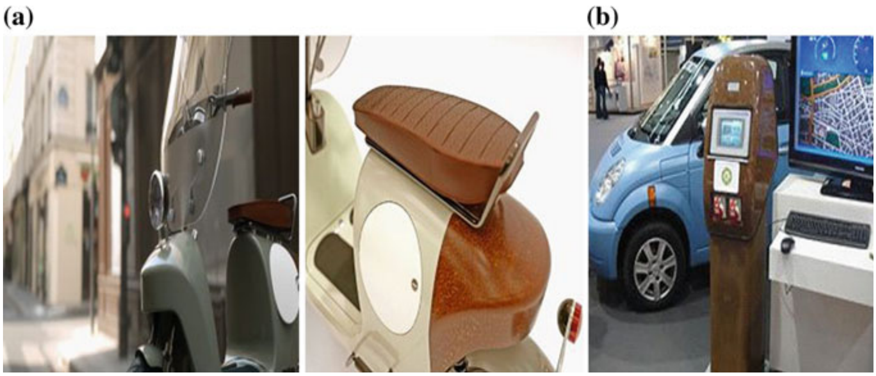

Fig. 18 Be. e electric scooter (**a**) and electric charge station (**b**). **a** www.dezeen.com, **b** www.materialstoday.com

Fig. 19 Hemp plane (**a**) and Lotus Elise Eco Concept Car (**b**). **a** http://altnonfic.com/hemp-car, **b** http://gearheads.org

The hemp plane and lotus eco concept car shown in Fig. 19a, b.

RLR 1 is modern and luxurious car with sustainability at the forefront of its design, having the metal and foam sections removed by 97% biodegradable or recyclable components that can be fully composted, at the end of life. It is primarily constructed from FSC certified plywood, combined with silk fabric and bio-resin derived from linseed oil based alternative to the existing typical glass fibers and chemical resins (richardlanderracing.blogspot.com). Furthermore, Kenneth Cobonpue and Albrecht Birkner designed a project to unveil the future of green vehicles using woven skins from organic fibers mated to composite materials powered by green technology in order to manage the wastes from old cars and build a Phoenix concept car. Developed concept car is the world's first 153 in. long biodegradable car, built in just 10 days from bamboo, rattan, steel, and nylon by product designed by Kenneth Cobonpue and Albrecht Birkner (http://inhabitat.com). The RLR 1 and Phoenix concept car are displayed in Fig. 20a, b. Renowned, Faurecia automotive exterior company also striding its research in the field of composites, through collaborations with world of academia and research laboratories. Currently, Faurecia are one of the leading

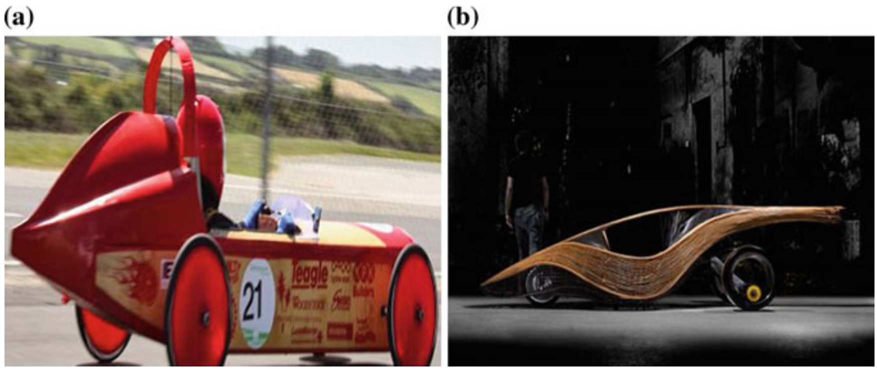

Fig. 20 The RLR 1 car (**a**) and Phoenix concept car (**b**). **a** richardlanderracing.blogspot.com, **b** http://inhabitat.com

company in designing the composite parts for automobiles, including both structural, semi-structural (roof, hood, hatchback, etc.) and visible components (painted or visible carbon parts) (http://www.faurecia.com).

A UK-based research consortium from the universities of Ulster (Art & Design Research Institute) and Warwick design an eco-friendly, green composites based formula 3 racing car using environmentally sustainable components centered on extensive research on the processing parameters of bio-resins. The process uses 3D flax yarn preforms with liquid moulding technology (http://www.iom3.org). Researchers also reported the development of green composites for seat paneling element and rail vehicles interior paneling, fulfilling the requirements of weight savings by 30% compared with glass fibers reinforced materials (Nickel and Riedel 2003). Besides this many hand friendly products presenting an interesting approach to a multitude of technical applications has been designed includings personal digital assistants (PDA), portable CD or MP3 players, cellular phones and CD-holder (Nickel and Riedel 2003). Faurecia exterior components, green formula 3 racing car and seat panel are displayed in Fig. 21a–c.

Biofore Concept car made by UPM's next generation biomaterials and Helsinki Metropolia University of Applied Sciences, implies the best environmental performances (shown in Fig. 22). The major parts conventionally made from plastics are replaced with UPM Formi and UPM Grada, a high quality, safe, clean, durable and odorless composite biomaterials. The interior panels, instrument panel, sill covers, floor and bow structures made from fossil raw materials constitutes a 15% of Biofore vehicle's weight (http://www.upm.com).

Additionally, Armstrong and Motive Industries introduced industrial hemp based biocomposites fully electric Kestrel car to influence the future of electric-car building, having zero emission vehicle (ZEV), in Jan 2010 in Vancouver Electric Vehicle (EV) Conference and Trade show (http://cannabisdigest.ca/hemp-bio-composite-electric-car). The hemp fibers effectively constitutes constructional material for car based body panels, boot and vehicle's shell. The Kestrel cars and

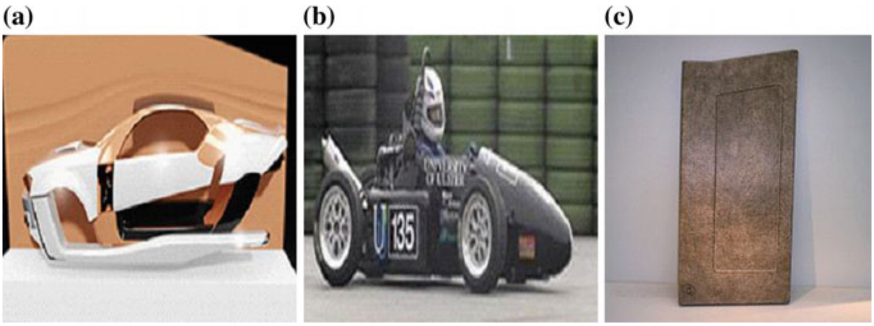

Fig. 21 Car exterior component (**a**), formula 3 racing car (**b**) and seat panel (**c**). **a** http://www.faurecia.com, **b** http://www.iom3.org, **c** Nickel and Riedel (2003)

Fig. 22 Biofore Concept car by UPM http://www.upm.com

doors made from hemp based biocomposites are shown in Fig. 23a, b. Car has the impact resistance of fiber glass, with the relatively green composites parts presenting fewer health risks for manufacturers and workers.

7.3.5 Aerospace and Aircrafts

Nowadays the green composites are also extending its applications towards the biggest consumer of the composites in aerostructures business such as aircraft components. More than 200 commercial, civil and military aircraft components are currently manufacturing through biocomposite materials worldwide. The significant benefits of the systems includes reduced fuel consumption, reduced weight, low GHG-emission, less noise, longer maintenance duration gap, better performance and reliability (Heimbs et al. 2010). The interior sophisticated components, propeller systems, trimmable horizontal stabilizer actuators, cabin equipment, wheels/brakes and flight safety parts for helicopters are also being designed and

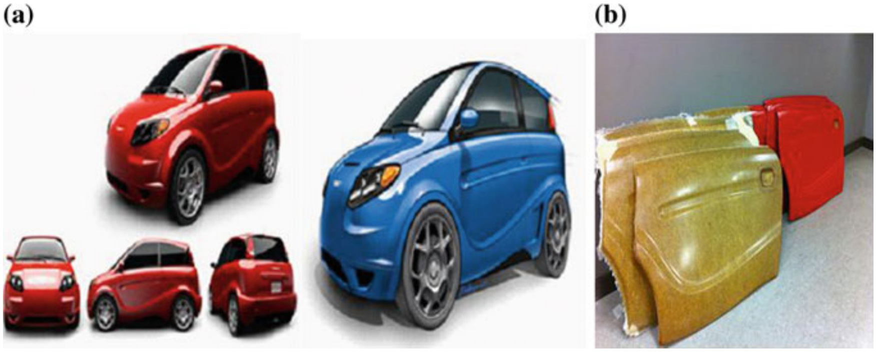

Fig. 23 Multicolored Kestrel cars (**a**) and hemp door (**b**) http://cannabisdigest.ca/hemp-bio-composite-electric-car

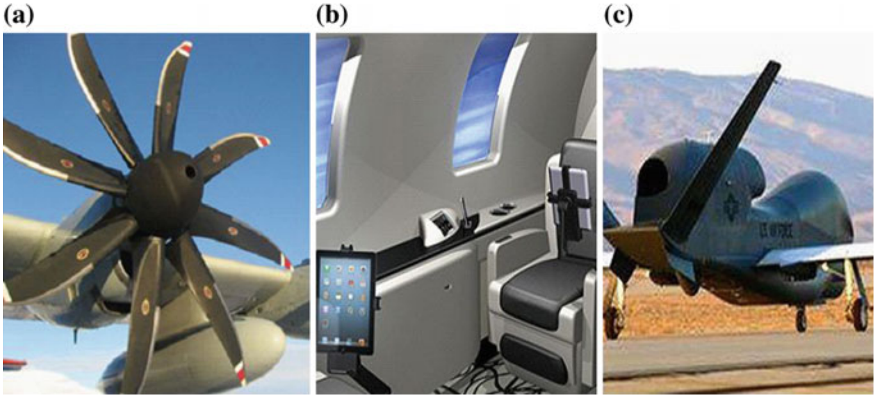

Fig. 24 The propeller systems (**a**), cabin equipment (**b**) and wheels/brakes of the aircraft (**c**) http://utcaerospacesystems.com

replaced by greener composite materials (Blasques et al. 2010; Milan 2005; Brunner 2015). The propeller systems of turboprop-powered aircraft, cabin equipment and wheels/brakes of the aircraft are presented in Fig. 24a–c.

7.4 Applications of Wood Based Bioplastic Composites (WPCs)

Wood based bioplastic composites also shows extensive applications and use in all areas of life as they are comparatively inexpensive and sustainable providing a huge attraction for innovative design (Chen et al. 2014). According to the study by Markarian (2008), the WPCs market, including thermoplastics and thermosets has

Fig. 25 Household products made of WPC http://lessbydesign.org

been estimated globally at 900,000 ton, where only 10% are consumed from Asia, 20% in Europe and major portion of 70% volume consumed by North America. In recent years, wood fibers/flour (WF) reinforced biocomposites, named WPCs, play a vital role in the social, economic and environmental growth of human history (Binhussain and El-Tonsy 2013; Gurunathan et al. 2015). The WPCs show characteristics features of moderate strength, high durability and lighter weight. Various wood and natural fibers have been used in the processing of WPCs, for example, hemp (Beckermann and Pickering 2008), cellulosic fibers (Beg and Pickering 2008) and flax (Bos et al. 2006). The WPCs are initially used for construction applications (decking, docks, landscaping timbers, fencing) and non-structural applications, but presently they are displaying more broader and wider range of applications, including automotive, gardening, outdoor products, profiles and decking (Alamri and Low 2013). Interestingly, WPC are also found suitable for further processing to produce toys or household products manufactured by both injection moulding and extrusion, shown in Fig. 25 (http://www.jeluplast.com). The JELU-WPC granulates also being used in making bottle openers and pen caps (Fig. 26) (http://www.jeluplast.com).

Fig. 26 Products of JELU-WPC http://www.jeluplast.com

8 Conclusions

Growing awareness and an escalating demand in society towards green sustainable and pollution free environment drive the material science and technology to manufacture the pioneering and advanced commercial products that are fully biodegradable and compatible with the environment. Fully green or biocomposite is the reply to the increasing concept of greener and renewable products and it opens new opportunities and avenues for both academicians as well as industries to manufacture a sustainable module. Presently green composite materials received greater commercial acceptance for both structural and non-structural applications where a combination of stiffness, high strength, renewability, durability and extremely low weight are key requirements. They display a wider versatility in materials just by varying the required bio-polymer to the particular product demands including PLA, PHA, vegetable oils and soy based matrix with different cellulosic based reinforcements. Green composites offer extensive and elaborative applications in the areas of construction, automotive interior components, aerospace, defense, marine-offshore, automotive/transport and specialty products such as wind turbine blades. Certainly, eco-friendly and fully biodegradable/compostable reinforced plastics or ‘green’ composite materials will play a key role in minimizing the wastes disposal problem, economy and ecological instability but positively leads to greening of the products in the future.

This review article expected to delivers valuable evidence or literature information for further research and in the elaborative study of novel green biocomposites derived from other agricultural or crop wastes. The future research work will involves the expansion of green composites in the construction of roads or multilevel bridges and sports products.

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Green Composites: Versatile Material for Future

Anshu A. Singh, Sadaf Afrin and Zoheb Karim

Abstract The growing concern towards environmental problems and the urgent need for more versatile environmental friendly materials has led to increasing attention about polymer composites, i.e. fillers/reinforcing materials coming from renewable sources and biodegradable, especially from forest. The composites usually referred to as "green", can find several industrial applications as discussed in this chapter. Biodegradable polymers coming from natural resources are also one important constituent of green composites. This chapter provides tactic for readers regarding the materials used for the fabrication and specific application of green composites in various fields. Furthermore, a discussion of the major material attributes of green composites is provided. From these focuses, a series of balancing application properties are explained. The chapter concludes that green composites have potential for use in a number of applications, but as with all design, one must carefully match the material to the application.

Keywords Reinforcing materials · Green composites · Biodegradable polymers · Plant fibers

1 Introduction

Man has been using materials since the beginning of the recorded history. Initially only natural materials like stone, clay, wood etc. were used. Materials have an important role in the life of modern man and have been making significant

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contribution to the techno-economic development of the modern world. Materials have been divided into three broad categories: (i) metals, (ii) ceramics, and (iii) polymers (Buschow et al. 2001). Composites based on metal, ceramic and polymer matrices have also been developed. Polymers (synthetic and biopolymers) and polymer composites have emerged as important materials. The two main constituents of a polymeric composite are: (i) a polymeric matrix, and (ii) a reinforcing material. A composite offers better properties than those of its constituent materials, due to synergistic properties of its constituent materials. In a composite, one of the constituent materials is in continuous phase, and is termed as the matrix, and the other is discontinuous or dispersed phase and is termed as the reinforcement or the reinforcing material. Polymeric composite include, mica or any other particle reinforced polymer composites; short aramid fibers or any other short fiber reinforced polymer composites; continuous carbon fiber reinforced epoxy or any other thermoset or thermoplastic polymer composites; nanoparticles or nanofibers reinforced polymer composites. Properties of a polymeric composite are governed by properties and amount of the polymeric matrix; properties (for example; aspect ratio, chemical nature, purity, distribution, orientation and geometry) and amount of the reinforcement; and the interfacial adhesion between the two. Thus, the properties of a composite are strongly influenced by the properties of their constituent materials, their amounts and distribution, and the fiber/matrix interfacial adhesion (Herrera-Franco and Valadez-Gonzalez 2004).

There are several advantages of such polymeric composite; however, the main limitation is the problem of suitable removal or recycling after the end of life and reuse of both the components quite difficult. Furthermore, the synthetic polymers (like polypropylene, polyethylene etc.) production requires a remarkable consumption of oil-based resources, which are notoriously non-renewable and as a result of declining oil reserves and increase in cost of production of fossil fuels; scientists and researchers are now exploring alternative sources that are renewable, environment friendly and are sustainable. Energy Information Administration (EIA) reported that the oil production is expected to decline at the rate of 4% per annum after year 2010 and therefore great effort has been made in the policy and promotion in search of engineering sustainable solutions in energy and the environment (Nirma et al. 2015; Holbery and Houston 2006).

In view of this, the concept of "green composites" is gaining more and more importance these days because of increasing environmental awareness, decreasing oil reserves and demands of legislative authorities. This green composite consists of biodegradable polymers as matrix materials and natural fibers as reinforcement materials. Recent advances in polymer composites offer significant opportunities for improved materials from renewable resources with enhanced support for global sustainability. The green composites from natural fibers and biodegradable polymers will render a major contribution in the 21st century due to environmental problem as this composite gives a possible solution to waste disposal problems associated with traditional petroleum derived polymers. Green composites are emerging as new eco-friendly polymeric composite material and are offering commercial and engineering applications along with techno-economic advantages

(Mohanty et al. 2002). Green composites deriving from renewable resources bring very promising potential to provide benefits to companies, natural environment and end-customers due to dwindling petroleum resources. Nevertheless these materials have very high pressure from the global market. In present day it is a challenge for scientists and researcher to find out the properties and suitability of various polymers available in current market to make sure whether they are right to be used as a matrix material for green composite or not (Paul et al. 2003).

2 Constituents of Green Composite

One of the main components of the green composite is the use of natural/bio-fiber as reinforcement materials. Reinforcing material or reinforcement are embedded in the matrix of the composite, and form the discontinuous or the dispersed phase of the composite material. It carries the applied load and stress, and imparts improved mechanical properties, including stiffness and strength, to the composite. Another important constituent of green composites are biodegradable polymers which act as a matrix or continuous phase and plays an important role in determining the demanding properties of the green composite. It provides protection to the composite against environmental and chemical attack, and holds and binds the reinforcing materials together and transfers load and stress to the reinforcement (Thakur et al. 2014; Karim and Afrin 2015; Karim et al. 2016a).

2.1 Reinforcing Bio-Fibers

Bio-fibers are renewable fibers that can be obtained from plant, animal and mineral resources and can be used as reinforcements in manufacturing of green composite in the same way as the synthetic fibers. The classification of bio-fibers based on their origin is shown in Table 1.

Table 1 Classification of bio-fibers

Bio-fibers	Examples
Animal fiber	(a) Wool/hair—sheep, camel, rabbit hair, goat hair, yak, horse hair
	(b) Silk—mulberry silk, coarse silk
Mineral	Asbestos, wollastonite
Plant fiber	(a) Wood fiber—hardwood, softwood
	(b) Non-wood Stalk fiber—bamboo, wheat, rice, grass, barley, corn, maize, oat
	Fruit fiber—coconut, betelnut
	Seed fiber—cotton, oil palm, kapok, alfalfa
	Leaf fiber—sisal, banana, palm, date palm, pineapple, henequen, agave
	Bast fiber—hemp, jute, banana, flax, kenaf sugarecane, ramie, roselle

Adopted from Refs. Mohanty et al. (2002), Holbery and Houston (2006), Thakur et al. (2014)

In recent years, natural plant based fibers, for example—jute, coconut, hemp, sisal, coir, banana etc., have been used as reinforcing materials in place of conventional fibers like glass, carbon, aramid, etc. The main advantages of using these natural fibers over conventional synthetic fibers are their easy availability, low cost, bio-degradability, renewability, recyclability, low density, acceptable specific strength and stiffness, reduced tool wear, non-abrasiveness, easy to manufacture, light weight and non-toxic nature. Dittenber and Gangarao (2012) and Ahmad et al. (2015) discussed the comparison between natural fiber and synthetic fiber on the basis of cost per weight, and cost per volume versus tensile modulus and tensile strength for natural fibers, synthetic fibers, natural fiber composites, and synthetic fiber composites and it was found that as compared to synthetic fibers, the natural fibers are generally cheaper in cost (Oksman et al. 2003; Ramamoorthya et al. 2015).

2.1.1 Plant Fibers

Plants from which natural fibers obtained are classified as primary and secondary depending on their utilization. Primary plants are those grown for their fiber content for example; jute, hemp, kenaf, and sisal and/or secondary plants, for example; pineapple, oil palm and coir (Corbiere et al. 2001). Plant fibers have also been classified according to their origin and the part of the plant from which the fiber is extracted. The classification of natural fibers based on their origin is shown in Table 2.

Wood Fibers

Wood fibers have been categorized into hardwood and softwood fiber. Hardwood fibers for example; fibers from aspen and birch and softwood fibers for example;

Table 2 Comparison between natural fibers and synthetic fibers cost

Properties	Natural fibers	Synthetic fibers
Resource	Infinite	Limited
Renewability	Renewable	Non-renewable
Recyclability	Good	Moderate
Bio-degradability	Bio-degradable	Non-biodegradable
CO_2 neutral	Yes	No
Density	Low	High
Mechanical properties	Moderate	High
Moisture sensitivity	High	Low
Thermal sensitivity	High	Low
Abrasiveness	Low	High
Toxicity	Non-toxic	Toxic
Cost	Low	Higher than natural fiber
Energy consumption	Low	High

Adopted from Refs. Oksman et al. (2003), Dittenber et al. (2012)

Table 3 Estimated average global production of different natural fibers

Fiber type	Origin	Production per year (Million Tonnes)	Largest producer country
Cotton	Seed	25	China, USA, India, Pakistan
Jute	Bast	2.3–2.5	India, Bangladesh
Flax[a]	Bast	0.5–1.5	China, France, Belgium, Belarus, Ukraine
Coir	Seed	0.45	India, Sri Lanka
Kenaf	Bast	0.45–0.97	China, India, Thailand
Sisal	Leaf	0.39	Brazil, China, Tanzania, Kenya
Ramie	Bast	0.15	China, Brazil, Philippines, India
Abaca	Leaf	0.10–0.07	Philippines, Costa Rice
Hemp[b]	Bast	0.10–0.2	China, France
Pineapple	Leaf	0.74	Philippines, Thailand, Indonesia
Henequen	Leaf	0.03	Mexico

[a] The real production of flax was underestimated because the production of flax in Canada is not considered for calculation

[b] China has announced plan to substantially increase the hemp production for textiles in the coming years to 1.5 million tonnes of fiber per year

Adopted from Refs. Bledzki et al. (2002), Niska and Sain (2008)

fibers from pines, spruces, larches; are obtained from conifer. Hardwoods except balsa wood are generally denser than softwoods but the growth rate of softwood is faster than that of hardwood. The anatomy of softwood is simple in most cases, as 90% or more of softwood volume is composed of longitudinal tracheid which transports water and gives mechanical strength to the wood. Softwood fiber reinforced polymeric composites have better stiffness than hardwood fiber reinforced polymeric composites and this is due to higher lignin content in softwood fiber compared to that in hardwood fiber. However, hardwood fiber reinforced polymeric composites showed better tensile strength, impact strength, and elongation which could be attributed to higher cellulose content (Joshi et al. 2004; Oma et al. 2012). Softwood fibers are preferred for composite applications as it has higher aspect ratio than hardwood fibers.

Non-wood Fibers

Non-wood fibers have been further categorized into bast fibers, leaf fibers, seed fibers, fruit fibers and stalk fibers. Table 3 indicates the average global production per year of some commonly used non-wood fibers.

Compositions of Plant Fibers

The structure, microfibrillar angle, cell dimensions, defects, and the chemical composition of plant fibers are the most important properties that determine the overall properties of the fibers (Saravana and Kumar 2010). The size and length of plant fibers obtained from various different plants of a particular type also varies depending upon the climatic conditions, location and age of the plants and the fiber extraction process. The overall structure of a plant fiber is very complex consisting of several layers and walls. The cell wall of a natural fiber is not homogeneous as it has a thin primary wall, which is the first layer formed during cell growth. Primary wall encircles secondary wall, which is made up of three different layers, known as outer layer, middle layer and inner layer. The transverse section of the unit cell in a fiber has a central hollow cavity (lumen). Each layer in the cell wall has been found to be composed of cellulose that embedded in a matrix of hemicellulose and lignin. The physical and mechanical properties of plant fibers differ among cited works, because different fibers were used, different moisture conditions were present, and different testing methods were performed. Mechanical properties of plant fibers can be affected by many factors for example; either single fiber or bundle of fibers is being tested. Table 4 represents the important mechanical properties of commonly used plant fibers. The physical properties of each natural fiber are critical, and include the fiber dimensions, defects, strength and structure. There are several physical properties for example; fiber dimensions, defects, strength, variability, crystallinity, and structure; that are important to know about for each plant fiber before that fiber can be used to reach its highest potential.

The chemical compositions of some of the commonly used plant fibers used as reinforcement are summarized in Table 5, and it is observed that plant fibers mainly consist of varying proportions of cellulose, hemicellulose, lignin and pectin (Nirma et al. 2015; Ahmad et al. 2015). In addition to these there are a number of non-structural components including waxes, inorganic salts and nitrogenous substances. Climatic conditions, age and the degradation process not only influence the structure of fibers, but also the chemical composition. The chemical compositions of the plant fibers are also influenced by the fiber growth time (days after planting), the botanical classification of the fiber and the stalk height (Dittenber and Gangarao 2012).

2.2 Biodegradable Polymer Matrix

The yearly disposal of synthetic polymers derived from petroleum products in both the US and EC country has raised the demands for managing this non-biodegradable waste. The commodity plastics for example; polyethylene, polypropylene, polystyrene and polyvinyl chloride etc. displaced metals, glasses, ceramics and wood products especially in the area of packaging and these polymers are available in variety of forms as films, bags, containers etc. They persist in environment, do not degraded after their disposal and thus giving rise to multitude of ecological and environmental concerns. Biodegradable polymers offered scientists and researchers a possible solution not only to the waste disposal problem associated with traditional petroleum based polymers but also to the rising oil prices

Table 4 Different physical and mechanical properties of natural fibers

Name of plant fibers	Density (g/cm^3)	Elongation (%)	Tensile strength (MPa)	Specific strength (MPa)	Young's modulus (GPa)	Specific modulus (GPa)	Specific gravity
Alfa	0.89	5.8	35	–	22	25	–
Bagasse	1.1–1.6	6.3–7.9	170–350	–	5.1–6.2	3.6–4.1	1.4–1.5
Bamboo	1.1	1.9–3.2	500–575	454	27–40	50–67.9	0.4–0.8
Banana	1.35	2.4–3.5	711–789	444	4.0–32.7	3.6–27.3	1.1–1.2
Betel nut	0.2–0.4	22–24	120–166	–	1.3–2.6	1.0–1.9	1.3–1.4
Coir	1.2–1.6	14–30	170–230	146	3.0–7.0	2.5–5.0	1.2–1.4
Cotton	1.5–1.6	2.1–12	200–600	179–373	5.0–15.1	3.3–10.1	1.5
Curaua	1.4	1.3–4.9	87–1150	113–521	11.8–96	39	–
Flax	1.3–1.5	1.1–3.3	340–1600	535–1000	25–81	16.7–54	1.5
Hemp	1.1–1.6	0.8–3	550–900	372–608	70	47.3	1.5
Henequen	1.2	3.7–5.9	430–570	–	10.1–16.3	11	–
Jute	1.3–1.5	1.4–2.1	385–850	269–548	9–31	6.9–20.7	1.3–1.5
Kenaf	0.6–1.5	1.6–4.3	223–1191	641	11–60	10–42.9	1.1–1.4
Oil palm	0.7–1.6	4–18	50–400	–	0.6–9.0	0.5–7.5	1.1–1.2
Pineapple	1.56	2.4	150–1627	–	11–82	7.8–57	1.4–1.6
Ramie	1.4–1.5	1.5–4	200–1000	147–625	41–130	27–81	1.5–1.6
Sisal	1.3–1.6	1.9–15	400–700	366–441	8.5–40	6.5–30.8	1.3

Adopted from Refs. Manita and Morreale (2011), Ahmad et al. (2015)

Table 5 Chemical compositions of different natural fibers

Name of plant fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)	Wax (%)	Ash (%)	Moisture (%)
Bagasse	28.3–55	20–36.3	21.2–24	NA	0.9	1–4	NA
Bamboo	48.2–73.8	12.5–73.3	10.2–21.4	0.37	NA	2.3	11.7
Banana	48–60	10.2–15.9	14.4–21.6	2.1–4.1	3–5	2.1	2–3
Betelnut	35–64.8	29–33.1	13–26	9.2–15.4	0.5–0.7	1.1–2.1	NA
Coir	19.9–36.7	11.9–15.4	32.7–53.3	4.7–7.0	NA	NA	0.2–0.5
Cotton	82.7	5.7	28.2	5.7	0.6	NA	10
Curaua	73.6	9.9	7.5	NA	NA	NA	NA
Flax	64.1	16.7	2	1.8	1.5	13.1	10
Hemp	55–80.2	12–22.4	2.6–13	0.9–3.0	0.2	0.5–0.8	6.5
Henequen	77.6	4–8	13.1	NA	NA	NA	NA
Jute	64.4	12	0.2	11.8	0.5	0.5–2.1	10
Kenaf	37–49	18–24	15–21	8.9	0.5	2.4–5.1	NA
Oil Palm	42.7–65	17.1–33.5	13.2–25.3	NA	0.6	1.3–6.0	NA
Pineapple	57.5–74.3	80.7	4.4–10.1	1.1	3.3	0.9–4.7	NA
Ramie	68.6	13.1	0.6	1.9	0.3	NA	10
Rice husk	38–45	12–20	–	–	–	20	–
Sea grass	57	38	5	10	–	–	–
Sisal	65.8	12.0	9.9	0.8	0.3	4.2	10.0

From kind Refs. Nirma et al. (2015), Ahmad et al. (2015)

(Satyanarayana et al. 1986; Ya et al. 2014; Mathew et al. 2014; Karim et al. 2014a, 2016b). The developments in emerging biodegradable polymers are impressive from a technological point of view and mirror their rapid growth in the market place (Mohanty et al. 2000; Azwa et al. 2013; Faruk et al. 2014; Karim et al. 2014b, 2016c, d).

2.2.1 Classification

Biodegradable polymers on the basis of their origin can be natural as well as synthetic. Almost all natural biodegradable polymers which can be obtained from the renewable resources degrade within a reasonable time scale. However, the synthetic biodegradable polymers also degrade if they contain chemical bonds which occur in natural compound (Mohanty et al. 2000; Karim et al. 2014b). International organizations for example: American Society for Testing Materials (ASTM) in connection with Institute for Standard Research (ISR), the European Standardisation Committee (CEN), the International Standardization Organization (ISO), the German Institute for Standardization (DIN) are all actively involved in developing definitions and tests for biodegradability of polymers in different environments. Some of the commonly used biodegradable polymers used as matrix in green composites are polylactic acid, polyhydroxybutyrate, starch etc. Of all the biodegradable polymers polylactic acid (PLA) is the most commonly used and studied matrix material for green composites.

3 PLA Based Green Composites

Several works has been reported on the kenaf fiber with PLA. Various reports have been discussed relating to chemical modifications, biodegradability, and the mechanical and dynamic mechanical properties of fabricated composites (Ochi 2008; Huda et al. 2008; Lee et al. 2009; Karim 2014). Significant improvement in mechanical properties has been reported by silane-treated kenaf fiber reinforced PLA composite. The heat deflection temperature (HDT) was higher compare to neat PLA. The biodegradability (weight loss with time) of kenaf/PLA decreased approximately 38% after four weeks of decomposition. Young's modulus (6.3 GPa) and the tensile strength (62 MPa) of the kenaf (70%)-PLA composites were in the line compare to conventional composites.

Flax fiber reinforced PLA composite was processed and the interfacial characterization was performed using the microbond testing method (Le Duigou et al. 2010). The interfacial mechanisms was explained and discussed; depends on thermal treatment (Le Duigou et al. 2010).

Abaca fiber and cellulose fiber reinforced PLA composites was processed using two-step extrusion coating process followed by injection molding and compared with each other. It was reported that with man-made cellulose of 30 wt%, the tensile strength and modulus increased by factors of 1.45 and 1.75 times in comparison to neat PLA. Reinforcing with abaca fibers (30 wt%) enhanced both the E-modulus and the tensile strength by factors of 2.40 and 1.20, respectively (Bledzki et al. 2009).

3.1 Processing

PLA based green composites are manufactured using the same processing technique as used for the conventional synthetic fiber reinforced polymer matrix composites. These processing techniques are broadly classified as open mold process and closed mold process. Open mold process includes hand layup, spray

Table 6 Processing and tensile properties of PLA based green composite

Composite	Process	Tensile strength (MPa)	Tensile modulus (GPa)	Reference
PLLA/kenaf (70%)	Wet impregnation	62	6.3	Nishino et al. (2003)
PLA/kenaf (70%)	Hot pressing	223	32	Nishino et al. (2003)
PLA/ramie	Hot pressing	52	–	Tao et al. (2009)
PLA/cotton	Compression molding	41.2	4.24	Graupner et al. (2009)
PLA/jute (40%)	Film stacking	100.5	9.4	Placketta et al. (2003)
PLLA/flax (30%)	Film stacking	99	9.52	Bodros et al. (2007)
PLA/flax (30%)	Extrusion, compression molding	53	8.3	Manita and Morreale (2011)
PLLA/flax (30%)	Injection molding	53.1	7.32	Duigou et al. (2008)
PLA/wood flour	Injection molding	58.28	6.22	Petinakis et al. (2009)
PLA/flax (30%)	Solution casting, hot pressing	21	0.137	Kumar et al. (2010)
PLA/bamboo flour	Injection molding	50	–	Kim et al. (2011)
PLA/wood flour	Hot pressing	41.33	3.00	Febrianto et al. (2006)
PLA/sugar beet pulp	Extrusion, injection molding	29.55	2.59	Finkenstadt et al. (2007)
PLA/coconut (0.5%)	Extrusion, compression molding	67.99	2.37	Tayommai et al. (2010)

up, tape layup, filament winding and autoclave method. The compression molding, injection molding and transfer molding are closed mold processes. However the most commonly used processing techniques are extrusion followed by injection molding or compression molding. Some examples are given in Table 6.

3.1.1 Factors Influencing Processing of Green Composite

Some typical problems related to the processing of green composites are the hydrophilic and hygroscopic nature of natural fibers which is used as reinforcement, their poor thermal resistance and also the type as well as its content in the green composite. Natural fibers must be processed at lower temperatures to avoid the possibility of its burning and degradation (Nishino et al. 2003). This limits the use of only those polymers as matrix resins for natural fiber composites that can be processed at lower temperatures, consequently, high performance and high glass transition temperature and high melting temperature polymers may not be used as matrix resins for green composites. Hydrophilic and hygroscopic reinforcing natural fibers have poor compatibility with hydrophobic polymer matrix, as a result of which, natural fiber reinforced polymer composites have weak fiber/matrix interfacial adhesion that limits load transfer from the fiber to the matrix and results in poor mechanical properties of the composites (Tao et al. 2009). The fiber/matrix interfacial adhesion needs improvement for use of natural fiber/polymer composites. Another drawback is the high moisture absorption by natural fibers in the green composites (Tao et al. 2009). Moisture swells the natural fibers in composites and adversely affects the dimensional stability and the mechanical properties of the natural fiber/polymer composites. The presence of humidity or moisture during the processing of green composite leads to the formation of water vapor which can, in turn, give rise to several problems, especially in the in the case of injection molding, if a venting or drying system is not present as it causes the formation of voids in the material and thus poor mechanical properties. Furthermore, it is a widely accepted step prior to the processing of green composite, to dry the natural fibers and this can be done by different ways such as hot air jets, rotating driers, ventilated ovens, in order to reduce the humidity level to approximately 2–3% (Graupner et al. 2009). Fiber treatment either chemically or physically can also reduce both the moisture content level and the rate of absorption very significantly. Bio-based polymers for example polylactic acid can be more sensitive to moisture than natural fibers. Moisture or water content in the sample also affects the mechanical properties (such as, compression, flexural and tensile) of the composites. Nowadays new extruder screw design (higher L/D ratio) allows better degassing and, consequently, lower moisture content. In addition, the machine's barrel must be redesigned. Type of natural fiber and its content is another important parameter that influences the processing of the green composite. The length of natural fibers (short or long), aspect ratio (length/diameter), and chemical compositions have great influence on the processing and therefore processing parameters are different for different fiber types (Placketta et al. 2003). In general, increase in fiber content in the composites increases the stiffness and strength of the composite.

3.1.2 Performance of Green Composite

The properties of a green composite cannot be achieved by any of the components acting alone. Overall, the properties of composite are determined by properties of the matrix, properties and aspect ratio of the reinforcing fiber, amount of fiber in the composite (fiber volume fraction), geometry and orientation of the fibers in the composite, and several others, including fiber/matrix interfacial adhesion, because the adhesion between the reinforcing fiber and the matrix polymer plays an important role in the transmission of stress from the matrix to the fiber and thus contributes towards the performance of the composite (Placketta et al. 2003; Bodros et al. 2007). The principal purpose of a matrix is not to be load carrying constituent but essentially to bind the fibers together, transfer load to the fibers, and to protect the composite. Each fiber must be separated from the other and uniformly coated by the matrix. Properties of the polymeric matrix govern the resultant properties of the polymeric composites. Thermal stability and temperature dependent properties and high temperature applications of a polymeric composite depend on its polymeric matrix. The fundamental role of fibers is to perform as the reinforcing materials and to carry or support the load, limit deformation, and enhance the mechanical properties of the polymeric composite such that the polymeric matrix experiences negligible stresses (Duigou et al. 2008). Reinforcing fibers provide stiffness, strength, and other mechanical properties. The fiber aspect ratio (length/diameter ratio) is a critical parameter in a composite material. Mechanical properties improve with increasing fiber aspect ratio. The greatest stiffness and strength occurs, when the fibers are very long compared to their diameter; however, although, short fiber reinforced polymer composites are limited by the short length of the reinforcing fiber; but they offer good properties. One of the significant factors determining the mechanical properties of a composite is the content of reinforcing fiber (fiber volume fraction) (Petinakis et al. 2009; Kumar et al. 2010). Stiffness and strength increases with increasing fiber contents, however, beyond a particular volume fraction of fibers, there is increase in stiffness, but no proportional increase in strength. The geometry of the fibers in a composite is also important, since fibers have their highest mechanical properties along their lengths, rather than across their widths (Kumar et al. 2010). Orientation of the fibers in the composite plays an important role in imparting isotropic or anisotropic properties to a composite. Composite properties depend on the fiber/matrix interfacial adhesion also. The ultimate mechanical properties of fiber reinforced polymeric composites depend not only on the properties of the fibers and the matrix, but also on the extent of interfacial adhesion between the fiber and the polymer matrix. Poor fiber-matrix interfacial adhesion limits the load transfer from matrix to fibers. In polymer matrix composites, the interface between the reinforcing fiber and the polymeric matrix is important for the overall performance of the composite as a structural material.

It is important to know the certain mechanical properties of each green composite in order to understand its highest potential. Mechanical properties of a composite material are important because these properties decide the applications and performance of a composite material. Among all the mechanical properties the most commonly studied are the tensile, flexural and impact properties. However, maximum work has been reported on tensile properties of green composite than any other mechanical property. Table 6 summarizes the processing techniques and tensile properties reported for PLA based green composites. Tensile test has been performed to measure the ability of a material to withstand the force that tends to pull it apart and the extent of its deformation before breaking. Tensile testing gives result for tensile modulus, tensile strength and elongation at break of a material (Tayommai et al. 2010). Tensile modulus indicates the stiffness of a material and can be determined from the stress-strain curve. Stress is the force applied to produce deformation in a unit area of a test specimen and is ratio of applied load to the original cross-sectional area. Strain is the change in the length per unit of the original length (Δl/l). Tensile strength is the maximum stress that a specimen can withstand during a tension test, and is measured in MPa. Tensile Modulus, also known as the Young's modulus, is a measure of the stiffness of the material and is the ratio of stress to corresponding strain below the proportional limit of a material; and is measured in GPa. Elongation at break of a material is the percentage increases in its length due to the applied tensile load up to its breaking point.

4 Green Composites in Future

The use of biodegradable polymers as matrix and natural fibers as reinforcement in composite materials contributes to enhancing the development of green composites in regards of performance as well as sustainability. Green composites have created substantial commercial markets for value-added products especially in packaging sector. Although PLA/kenaf fiber composites have been used for spare tire cover, circuit boards (Nakamura et al. 2009) and so on Bax and Mussing (2008) proposed the application in automotive and electronic industry. Graupner et al. (2009) suggested their applications for furniture, suitcase, car parts, grinding discs, safety helmets. However, to cover other fields, scientists and researchers still need to think about the up scaling of products. To launch various lab scale ideas into market a concise effort is required from scientific community.

In the future, these green composites will see increased use in structural applications. Various other applications depend on their further improvements and research. But there are still a number of problems that have to be solved before green composites become fully competitive with synthetic fiber composites.

In recent years, the major advancement lies within the establishment of nanocomposites (i.e., the use of nano cellulose in the form of crystal or fibers produced from natural fibers). Natural fibers consist of approximately 30–40% cellulose and about half of that is crystalline cellulose. It was reported that this nano cellulose could compete with components made from conventional materials. Nanotechnology shows numerous opportunities for improving the properties of green composite products. The use of cellulose nanocrystal and cellulose nanofibers is being explored for a variety of uses since it is stronger than steel and stiffer than aluminum. Cellulose nanocrystal reinforced composites could soon provide advanced performance, durability, value, service-life, and utility while at the same time being a fully sustainable technology.

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Design and Fabrication of Green Biocomposites

Faris M. AL-Oqla, Ahmad Almagableh and Mohammad A. Omari

Abstract Many traditional materials that have been used in various engineering applications for long periods of time are being switched by new green materials to contribute meeting the demand of weight reduction, environmental issues as well as customer satisfaction attributes. Since natural fibers have many advantages, such as low cost, lightweight and environmentally friendly, researchers start put more effort in this area to utilize its benefits in producing bio-composite materials. However, design in green bio-composites has many challenges. One of the most important challenges is the limited availability of design data due to the large variety of fibers, matrices, and manufacturing processes. In consequence, several factors must be considered in the design process of green bio-composites, namely: processing consideration, selection of additives, selection of polymers, as well as good part design. Moreover, high coefficients of safety are still being used because of the difficulty to precisely model the material behavior, which in turn leads to oversize the structures. This is mainly due to the fact that the variation of material's properties is not linear; however, it depends on how far the material is from failure. Therefore, proper testing, evaluation and manufacturing processes have to be considered by designers to be capable of producing functional produces regarding both macro and nano-scale bio-composite.

Keywords Composites performance · Design of composites · Biocomposites · Green products

1 Introduction

The growing awareness regarding global environmental issues as well as concepts of sustainability, have together prompted the search for both new products and processes that are compatible with the environment. Designers and engineers are

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always looking for new materials and improved processes to be utilized in developing better products to maintain competitive and enhance their profit margins. Various materials that have been used in various engineering applications for long periods of time are being switched by new green materials to contribute meeting the demand of weight reduction, environmental issues as well as customer satisfaction attributes (AL-Oqla and Sapuan 2014c). As the accessible set of materials is increasing both in type and number, complex relationships between the various selections parameters appear and made the selection of a material for a particular application is a difficult task (Dweiri and Al-Oqla 2006; Al-Oqla and Omar 2015; Al-Oqla and Omar 2012; Jahan et al. 2010). It is estimated that more than 80,000 material types including metallic alloys and nonmetallic engineering materials are available in the world. Such materials include ceramics, glasses, plastics, composite materials, and semiconductors.

Designers and engineers have to consider several factors and materials related features during material selection process to achieve low-cost successful design. These factors include physical properties, mechanical properties, magnetic characteristics, electrical properties manufacturing abilities, material cost, durability, material impact on the environment, recyclability, availability as well as others. Moreover, metaphysical properties as well as the user-interaction aspects like perceptions, appearance and emotions are also considered during selecting materials (AL-Oqla et al. 2015c; AL-Oqla and Hayajneh 2007; Al-Oqla and Omar 2012; AL-Oqla and Sapuan 2014b, c). The user-interaction features usually affect the usability and nature of a product and formulated as intrinsic material properties. Therefore, the process of material selection is an interdisciplinary work and it often needs various fields of study including industrial engineering, material science and engineering, as well as other experts regarding the field of application.

On the other hand, design of an engineering element usually requires three interrelated tasks, which are 1—Choosing the material. 2—Identifying the geometry, and 3—Selecting a manufacturing process. To perform this properly right the first time via determining the optimal combination as proper design has huge benefits to any business. Such proper selection usually guarantees lower product costs, reduces the number of failures during service, fasters time-to-market, and, sometimes, significant advantages relative to business competition (AL-Oqla et al. 2015a; Alves et al. 2010).

Composite materials are on the other hand, one of the most functional types of materials for various applications. They are materials that contain at least two distinguished separated components one from another and uniformly filling its volume. They are usually produced in order to create particular desired characteristics (Bajpai et al. 2012; AL-Oqla and Sapuan 2014b; Aridi et al. 2016). Fiber reinforced polymeric composites have also been implemented in various structural applications due to their desired specific strength as well as modulus compared to metals. Such composites were initially developed for the aerospace and automotive industries, advanced composites are recently found in applications from circuit boards, to building materials as well as specialty sporting goods, energy saving and medical applications (AL-Oqla et al. 2015d; Al-Widyan and Al-Oqla 2011, 2014).

Most of these composites are designed for long-term durability and are prepared from non-degradable resins, such as polyurethane, polyethylene and epoxies in addition to high-strength fibers, like graphite, glass and aramids. As composites are formed from various dissimilar materials, it is not easy to recycle or reuse them. Moreover, most composites culminate in landfills, whereas some are burned after use, despite of some efforts for recycling and reusing.

On the other hand, the recent environmental awareness, high rate of petroleum reduction, in addition to the new environmental regulations have together prompted finding new generation of green materials. Thus, most main producers have policies to make their products green and pay efforts to enhance their recyclability to be consistence with sustainability themes. Undoubtedly, fully biodegradable plastics or green composites will have a major role in the future greening.

2 Greener Alternative Materials

Since natural fibers have many advantages, such as low cost, lightweight and environmentally friendly, researchers start put more effort in this area to utilize its benefits in using the natural fibers as reinforcement in polymers (AL-Oqla and Sapuan 2014a; Bledzki et al. 2006; Al-Oqla et al. 2016). Natural fibers play a major role in producing a wide range of composites for many applications. Comparison between glass fiber and natural fiber on environmental performance shows the superior advantages of fibers over glass in many aspects such as environmental effects during production processes, environmental pollution after use the product, and the light weight of the natural fiber composites makes it suitable in the automobile applications, so the fuel efficiency is increased, thus, emissions to the environment is decreased (AL-Oqla and Sapuan 2014c). Fiber reinforced polymeric composites have also high specific strength and modulus compared to metals. For all those reasons, fiber reinforced composites are used in wide variety of applications such as; aerospace industry, automotive parts, building materials, sporting goods, circuit boards, etc.

Currently, most of composites are made using either non-degradable polymeric resins, such as epoxies and polyurethane, or high-strength fibers, such as graphite, aramids, and glass. Many of these polymers and fibers are derived from petroleum which is a non-renewable product. For this reason using composites in place of common plastics will improve performance and reduce weight and cost of products. Since composites are made from two or more materials, it is difficult to get rid or recycle it. Most composites end up in landfills, while some are burned after use, although; some of them are recycled in expensive and complicated processes. In many applications products have been overdesigned. That is; increasing the mechanical properties for no specific reasons. A proper strength will be enough to stand the application. For instance, secondary structures, packaging, prototyping products… etc., using green composites would be strong enough to stand such applications. On other hand, get benefits from their overwhelming pros (AL-Oqla et al. 2015b).

3 Design of Green Bio-Composites

3.1 Design in Engineering

Design in engineering is a systematic way or steps used for creating functional products and/or processes. Many factors should be considered in designing a new product, some of those factors can be summarize into the following (Ashby and Johnson 2013; Dweiri and Al-Oqla 2006):

- Fitness for Purpose.
- Choice of Materials.
- Use of the product.
- Ease to manufacture.
- Quantity to be manufactured.
- Cost of the product.
- Finishing quality.
- Durability.
- Ease of Maintenance.
- Efficiency.
- Running Costs.
- Safety.
- Environmental and Social Considerations.

A design process model called Total Design in Product Development (TDPD) was established by Pugh (Pugh and Clausing 1996) to enhance engineering design process. TDPD includes several stages consist of market investigation, conceptual design, product design specification, detail design, manufacture, and sale. On other hand, many authors included embodiment design as an intermediate stage between conceptual and detail design (AL-Oqla and Sapuan 2014c; Ashby and Johnson 2013; Bledzki et al. 2006). Ashby have provided useful guidelines for product development include; geometrical design of natural fiber composites and materials selection process as shown in Fig. 1.

Generally, for design purpose one of the following well-known failure theories can be followed:

(1) Maximum shear stress theory.
(2) Maximum normal stress theory.
(3) Maximum strain energy theory.
(4) Maximum distortion energy theory.

However, the maximum normal stress theory is only applicable for brittle materials, whereas others are applicable for ductile ones (Kaw 2005). Since the natural fiber reinforced polymer 8 composites are neither isotropic nor exhibit gross yielding, other methods will be discussed in the below sections.

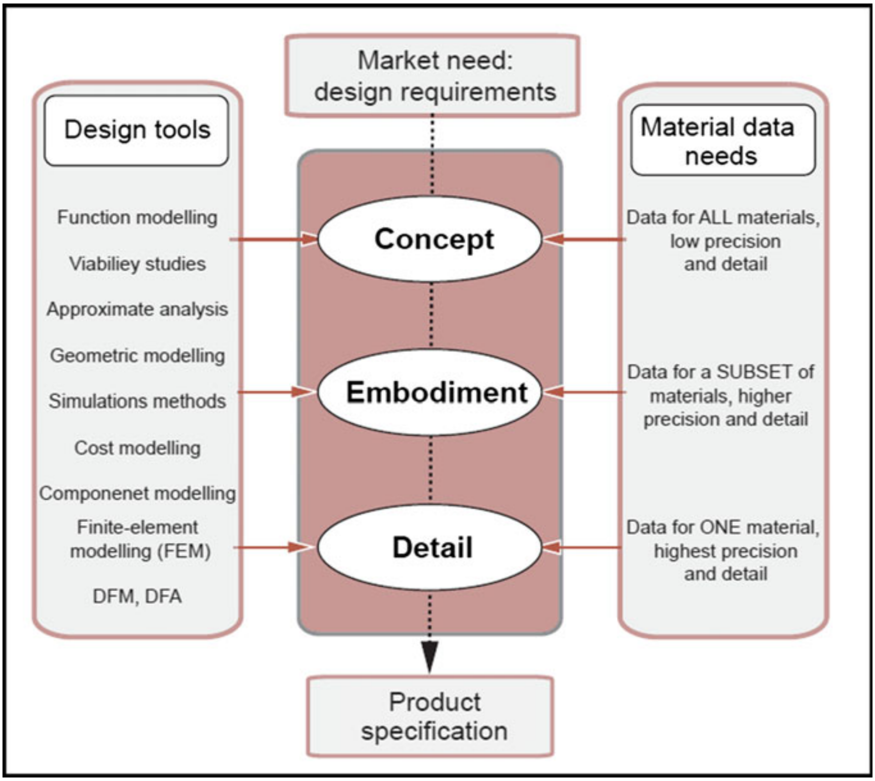

Fig. 1 Product development activities (Ashby and Johnson 2013)

3.2 Design in Composites

Design in composites has many challenges: one of the most important challenges is the limited availability of design data since the large variety of fibers, matrices, and manufacturing processes (AL-Oqla and Sapuan 2015; AL-Oqla et al. 2014a). Those changes appear because of different reinforcements materials, different fiber geometry, orientation and fiber arrangement been use. Therefore, composites have several design variables. They include the choice of material for the matrix and the reinforcement in addition to its shape, scale and configuration. The design variables in composites are demonstrated in Fig. 2.

Moreover, another serious challenge is the design against fatigue one. Since fatigue is the most common cause of structural failures in composite materials; high coefficients of safety are generally used because of the difficulty to precisely model the material behavior, which in turn leads to oversize the structures. The problem here in composites is that the variation of material's properties is not linear; however, it depends on how far the material is from failure. Therefore, safety

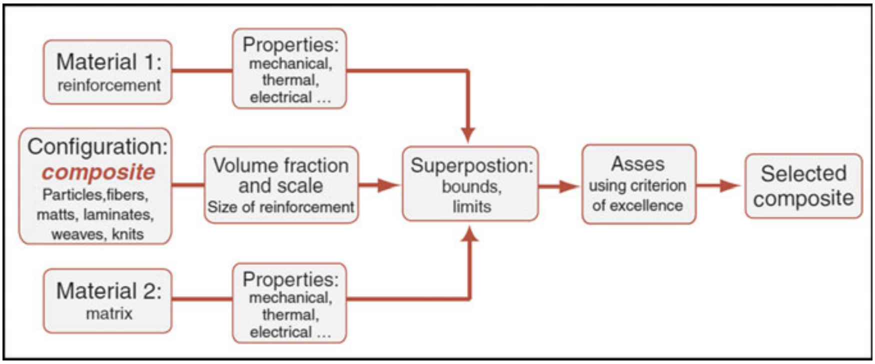

Fig. 2 The design variables in composites (Ashby and Johnson 2013)

Table 1 Safety factors for composite materials according to the loading type (Gay 2014)

High volume composites	Static loading	2
	Intermitted loading over long term	4
	Cyclic loading	5
	Impact loading	10
High performance composites		1.3–1.8

factors have to be seriously considered in the design of such composites. Safety factors for composite materials depending to the loading type are demonstrated in Table 1 (Gay 2014).

The reinforcement's variation could be in many aspects: it can be in; raw fibers; intermediate materials; or in finished items. Other ways of variation in reinforcement are fiber length, fiber arrangements (random chopped, woven roving, and nonwoven fabrics), as well as fiber types (glass, carbon, and Kevlar) fibers (Mayer 2012). In this chapter the design of green composites are considered since they have some especial treatment and behavior.

3.3 Design for Green Composites

If there were no needs for change, things would stay the same. However, in fact things are changing faster now than ever before due to several needs as shown in Fig. 3. The developing circumstances of the modern world change the boundary conditions for design. Among these circumstances are those for selecting materials and processes. These changes are driven by a number of needs. First, there is the market pull: the demand for materials that are lighter, cheaper, tougher, stiffer, stronger, and more tolerant of extremes of environment, and that offer greater functionality. Second, there is the science-push: where the curiosity-driven investigates of materials experts in

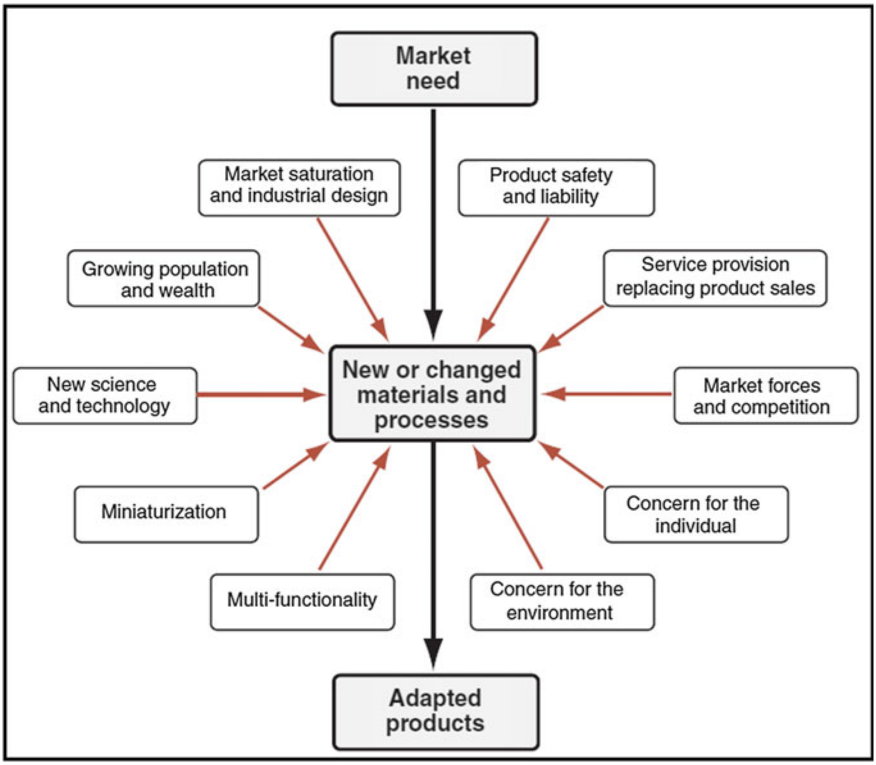

Fig. 3 Forces for change for developing new materials for product design (Ashby and Johnson 2013)

industries, universities and governments. In fact, there is a driving force of what might be called mega-projects such those of developing of nuclear powers, various defense programs as well as the space-race ones. But, today, one might think of alternative energy technologies, maintaining an ageing infrastructure of roads, drainage, bridges, and aircraft, and the threat of terrorism. In addition, the trend to miniaturization while enhancing the functionality of products is notably considered. Moreover, there is legislation regulating product safety and the liability conventional by recent legal precedent (Ashby and Johnson 2013).

In consequence, several factors must be considered in the design process of green fiber composites, namely: processing consideration, selection of additives, selection of polymers, as well as good part design (Al-Oqla et al. 2014a, b, 2015d; Al-Oqla and Sapuan 2014b). For design purposes, failure stresses of materials need to be evaluated. This can be done experimentally and/or by Finite Elements Analysis (FEA) techniques. Since the NFCs are neither isotropic nor exhibit gross yielding, the previous failure theories are not appropriate for them as these theories were developed for metals or other isotropic materials (Ihueze et al. 2013). As an alternative, various new failure theories were suggested for the NFCs, some of which will be discussed here.

3.4 Failure Prediction in a Unidirectional Lamina

Failure in composite could be caused by various deformation modes. The operative failure mode mainly be influenced by the microstructure and the loading conditions of a particular composite system. The microstructure means here fiber diameter, fiber distribution, fiber volume fraction as well as damage causing from thermal stresses, which may grow during fabrication and/or in service. Therefore, a multiplicity of failure modes may be observed in a given composite system due such many factors that do contribute to the fracture process in composites.

Plane stress condition of a general orthotropic lamina containing unidirectional fibers at a fiber orientation angle of θ with respect to the x axis (Fig. 4) will be discussed here as it is strongly suitable for the natural fiber reinforced polymer composite materials and their designs.

For such failure prediction, first, one needs to calculate the four independent elastic constants, namely, E11, E22, G12, and ν12 which are the moduli of

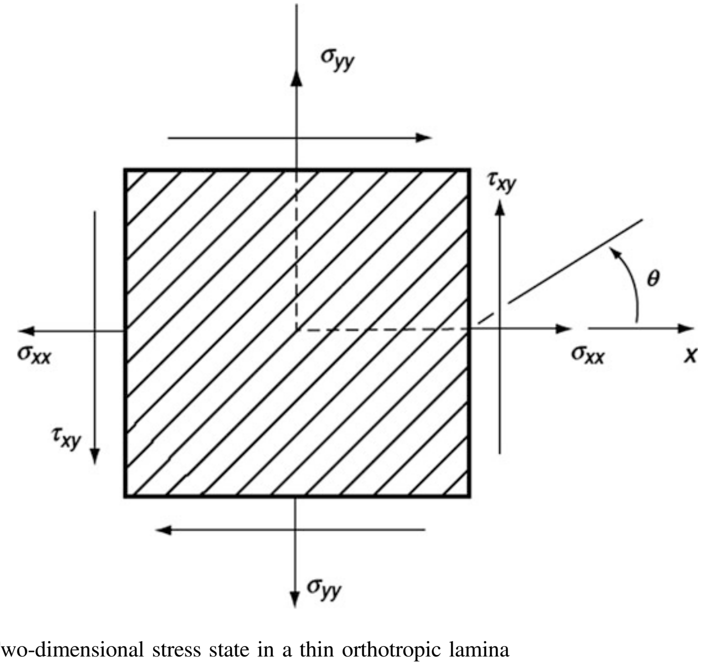

Fig. 4 Two-dimensional stress state in a thin orthotropic lamina

elasticities, modulus of rigidity and Poisson's ratio with respect to directions 1 and 2, in order to define elastic characteristics and properties namely:

S_{Lt} = longitudinal tensile strength
S_{Tt} = transverse tensile strength
S_{Lc} = longitudinal compressive strength
S_{Tc} = transverse compressive strength
S_{LTs} = in-plane shear strength

Then, based on of the following theories one can predict the failure in a unidirectional lamina under plane stress conditions.

3.4.1 Maximum Stress Theory

In this theory, failure is proposed to occur when any stress in the principal material directions equals or exceeds the corresponding ultimate strength. That is;

Normal stress (σ11 and 22) as well as the shear stress (τ12) must be within the following limits as:

- $S_{Lc} < \sigma 11 < S_{Lt}$,
- $S_{Tc} < \sigma 22 < S_{Tt}$,
- $S_{LTs} < \tau 12 < S_{LTs}$.

3.4.2 Maximum Strain Theory

According to the maxi mum strain theory, failure occurs when any strain (ε) in the principal material directions is equal to or greater than the corresponding ultimate strain.

- $\varepsilon_{Lc} < \varepsilon_{11} < \varepsilon_{Lt}$
- $\varepsilon_{Tc} < \varepsilon_{22} < \varepsilon_{Tt}$,
- $\gamma_{LTs} < \gamma_{12} < \gamma_{LTs}$.

3.4.3 Azzi-Tasi-Hill Theory

Here, failure will occur in an orthotropic lamina if the following equality is satisfied:

$$\frac{\sigma_{11}^2}{S_{Lt}^2} - \frac{\sigma_{11}\sigma_{22}}{S_{L1}^2} + \frac{\sigma_{22}^2}{S_{Tt}^2} + \frac{\tau_{12}^2}{S_{LTs}^2} = 1$$

Where σ_{11} and σ_{22} are tensile stresses.

3.4.4 Tasi-Wu Failure Theory

According to this theory, a failure may occur in an orthotropic lamina if the following equality is satisfied

$$F_1\sigma_{11} + F_2\sigma_{22} + F_6\tau_{12} + F_{11}\sigma_{11}^2 + F_{22}\sigma_{22}^2 + F_{66}\tau_{12}^2 + 2F_{12}\sigma_{11}\sigma_{22} = 1$$

where F1, F2,…etc. are the strength coefficients, and are expressed as:

$$\begin{aligned} F1 &= \frac{1}{S_{Lt}} - \frac{1}{S_{Lc}} \\ F2 &= \frac{1}{S_{Tt}} - \frac{1}{S_{Tc}} \\ \mathrm{F6} &= 0 \\ F11 &= \frac{1}{S_{Lt}S_{Lc}} \\ F22 &= \frac{1}{S_{Tt}S_{Tc}} \\ F66 &= \frac{1}{S_{LTs}^2} \end{aligned}$$

and $F12$ is a strength interaction term between σ_{11} and σ_{22}. $F1$, $F2$, $F11$, $F22$, and $F66$ can be found using the strength properties (tensile property, compressive, and shear ones) in the principal material directions in MPa (Tsai 2008) (Fig. 5).

3.5 *Failure Prediction for Unnotched Laminates*

For un-notched laminates, ultimate failure prediction theory will be used. In this theory the following steps can be tracked:

1. Compute stresses and strains using the lamination theory for each lamina.
2. Utilize the suitable failure theory for predicting the first failed lamina.
3. Give reduced stiffness and strength to the failed lamina.
4. Recalculate stresses and strains in each of the remaining laminas using the lamination theory.
5. Complete steps 2 and 3 to predict the next lamina failure.
6. Repeat steps 2–4 until ultimate failure of the laminate occurs.

Stress and strain are calculated in each lamina utilizing the lamination theory by following steps:

1. Finding the laminate stiffness matrices.

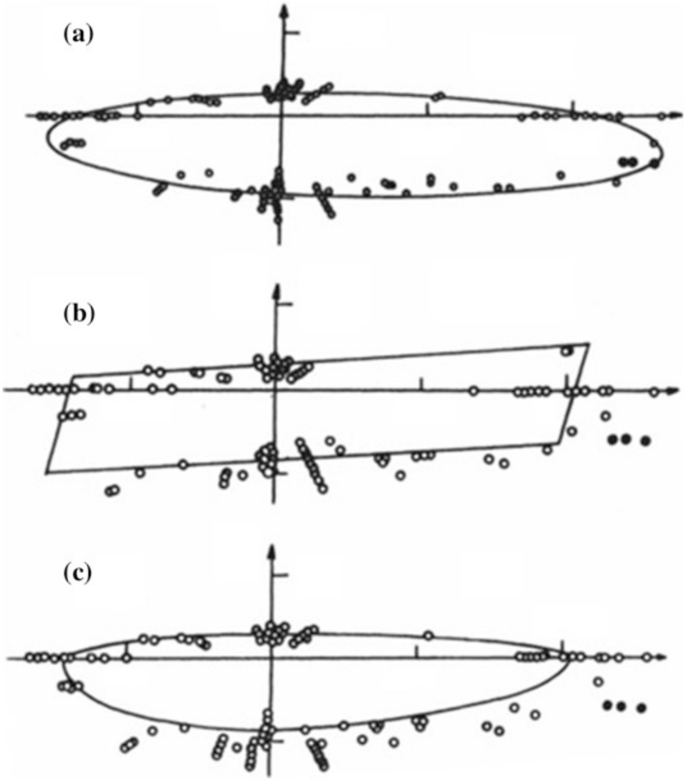

Fig. 5 Comparison of **a** Tsai–Wu, **b** maximum strain, and **c** Azzi–Tsai–Hill. Failure theories with biaxial strength data of a carbon fiber-reinforced epoxy composite where stresses are in MPa (Tsai 2008)

2. Computing the laminate mid-plane strains and curvatures corresponding to a given applied loading (forces and moments).
3. Calculating the in-plane strains ε_{xx}, ε_{yy}, and γ_{xy} for each lamina.
4. Calculating the in-plane stresses σ_{xx}, σ_{yy} and τ_{xy} in each lamina.

3.6 *Failure Prediction in Random Fiber Laminates*

The most common methods in predicting laminates failure in randomly oriented discontinuous fibers-based composites is the Hahn's method. Here, failure can be predicted if the laminate's maximum tensile stress equals a certain strength averaged over all possible fiber orientation angles (Mallick 2007) as:

$$S_r = \frac{4}{\pi}\sqrt{S_{Lt}S_{Tt}}$$

where,

S_r = the random fiber laminate strength

S_{Lt} = longitudinal strength of a 0° laminate

S_{Tt} = transverse strength of a 0° laminate.

3.7 Material Modelling

In the analysis of green composites many challenging concerns have to be considered including the complexity of the mechanical interactions between the composite ingredients, principally when the applied loads can generate local damage and successive failure. The failure mechanisms in natural composite components are totally unlike from that of conventional metal components. Moreover, the static/dynamic failure includes matrix cracking, fiber break, and layer delamination. The mechanical response complexity in natural fiber composites shows several problems in predicting reliable performance of such composites; however, finite element method (FEM) became a very common tool for simulating such engineering material problems. It is believed that material characterization needs to be performed looking towards the overall size and behavior of the structure. Finite element models are in substantial agreement with the small scale tests while larger differences may be found with the large scale ones. Besides to the manufacturing defects, which is more obvious to be higher in larger structures, the interaction of failure modes may lead to lower material strength. An example of a FE model with the consistent experimental test is shown in Fig. 6.

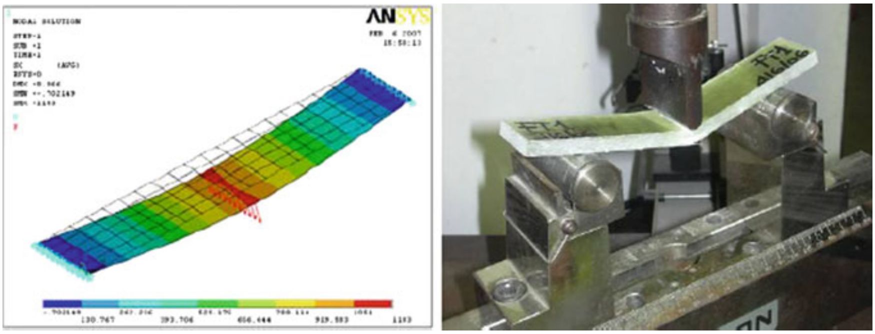

Fig. 6 Consistency between FE model and experimental test

4 Nano-Composites for Engineering Design

Conventional composites are no longer able to satisfy outstanding demands for materials with improved properties (particularly mechanical and thermal), nor can they be designed to be with controlled properties at the microscopic scale. Such controlled properties are highly needed as the macroscopic properties are highly influenced by their molecular structure particularly under external loading like that of impact and thermal energy. Fortunately, nanocomposite materials are now engineered at the atomic level to create large structures with primarily new molecular network.

4.1 Nanofibers from Natural Fibers

Nanofibers are fibers that have diameter equal to or less than 100 nm. One major feature of nanofibers is the huge availability of surface area per unit mass. Such area of nanofibers offers a notable capacity for attaching or releasing functional groups, catalytic moieties, absorbed molecules, ions and nanometer scale particles of many kinds. Nanocomposites become attractive due to the tremendous interaction between nano-metric particles and the polymeric matrix within the structure, for example, an interphase of 1-nm thickness occupies about 30% of the entire volume for nano-composites but 0.3% of the total volume of polymer for micro-filled composites. Such large interfaces within the nanocomposites promotes adhesion energy, increasing molecular bonding, leading to an increase in the chemical bonding that enhances the crosslinking in polymers. This in order resulting in improvements in mechanical properties (Ye et al. 2007). On the contrary, a small participation due to the interphase offers diverse potential of performance tailoring and is capable of influencing the characteristics of the polymers to a much higher extent under rather low particle content. Moreover, to show excellent mechanical properties that are visible gains for nanocomposites, nanotubes, for instance, are predicted to have an fascinating mode of plastic performance, showing a step-wise diameter reduction (local necking) and lattice orientation change. Such highly flexible elastic mobility is extremely functional and could play a significant role in increasing the toughness of nanotube reinforced composites by increasing the energy absorption under deformation (Ye et al. 2007).

4.2 Nanoclay

For more sustainable design possibilities there is a considerable progress in the mechanical and physical properties of clay reinforced composites at a very low silicate loading (4 wt%). The field of polymer/nanoclay composites has gained

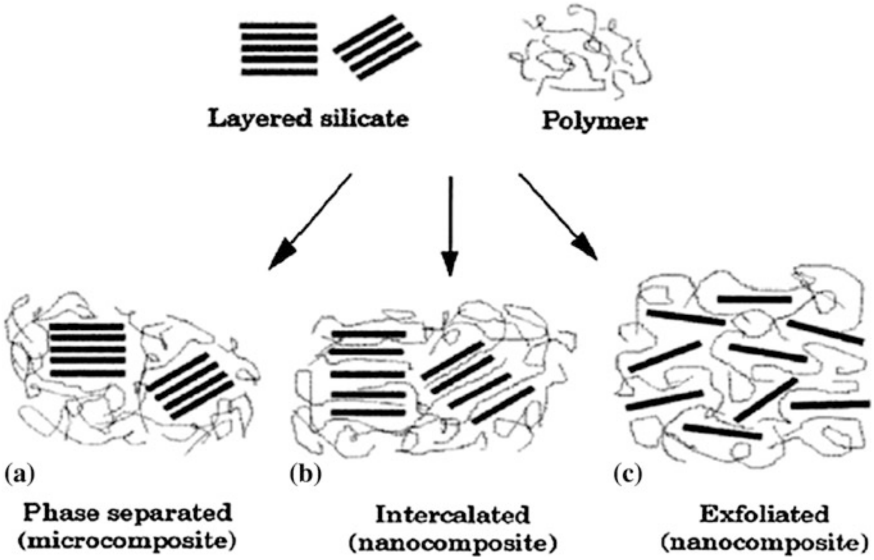

Fig. 7 SEM images of **a** intercalated, **b** expanded, and **c** sonicated (exfoliated) silicate nanocomposites (Alexandre and Dubois 2000)

attention due to the fact that it is feasible to melt-mix resin with silica layers, and no need to use organic solvents. Polymer- silicate nanocomposites could have three types of morphological structures (Alexandre and Dubois 2000). A phase divided composite is obtained when matrix is incapable to intercalate between the silicate layers as shown in Fig. 7a. In intercalated formation, more than one matrix molecules is intercalated between clay layers as shown in Fig. 7b but the layers remain parallel. In fully exfoliated structures, the silica platelets are no longer close to each other and the nano-metric layers are fully distributed in the matrix Fig. 7c.

4.3 Exfoliated Graphite Nanoplatelet (XGnP)

Natural graphite is a black carbon stone, hardest material exists in nature. Its elastic stiffness is about 1000 MPa. The basic element of graphite is the graphene, in which a huge number of benzene rings are reduced to form a firm planar layer. The interlayer spacing is around 3.35 Angstrom and the force between the layers is Van der Waals type (Matsumoto et al. 2012).

Graphite allows to link with various atoms, ions, and molecules in the space provided between its hexagonal sheets of carbon atoms through physical and chemical treatment process. This process is called intercalation. Exfoliated graphite exhibits high aspect ratios, which can reach 1000, once intercalated and exfoliated by chemical processes. Graphite platelets reinforced nanocomposites show excellent electrical and thermal conductivity in addition to enhancements in strength, stiffness, heat distortion temperature (Matsumoto et al. 2012).

5 Natural Fiber Composites Tests

As in metals, mechanical features of natural fiber need to be tested and improved. The most important properties here are the tensile strength, flexural, impacts, fatigue and creep. Natural fibers generally are appropriate to reinforce polymers due to their relative high strength, stiffness and low density (AL-Oqla et al. 2015a, b).

5.1 Tensile Testing of Bio-Composites

The tensile test is the most important test in bio-composites as in metals. The properties taken from tensile test are vital factors for the selection of an exact cellulosic fiber for a precise application. Moreover, tensile properties can be improved, for example, to increase the tensile strength of HDPE/hemp fiber composites, silane as well as the matrix-resin pre-impregnation of the fiber should be done. Experiments presented that the longitudinal tensile strength dramatically increased for the silane-treated fibers. On the other hand, transverse tensile strength was not significant in natural composites. It is obvious that the performance of natural composites is fiber controlled, due to the fact that the longitudinal fiber direction is much greater comparable to the transverse direction.

General experimental conclusions in the area of natural fiber composites can be generally dedicated for the purpose of design as:

- The tensile modulus depends upon the amount of fiber loading as mentioned by the modified rule-of-mixture equation.
- The tensile strength for particular natural fiber/polymer composites tends to decrease with fiber loading, due to the poor adhesion between the matrix and the fibers.
- Tensile strength might be increased when natural fibers chemically treated.
- The following factors should be also considered to study the tensile properties for the thermoplastic matrices: moisture absorption, the effect of surface treatment (using NaOH), the performance of hybrid natural fiber reinforced polymer composites, the fiber size, and the fiber orientations in the composites.
- For natural fiber reinforced thermosets the following factors should be considered via the siloxane treatment of polyester-based and epoxy-based composites to determine the tensile properties; the temperature as well as the effects of a

differing geometry in the composites, the effect of moisture absorption, the effect of fibers volume fraction, and the impact of the fiber orientation, The hybridization and chemical mode-fictions of fiber-natural rubber composites, the impact of high temperature on biodegradability of resin composites, the result of biodegradable matrix sort like that of PLA, PHBV, and PBS on renewed cellulosic/biopolymer composites, as well as others (Faruk et al. 2014; Favaro et al. 2010; George et al. 2013; Sapuan et al. 2013; Satyanarayana et al. 2009).

5.2 Impact Test of Bio-Composites

Major challenge of bio-fiber reinforced composites is the impact strength. Continuous improvement of new fiber manufacturing techniques along with enhancement of filler/matrix adhesion is required to pass out this challenge. Charpy impact test showed increases in impact strength, in some cases the strength be doubled comparable to values in the literature. Compared four types of boards made from composites consisting of HDPE and types of rice straw components (rice husk, straw leaf, straw stem, and whole rice straw) formed by melting and compression molding (Shah and Lakkad 1981); the results revealed that panels with rice husk demonstrated the best impact strength. However, no significant changes occurred regarding the impact properties for boards made from leaf, stem, and whole straw fibers. On other hand, the recycled HDPE composites had better impact strength than the virgin ones (Shah and Lakkad 1981). Moreover, they have demonstrated that the toughness of natural composites can be subjective to various number of factors including the matrix intrinsic properties, the fiber volume fraction, and the filler-matrix bond strength (Anyakora 2013).

6 Manufacturing Processes of Bio-Composites

The public feature in all polymeric-based composite methods is the joining of a resin, a curing agent, some type of fillers, and sometimes a solvent. Usually, both heat and pressure are utilized to shape as well as curing the mixture into a final product. In natural fiber reinforced composites materials the resin holds the fillers together in addition to their protection as well as transferring the load to the fibers in the composite. The curing agent (or hardener) on the other hand, usually acts as a catalyst to help the curing process of the resin to a hard plastic. Several manufacturing process for green composites are usually utilized such as:

6.1 Hand Lay-Up

Fibers are trimmed here and spread over a mold after being designed to the wanted shape. Some layers may be necessary. After making, a vacuum bag is wrapped all over the place of the lay-up, where vacuum is utilized in this process to eliminate air, compressed the part and make a barrier for the assembly when it is located in an autoclave for curing under both heat and pressure.

6.2 Resin Transfer Molding

Resin transfer molding is utilized for making smooth surface parts with low pressure. Fibers are usually laid by hand into a mold then resin mixture is poured into its cavity. The part is then cured under heat and pressure. Pictorial view for the resin transfer molding is shown in Fig. 8.

Resin transfer molding has several advantages (Kim and Pal 2010) such as:

1. Large and complex shapes can be prepared efficiently and inexpensively.
2. Faster than the layup process.
3. Low clamping pressures is required.
4. Better surface definition than layup.
5. Inserts and special fillers can be easily added.
6. Operators may be unskilled.
7. Part consistency is good.
8. Worker exposure to toxic chemicals is minimized.

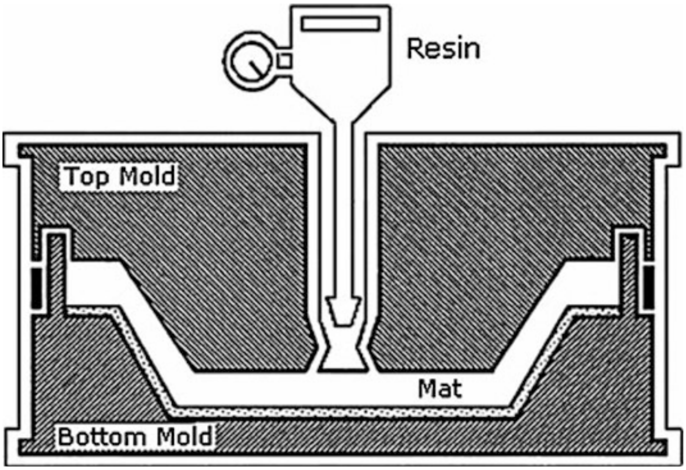

Fig. 8 Resin transfer molding

However the disadvantages including that the mold design is complex, produced material properties are good, but not optimal, resin to fiber ratio is hard to be controlled, and will vary in areas such as corners in addition to that reinforcement may move during injection causing problems in the produced parts.

6.3 Pultrusion

Pultrusion is a process where continuous roving strands are pulled from a creel through a strand-tensioning device into a resin bath. The coated strands are then passed through a heated die where curing occurs (Kim and Pal 2010). The continuous cured part is then cut into desired lengths. A schematic diagram of the pultrusion process is demonstrated in Fig. 9. It has some advantages (Kim and Pal 2010) such as:

1. Good material usage.
2. High throughput can be achieved.
3. Good resin contents.

The disadvantages are:

1. Needs uniform cross Section.
2. Fiber and resin might accumulate at the die opening resulting in increasing friction causing jamming and breakage.
3. If excess resin is used, part strength will decrease.
4. Voids can result if die is not conforming well to the fibers being pulled.
5. The strength of the produced part may be decreased due to the quick curing system.

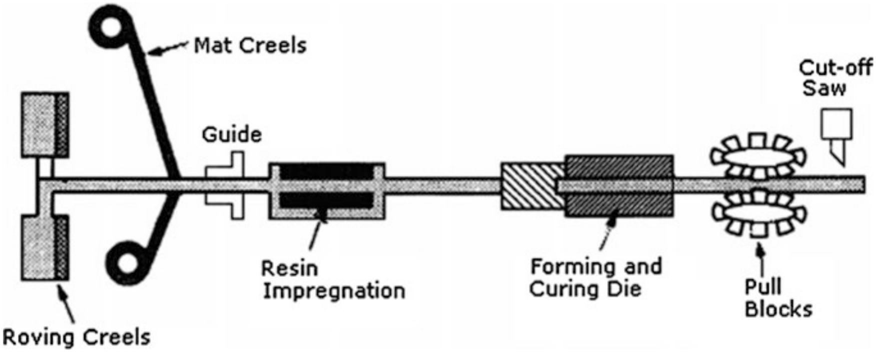

Fig. 9 Schematic view of pultrusion (Kim and Pal 2010)

6.4 Extrusion Processes

It is forcing a thick, viscous liquid through small holes of a device called a spinneret to form continuous strings (filaments) of semi-solid polymer. This process usually achieved by heat and pressure in case the polymers are thermoplastic synthetic, this kind of thermoplastics can be processed by heat, or by dissolving in a suitable solvent in case they are non-thermoplastic. Recently, new technologies have been developed for some specialty fibers made of polymers that do not melt, dissolve, or form appropriate derivatives by reacting with small fluid molecules. The most important part of this process is the spinneret. The spinneret looks like the bathroom shower head, i.e. it is a plate made from a corrosion-resistant metals has a bunch of small holes. Since those holes are small, they need a special kind of treatment; such that filtering the liquid that will feed them, maintenance, and schedule for disassemble and clean them regularly.

There are four methods of spinning filaments (solidification of the liquid polymer when exit from spinneret) of manufactured fibers: wet, dry, melt, and gel spinning.

6.4.1 Wet Spinning

It is used for fiber-forming substances that have been dissolved in a solvent. The spinnerets are submerged in a chemical bath and as the filaments emerge they precipitate from solution and solidify. Because the solution is extruded directly into the precipitating liquid, this process for making fibers is called wet spinning. Acrylic, rayon, aramid, modacrylic and spandex can be produced by this process.

6.4.2 Dry Spinning

The same as wet spinning but instead of the use of chemical reaction solidification is achieved by evaporating the solvent in a stream of air or inert gas.

6.4.3 Melt Spinning

In melt spinning, the fiber-forming substance is melted for extrusion through the spinneret and then directly solidified by cooling. Different cross-sectional shapes can be produced in this method such as; round, trilobal, pentagonal, octagonal, and others. For instance, to decrease soil and dirt in carpet make, it is recommended to use pentagonal-shaped and hollow fibers.

6.4.4 Gel Spinning

Gel spinning Uses to produce special fiber properties such as, high strength. The tensile strength can be increased by keeping the polymer in thick liquid state during extrusion process. The polymer chains will bound together at numerous points in liquid crystal form.

6.5 Natural Fiber Injection Process

The most widely used molding method in the industry to produce polymer composites due to its simplicity and fast processing cycle. Injection molding machine mixes and injects a pre-calculated amount of matrix and fiber mixture into the mold resulting in the desired product. It consists of three major sections: the injection unit, mold, and ejection & clamping unit.

The injection unit: contains a heated screw barrel having a compression screw. The function of each part is clear from its name. i.e., heated barrel provides heat to the polymer matrix to melt before injection, the screw carries and compress the pellets from the hopper into the heated barrel, mix the polymer matrix and fiber, and inject the mixture into the closed mold having the product final shape. The molds are as any other mold that uses in regular injection process. Molds are made by Computer Numerical Control (CNC) machining processes, they have cooling/heating coils to regulate the temperature of the mold itself and ejectors to eject the final product outside the mold when the processes complete.

7 Future Perspective

Bio-composites have been stressed to be implemented in wide range of industrial applications and have been slowly switching conventional materials. The upward interest in long-term sustainability as well as the awareness of the environmental issues, have made a need for design with green bio composite materials as they have greater specific strength and stiffness, greater fatigue strength and impact absorption capacity better resistance to corrosion, recyclability, natural hazardous environments, lower life-cycle costs, and non-toxicity. As green composites are developed to be involved to more structurally demanding components they have to be designed considering various conflicting factors. The mechanisms of failure in green bio-composite components are entirely different from that of conventional metal components. Static and dynamic failure includes matrix cracking, fiber break, and layer delamination. The complexity of the mechanical response of natural fiber composites presents great difficulties in predicting reliable performance of such composites. This in order makes the proper selection of the bio-composites constituents is mandatory issue utilizing new combined evaluation criteria for both macro and nano-scale of green products.

8 Conclusions

The interfacial bonding between bio-composites constituents is crucial in governing their mechanical performance. It is essential to attain the most constructive reinforcement conditions to minimize failure inside the composites. The fabrication process would dramatically affect the final behaviour of the green composites as they may destroy the desired properties of the reinforcement. Therefore, for design purposes, failure stresses of materials need to be evaluated. This can be performed experimentally and/or by Finite Elements Analysis (FEA) techniques. Since green composites are neither isotropic nor show gross yielding, failure theories established for metals or other isotropic materials are not applicable to those kinds of materials. Instead, many new failure theories have been proposed for such bio-composites.

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Cellulosic Biocomposites: Potential Materials for Future

A.H. Bhat, Y.K. Dasan, Imran Khan and Mohammad Jawaid

Abstract Bionanocomposite is one of the remarkable achievements of nanotechnology in material science to replace conventional non-biodegradable petroleum based plastics for packaging applications. In general, bionanocomposites are made up of biodegradable polymers (biopolymers) and bio based reinforcing material in the size range of 10–100 nm in one or more dimensions. Bio based materials could provide a solution for petroleum shortage and waste management problems. One of the potential reinforcing agents is agro industrial based is cellulose. Such composites demonstrate improved properties as compared to the neat biopolymers due the large surface area and high aspect ratio of nanoparticles. This study has given a clear overview of nanocellulose based composites by describing their isolation, surface modification, composite preparation, properties, and applications. Furthermore, the obtained results for developed bionanocomposites materials shows that it can be a promising alternative for conventional packaging materials with improved properties.

Keywords Nanocellulose · Biocomposites · Bionanocomposite · Polymers

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1 Introduction

The increasing environmental and sustainability concern have played a major role in guiding to the exploitation of the next generation products, processes and materials (Abdelwahab et al. 2012). Bionanocomposite is one of the emerging group of materials comprise of biopolymer matrix reinforced with organic nanoparticle owning at least one dimension in the range of 10–100 nm (Bhat et al. 2011). Such composites demonstrate improved properties as compared to the neat biopolymers due the large surface area and high aspect ratio of nanoparticles. Moreover, the properties inherent by bionanocomposites, such as biodegradability provides solution for depletion of petroleum and disposal methods of persistent packaging materials (Darder et al. 2007).

Nanocrystalline celluloses are discerned as one of the promising reinforcing agents of bionanocomposite due to the interaction between the nano-sized components that form a percolated network connected by hydrogen bonding (Zhou et al. 2012). Nanocrystalline cellulose (NCC) is a fine, odorless, white, crystalline powder with rod shaped crystalline domain with 1–100 nm in diameter and 10–100 nm in length depending upon the resources of cellulose. Furthermore, it has a perfect crystalline structure with high aspect ratio and large surface area of 70 and ca. 150 m^2/g respectively (Valentini et al. 2013; Haafiz et al. 2013). The major resources of cellulose are wood of forest, non-wood lignocellulose (cotton, hemp, ramie, kenaf etc.), and agricultural biowaste (corncob, rice husk, sugarcane bagasse and oil palm biomass) (Ng et al. 2015; Espino et al. 2014). The utilization of agricultural biowaste is encouraged as it is renewable, abundant and cheap. Oil palm empty fruit bunch fiber (OPEFB) is one of the major industrial by product which has been incinerated at plantation areas without any profit (Shinoj et al. 2011; Khalil et al. 2013). However, OPEFB fiber is one of the potential sources of cellulose as the fibers are composed of 40–50% of cellulose, which is highest as compared to coir, bagasse, corn, and kenaf fiber. This agricultural biowaste presents unique characteristics including, good thermal properties, lower density and cost, and high specific strength (Lani et al. 2014). Generally, NCCs extracted from cellulosic fibers through acid hydrolysis process, which dissolves the amorphous region of fiber by retaining crystalline fractions. Sulphuric acid (H_2SO_4) hydrolysis is a well-known process to obtain stable colloidal suspension of NCCs due to the repulsion force induced by negatively charged sulfate ions on the crystals surface (Bondeson et al. 2006; Peng et al. 2011).

Biopolymers are an important ingredient in bionanocomposite preparation process. Among the biodegrable polymers, poly (lactic acid) (PLA) and poly (3-hydroxybutyrate-co-3 hydroxyvalerate) (PHBV) are of increasing commercial interest for packaging applications. PLA is a transparent and crystalline biopolymer which can be synthesized via ring opening polymerization through the lactide formation or by the condensation polymerization of the lactic acid. This biopolymer exhibits high mechanical strength, thermoplastic characteristics and biocompatibility. Moreover, thermal instability, low elongation at break, poor water vapor barrier properties and brittleness are potential drawbacks for this polymer. Poly (3-hydroxybutyrate-co-3 hydroxyvalerate) (PHBV), also known as a bacterial polyester and it is a copolymer of hydroxybutyrate (HB) and hydroxyvalerate (HV). PHBV exhibits lower melting point with improved melting stability and higher flexibility as compared to the homopolymer, poly (3-hydroxybutyrate) (PHB). However, PHBV has mellow crystallization rate, high production cost and development of interlamellar secondary crystallization on storage. Therefore, the blend of these two biopolymers was proposed in order to combine the advantage of both polymer and to overcome their drawbacks. Several research studies show that the blend PLA-PHBV could improve crystallinity of PLA while improving the stiffness of PHBV (Arrieta et al. 2014; Bhardwaj et al. 2006; Ten et al. 2013).

The major challenge in the development of bionanocomposite is to increase the compatibility between NCC and biopolymer blend in order ameliorate the dispersion of nanocrystalline cellulose. Nanocrystalline cellulose reinforced composites exhibits poor dispersion of filler in the matrix due to the hydrophilic and hydrophobic nature respectively (Lindström and Aulin 2014). Therefore, surface modification process is an important step in order to improve surface functional groups and hydrophobic nature of NCC surface. On the contrary, solution casting and evaporation technique is one of the easiest methods of preparing bionanocomposite film with good dispersion and reinforcement results (Rebouillat and Pla 2013).

2 Natural Fibers as Fillers in Polymer Composites

Natural fibers symbolize a traditional class of renewable composite material which is known as biocomposites. It has gained tremendous attention among researchers due to its ecofriendly nature.

2.1 Source and Classification of Natural Fibers

Generally natural fibers are categorized according to their origin, which include plants, animal and/or minerals. Vegetable fibers which include cotton, jute, flax, ramie, sisal and hemp are generally referred as cellulosic fibers as cellulose is the primary structural component of all plants. Typically, natural animal fibers such as silk, wool, angora, mohair, and alpaca are composed of protein. Furthermore, mineral fibers are naturally occurring fibers or slightly modified fibers obtained from minerals. (Chandramohan and Marimuthu 2011). However, plant based natural fibers has received more attention due to their wide availability and renewability nature (Cristaldi et al. 2010). A broad classification of natural and synthetic fibers is represented schematically in Fig. 1.

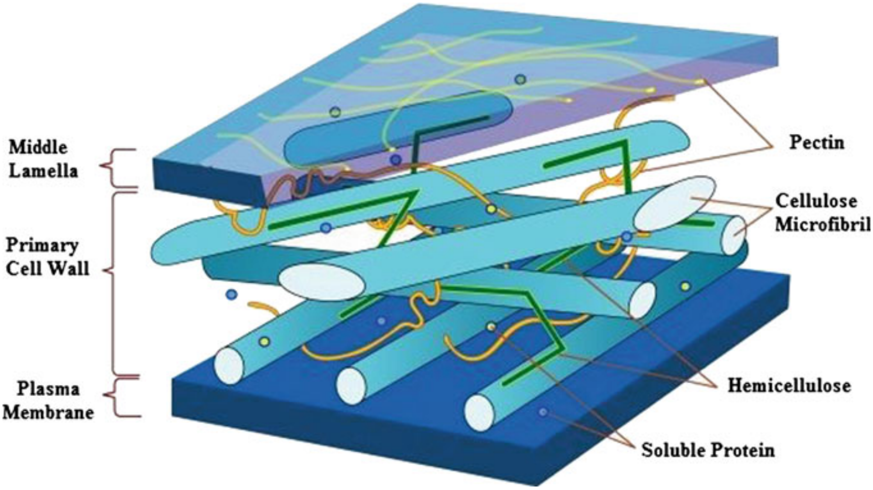

Fig. 1 A schematic diagram of plant cell wall structure (Sticklen 2008)

2.2 Chemical Compositions of Natural Fibers

The structure and chemical composition of a natural fiber depends on their climatic conditions, age and the degradation process. Natural fibers composed mainly of cellulose, hemicelluloses, lignin, and other extractives such as waxes, ashes, protein, starch and inorganic elements are shown in Fig. 1. The chemical components are distributed throughout the cell wall, which is composed of primary and secondary wall layers. The chemical composition varies from plant to plant, and within different parts of the same plant which is shown in Table 1 (Faruk et al. 2012).

Cellulose is the primary load bearing component of every plant cell wall. Polymerization of ∼30–36 chains of β−1, 4-linked glucose units form insoluble and rigid crystalline materials around the cell wall. Furthermore, hemicelluloses are plant polymers that make up of neutral and acidic polysaccharides such as xyloglucans, xylans, glucomannans and galactoglucomannans. Therefore, cellulose fibrils are coordinated with high molecular weight hemicelluloses molecules through hydrogen bond and engrafted in a matrix of pectin and lignins. Hemicelluloses act as clamp in between cellulose and, in some walls, with lignin (Scheller and Ulvskov 2010). Besides that, lignin act as a coupling agent and increase the strength of the cellulose-hemicellulose network (Stamboulis et al. 2001).

Table 1 Chemical composition of common lignocellulosic fibers (Faruk et al. 2012; Jawaid and Abdul Khalil 2011; Khalil et al. 2012)

Type of fiber	Composition (wt%)			
	Source	Cellulose	Hemicellulose	Lignin
Wood	Hardwood	31–64	25–40	14–34
	Softwood	30–60	20–30	21–37
Nonwood	Bagasse	32–55.2	16.8	19–25.3
	Coir	32–43.8	0.15–20	40–45
	Corn cobs	26.1	45.9	11.3
	Corn stalks	35	25	35
	Cotton	82.7	5.7	<2
	EFB	43–65	30	19
	Oil palm frond	56.03	27.51	20.48
	Flax	62–72	18.6–20.6	2–5
	Hemp	68–74.4	15–22.4	3.7–10
	Jute	59–71.5	13.6–20.4	11.8–13
	Kenaf	31–72	20.3–21.5	8–19
	Ramie	68.6–85	13–16.7	0.5–0.7
	Sisal	60–78	10–14.2	8–14
	Sunn	80	10	6
	Wheat straw	43.2	34.1	22
	Curua	70.7–73.6	9.9	7.5–11.1
	Abaca	56–63	20–25	7–13
	Alfa	45.4	38.5	14.9
	Bamboo	26–65	30	5–31
	Banana	63–67.6	10–19	5
	Coconut	36–43	0.15–0.25	41–45
	Soy hulls	56.4	12.5	18
	Rice husk	25–35	18–21	26–31
	Rice straw	59.1	18.4	5.3

3 Chemistry of Cellulose

Cellulose is a sustainable, abundant and naturally occurring biopolymer derived from biomass. Cellulose structure is organized into fibrils, which are surrounded by a matrix of lignin and hemicellulose (Rosa et al. 2010). It is a classic example of a renewable and biodegradable structural plant polymer which can be processed into fibrils (Haafiz et al. 2013). According to researchers, the estimated worldwide production of this biopolymer is more than 7.5 × 1010 tones each year. However, of this only about 6 × 109 tones are processed by paper, textile, material and chemical industries (Lavoine et al. 2012).

3.1 Structure and Properties of Cellulose

Cellulose, a high molecular weight carbohydrate polymer of β−1,4-linked anhydro-D glucose units is represented in Fig. 2 (Nguyen et al. 2013). This structure is secured by an intramolecular hydrogen bonds between the hydroxyl groups and oxygen of adjacent molecules. Cellulose molecular chains are biosynthesiszed and self-assembled into microfibrils in which crystalline regions alternate with amorphous regions (Haafiz et al. 2013). Cellulose microfibrils posseses diameter in the range of 10–30 nm and are made up of 30–100 cellulose molecules in extended chain confirmation and provide mechanical strength to the fiber (Kalia et al. 2011a, b, c). The hydrophilic nature of cellulose macromolecules is due to the three alcoholic hydroxyl (-OH) groups (Oksman et al. 2009). Therefore, unbonded hydroxyl group that mainly presents in amorphous region of cellulose plays the major role for their reactive nature during hydrolysis process whereas crystalline region of cellulose remain intact (Puri 1984).

The degree of crystallinity and degree of polymerization is very important in order to determine digestibility and mechanical properties (Gupta and Demirbas 2010). Furthermore, these two properties of cellulose may vary according to their source, age and pretreatments (Clarke 1996). Cellulose crystallinity is quantified based on the ratio of crystalline to amorphous cellulose and it is believed to play major role in the micro-accessibility of cellulose as well as in its effectiveness (Karimi 2015). X-ray analysis proves the existence of crystalline nature in cellulose with submicroscopic units, called crystallites or micelles, of varying length but of fixed breadth and thickness. Moreover, it shows the existence of smallest morphological units of ordered native cellulose on the surface of elementary fibrils, with diameter of about 3.5 nm. The average degree of polymerization (DP) of a cellulose is significantly related to their mechanical properties and also being used to access the degradation of cellulose by physical, chemical, or radiation damage.

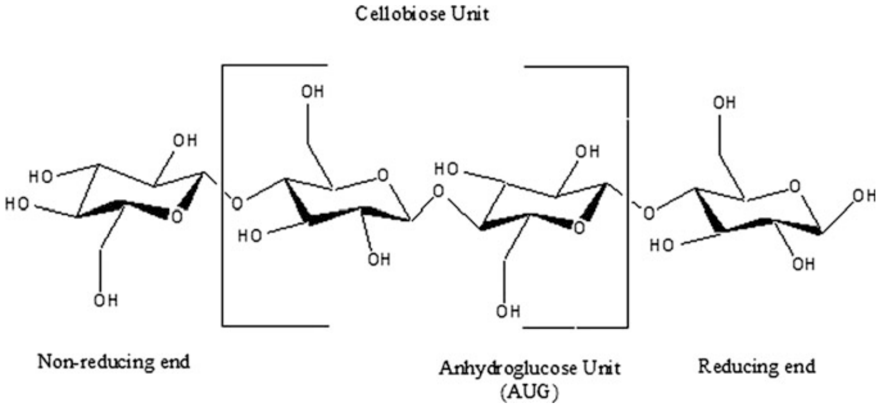

Fig. 2 The cellulose polymer chain structure

The DP of cellulose from primary cell wall is relatively low and heterogeneous (DP 2,000–6,000), while secondary cell wall cellulose is characterized by higher degree of polymerization and it is more homogeneous (DP 14,000) (Clarke 1996).

3.2 *Nanocellulose and Their Characteristics*

Nanocellulose, generally refers to the natural material that possess at least one dimension in the nanometer range which is extracted from native cellulose (Fig. 3) (Lin and Dufresne 2014; Khalil et al. 2014). There are three different types of nanocellulose which include nanocrystalline cellulose (NCC) or cellulose nanowhiskers (CNW), nanofibrillated cellulose (NFC), and bacterial cellulose (BC) which are categorized based on their dimension, function, preparation methods, and cellulosic source (Lin and Dufresne 2014; Brinchi et al. 2013). Nanocellulose has attracted great attention due to their unique characteristics such as sustainability, biodegradability, low density (~ 1.566 g/cm^3), abundant availability and low cost. Additionally, the nanoscale dimension of cellulose possess a very large surface to volume ratio, high modulus of elasticity (~ 150 GPa), high tensile strength, high stiffness, flexibility, electrical, good thermal and optical properties. Furthermore, the materials that are present in nanoscale range possess a different electronic, property, which successively affects its optical, catalytic, and other reactive properties (Silvério et al. 2013). The nanoscale dimensions and its capacity to form a strong entangles of nanoporous network have changed the emergence of new high value applications (Fig. 4).

Nanocellulose that is produced through mechanical processes is known as nanofibrillated cellulose (NFC), while nanocrystalline cellulose (NCC) is produced by acid hydrolysis which removes the amorphous segments and attain crystalline region of cellulose (Grossman et al. 2013). Nanofibrillated cellulose (NFC) was introduced by Turbak et al. in early 1980s as a cellulosic material, where high pressure homogenizer was used to produce cellulose from softwood with a diameter in nanometer scale (Nechyporchuk et al. 2015). NFC is composed of interconnected fibrils and microfibrils, whose diameter is 10–100 nm and length varies from 100 nm to several micrometers depending on the source of cellulose. They are comprised of alternating crystalline and amorphous domain. Furthermore, it

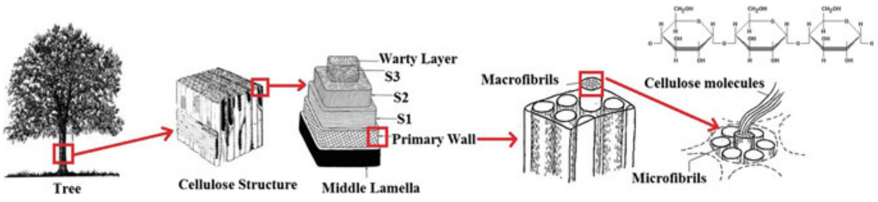

Fig. 3 Hierarchy of plant fiber

Fig. 4 Applications of nanocellulose

exhibits gel like properties in water with highly viscous dispersion at relatively low concentration i.e. 2% aqueous suspension (Besbes et al. 2011).

Nanocrystalline cellulose (NCC), also known as a cellulose nanowhiskers is a needle shaped cellulose particles with a diameter range of 2 to 20 nm and the length varies between 100 nm to several microns (Liu et al. 2011). Cellulose particles with rod like structure can be obtained through acid hydrolysis by removing amorphous region of cellulose chain. However, the degree of crystallinity, dimensional diversity and morphology depends on the source of cellulosic material and preparation conditions. These cellulose nanocrystals possess degree of crystallinity less than 400 and not more than 10% of the material has a particle size of less than 5 µm (Grossman et al. 2013).

Bacterial cellulose (BC) is an extracellular secretion of “vinegar bacteria” which is composed of cellulose nanofiber. Louis Pasteur in his study described them as *“a sort of moist skin, swollen, gelatinous and slippery…”* even though it has solid

Table 2 Nanocellulose dimensions (Khalil et al. 2012)

Cellulose structure	Diameter (nm)	Length (nm)	Aspect ratio (L/d)
Microfibril	2–10	>10,000	>1000
Microfibrillated cellulose (MFC)	10–40	>1000	100–150
Cellulose whiskers	2–20	100–600	10–100
Microcrystalline cellulose (MCC)	>1000	>1000	~1

content less than 1%. Moreover, it has no lignin and other foreign substance (Iguchi et al. 2000). Table 2 illustrates the classification of cellulosic fibers according to their physical characteristics. BC can attain a thickness of 25 mm under pure cultivation in carbohydrate media (Yamanaka et al. 1989).

4 Extraction of Nanocrystalline Cellulose (NCC)

The hierarchical structure of natural fibers needs to be broken down in order to obtain nanostructured cellulose molecules with high crystallinity and surface area. There is numerous extraction methods which have been reported to obtain nanodomain of cellulose nanofibrils by breaking up the glycosidic bonds. These methods include mechanical, chemical, Biological treatment, as well as combination of any of the two or several of the aforementioned methods. Furthermore, all these treatment methods lead to the different types of nanostructured cellulose molecules depending on their disintegration process.

4.1 Mechanical Treatment

Generally mechanical disintegration of cellulosic fiber produces nanofibrillated cellulose which is also called as a cellulose nanofiber. There are several mechanical approaches used to obtain cellulose nanofibers including, homogenizing, cryocrushing, microfluidization, grinding and high intensity ultrasonication (Khalil et al. 2014).

4.1.1 High Pressure Homogenizer

High pressure homogenization (HPH) (Fig. 5) is solely a mechanical process, where the fluid sample is forced to pass through the narrow gap of the homogenizing nozzle at high pressure (150–200 MPa). During the homogenization process the cellulosic fiber suspension is subjected to high pressure drop with shearing and impact force which leads to a high degree of fibrillation, resulting in the formation of cellulose nanofibrills. High pressure homogenizing (HPH) treatment is an efficient way of refining cellulosic fiber, referable to its simplicity, efficiency, reproducibility, ease of scaling up in the industry and noncompulsory usage of organic solvent (Li et al. 2012; Wang et al. 2015). The application of HPH for isolation of cellulose nanofibrills was first introduced by Tubak et al. and Herrick et al., using Gaulin laboratory Homogenizer in year 1983 (Missoum et al. 2013). Since then, many researchers have used HPH to isolate cellulose nanofibrills from various raw materials. In the year 2007, Leitner et al., have used HPH to produce nanofibrillated cellulose from bleached sugar beet by 10–15 cycles at 30 MPa. Followed by Habibi et al. (2008) where nanofibrillated cellulose was isolated from bleached cellulose residue from the skin of prickly pear extract with a diameter of 2–5 nm by 15 passes through HPH at 50 MPa at a temperature below 95 °C, and Lee et al. (2009) has used HPH to produce nanofibrillated cellulose from microcrystalline cellulose (MCC) with a diameter range of 28–100 nm by 10 passes.

Even though, HPH is considered as efficient method in producing cellulose nanofibrills, insoluble properties of nanocellulose in water and most of the solvents causes clogging problems which leads to difficulty in obtaining uniformity (Lim et al. 2008). Therefore, it is necessary to reduce the size of cellulosic fibers prior to homogenization. Considering this, various pretreatment methods was employed prior to HPH process. Pretreatments such as refining and cryocrushing were applied for kenaf bast fibers which produces nanofiber with a diameter of 10–90 nm. While, kenaf core and stem was grinded prior to HPH process which produces nanofibrillated cellulose ranged from 20–25 to 15–80 nm. Zimmermann et al. introduced a milling pretreatment to obtain homogeneous cellulose fibrils bundles from wheat straw and wood fibers before using homogenizer with 150 MPa to produce nanofibrillated cellulose.

4.1.2 Microfluidization

Microfluidizer (Fig. 6) is another instrument which is similar to HPH where the cellulose suspension is injected into the high pressure chamber fibrillation to produce cellulose nanofibrills (CNF). The fiber slurry is accelerated into the interaction

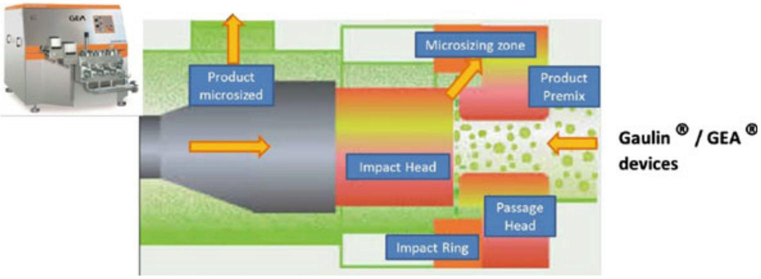

Fig. 5 High pressure homogenizer (HPH) (Missoum et al. 2013)

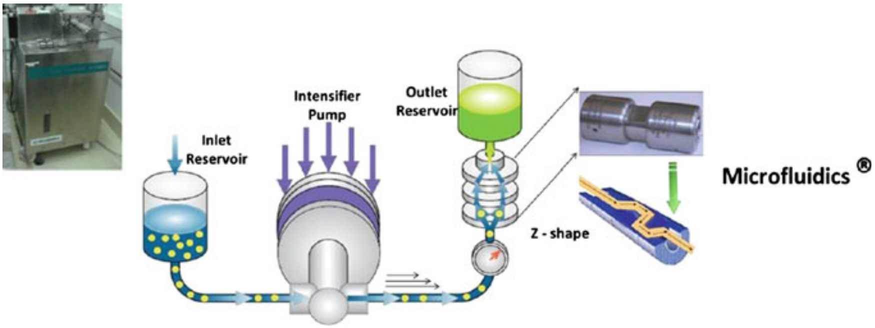

Fig. 6 Microfluidizer (Missoum et al. 2013)

chamber resulting from high pressure generated through pump intensifier. Once the pressurized product enters the interaction chamber, it passes through geometrically fixed micro channels, very high velocities are achieved. Apart from this, the degree of fibrillation is also determined by Z-chamber sizes (400–200–100 μm). There are several nanofibrillation works performed by using microfluidizer (Missoum et al. 2013).

Microfludizer has been used in order to obtain nanofibrillated cellulose, where Charani et al. (2013) has obtained improved microfibrillated cellulose of kenaf unbleached pulp quality from higher pulp consistency of 5.5%, Jihua et al. (2014) have produced nanocellulose with smaller diameter ranged 5–12 nm and Bandera et al. (2014) has isolated of long and thin cellulose nanofiber from microcrystalline cellulose (Li et al. 2014). Furthermore, microfluidizer is used to improve the properties of reinforcement where Khan et al. (2014) improved the mechanical properties of CNC reinforced bionanocomposites by optimized microfluidization process (Khan et al. 2014). Microfluidizing procedure possess unique characteristics, such as efficient and rapid mixing which leads to rapid chemical reaction, homogeneous reaction environment, continuously varied reaction condition and also due to the precise time intervals for addition of reagent during reaction (de Moura et al. 2012).

4.1.3 Grinding

Grinding equipment (Fig. 7) was first proposed and developed by Masuko Sanyo Co., Ltd., Japan, which involves breakdown of the cell wall structure using shearing force generated by two grinding stones with countersense rotation. In grinding device, the pulp is passed between a static and rotating grinding stone at desired speed (Missoum et al. 2013). The first reported work of grinding process for fibrillation method is in 1998 by Taniguchi and Okamura (1998). The shearing force occurring between two ceramic stones resulted in the fibrillation of fibers. Furthermore, the fiber was treated sequentially by passing several times through the

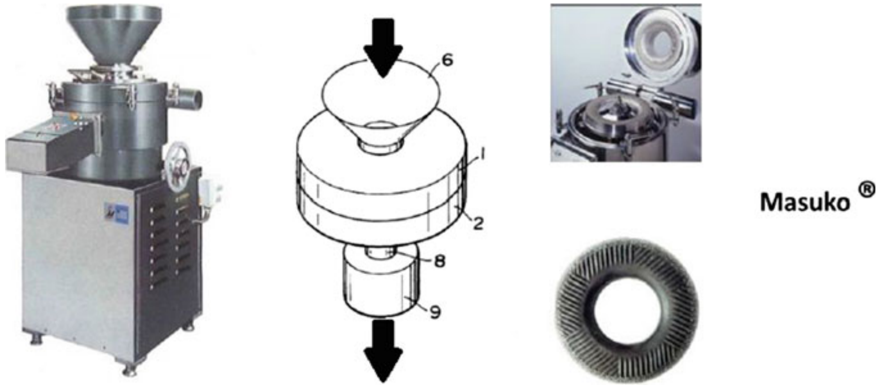

Fig. 7 Grinder (Missoum et al. 2013)

adjustable clearance between grinding stones until the desired quality was obtained (Iwamoto et al. 2007). Afterwards, many researchers have used grinding method in order to obtain nanofibrillated cellulose from various raw materials including, wood fibers (Abe et al. 2007), sludge fibers (Jonoobi et al. 2012), kenaf pulp (Jonoobi et al. 2010), bamboo pulp (Visakh et al. 2012), Agava tequilana and barley (Espino et al. 2014), and bleached Kraft pulp (Nair et al. 2014).

Apart from this, some researchers have combined this grinding process with mild chemical pretreatments, homogenization and ultrasonication processes in order to remove impurities such as lignin and pectin, also to improve their mechanical properties. Zhao et al. (2015) has prepared cellulose nanofibrills from coconut palm petiole powder by combining grinding/homogenization and grinding/ultrasonication with better tensile properties and transmittance (Zhao et al. 2015). On the other hand, Panthapulakkal and Sain (2013) and Karimi et al. (2014) have combined mild chemical pretreatments such as alkali pretreatment and bleaching prior to grinding process (Panthapulakkal and Sain 2013; Karimi et al. 2014). Grinding process has been used widely due to its simplicity, robustness with low cost and energy consumption. Furthermore, it doesn't have blocking problems like in homogenization process due to large fiber sizes (Josset et al. 2014).

4.1.4 Cryocrushing

Cryocrushing is a process where refined cellulose fiber is immersed in liquid nitrogen to free the water content in fibers and subsequently crushed by high impact grinding (Chakraborty et al. 2005). Microfibrils are generated from frozen fibers, in resultant of cell wall rupture due to exerted pressure of ice crystals generated by high impact forces. The resulting cryocrushed fibers might be dispersed uniformly into water suspension using disintegration before proceeding with the high pressure defibrillation process (Kalia et al. 2011a, b, c). Cryocrushing method has been adopted by many researchers in order to obtain nanofibrillated cellulose from soy bean stock (Wang and Sain 2006), chemically treated flax and hemp fibers (Wang et al. 2007), wheat straw fibers (Alemdar and Sain 2008), and curava fibers (Souza et al. 2010). Cryogenic grinding could overcome drawbacks of conventional grinding such as produces extremely fine grinding due to brittleness, more uniform dispersal of product, reduced visual speckling, settling rates in liquid preparations, increases throughput and reduces grinding power consumption (Manohar and Sridhar 2001).

4.2 Chemical Treatments

4.2.1 Alkali Pretreatment

Alkaline pretreatment is employed to break down the lignin structure, hence improving the susceptibility of the remaining polysaccharides (cellulose and hemicelluloses) for other treatment (Sun and Cheng 2002). Generally, NaOH, KOH, $Ca(OH)_2$, hydrazine and ammonium hydroxide are used as a pretreatment agents for alkaline hydrolysis (30, 31). Alkaline hydrolysis is usually conducted under mild condition (below 140 °C) as compared to other pretreatment technologies. During the pretreatment, intermolecular ester bond, which cross links Xylan (hemicelluloses) and lignin are saponified subsequently to increase their porosity (Sun and Cheng 2002). Furthermore, nucleophilic acyl group in the presence of alkaline salt substitutes the cleavage of this ester linkage to form a carboxylic salt and an alcohol (Pedersen and Meyer 2010). Moreover, ferulic acid and p-coumaric acid are produced when two types of aryl ether bonds split during the alkaline hydrolysis. Besides that, alkalis are good swelling agent, increases internal surface area and also decreases the degree of polymerization and crystallinity of cellulose. However, the removal of hemicelluloses component from lignocellulosic material with diluted acid treatment is required before alkali pretreatment in order to avoid over degradation of cellulose to sugar. It is because, lignin act as a protective layer for cellulose during solubilization of hemicelluloses, thus increases the cellulose yield for nanocellulose synthesis. However, it needs further separation process in order to dissolve strong poly-ring bonds C-O-C, C-C of the lignin matrix while maintaining the recovery rate of nanocellulose production (Sánchez et al. 2011).

4.2.2 Acid Hydrolysis

Controlled acid hydrolysis is one of the most common methods in dissolving amorphous domains of cellulose fiber and hence longitudinal cutting of the microfibrils. The resulting particles are generally named as a cellulose nanocrystal (CNC). Acid concentration, reaction time, and reaction temperature are some of the most important parameters for controlling the acid hydrolysis process. If the temperature of acid treatment is low (25–30 °C) then hydrolysis process needs long time too. On the other hand, if the hydrolysis temperature is higher than 60 °C darkening of cellulose particles takes place due to hydration and carbonization. Therefore, the optimal temperature of the acid treatment is in the range of 45–55 °C. Furthermore, the low acid to cellulose ratio of below 5 wt% leads to wide distribution in particle size. Therefore, homogenous acid treatment is performed at acid to cellulose ratio of more than or equal to 20 wt% (Ioelovich 2012). The nanocrystalline cellulose that is formed through the acid treatment is of colloidal dimensions and forms an aqueous suspension when stabilized. The critical concentration of colloidal suspension, which is the lowest concentration where the whiskers self- organizes, depends on particle size, acid treatment, preparation condition, aspect ratio, and ionic strength (Börjesson and Westman 2015). Hydronium ions that are present in acid breaks down the rigid structure of cellulosic fibers by attacking the glycosidic bonds, which release individual crystallites (Dufresne 2013). There are various types of acids used for lignocellulosic fiber hydrolysis which includes Sulphuric acid (H_2SO_4), Hydrochloric acid (HCl), Hydrobromic acid (HBr), Phosphoric acid (H_3PO_4), and Nitric acid (HNO_3). However, H_2SO_4 is the most common acid used for this purpose. This is because, it produces CNC particles grafted with the sulfate ester group. The presence of these negatively charged groups makes the CNC particles as negative electrostatic repulsion force to promote uniform dispersion in water. Furthermore, H_2SO_4 gave the highest crystallinity index followed by H_3PO_4. The mixture of acetic and nitric acid solution and hydrochloric acid contributes to the lowest crystallinity index due to higher tendency to promote the breakage of the hydrogen bonds in crystalline region of cellulose. Moreover, both the mixed acetic and nitric acid solution and, hydrochloric acid have better capability to swell cellulose, thus facilitates the breakage od intra- and inter molecular hydrogen bonds in the crystalline region of cellulose (Börjesson and Westman 2015).

The usage of concentrated acid for nanocellulose preparation requires extreme care in handling and processing and therefore it is expensive. However, the recovery and reusage of concentrated acid makes it more economical and environmental friendly (Harmsen et al. 2010). Besides that, many researches has been reported on the usage of diluted acid hydrolysis as it is more cost effective and less hazardous (Li et al. 2010; Moe et al. 2012).

4.2.3 Oxidizing Agent

Delignification process can also be catalyzed by oxidizing agent such as organic peroxide (H_2O_2, $C_2H_4O_3$), ozone, oxygen, or air (Abdel-Halim and Deyab 2011). Generally, oxidation agents are used to enhance the effects of alkaline pretreatments. Furthermore, this treatment oxidizes the aromatic ring of lignin and a part of hemicellulose polymer to carboxylic acids compounds. Therefore, oxidative delignification is one of the promising pretreatment for extraction of cellulose as it is more aggressive on lignin and partially on hemicellulose, while it retains cellulose from getting decomposed (Miron and Ben-Ghedalia 1982).

Hydrogen peroxide is an effective method for delignification of lignocellulosic biomass. However, it is strongly pH dependent with an optimum pH of 11.5–11.6 pKa for the dissociation reaction of H_2O_2. Studies have shown that hydrolysis of Hydrogen peroxide under alkaline condition solubilize the lignin to form lower molecular weight, water soluble oxidation products which is hydroxyl radical (OH). Furthermore, the removal of lignin leads to the exposure of cellulose in the end product. According to some researchers, 50% of lignin and most of the hemicelluloses has been removed during hydrolysis reaction using 2% H_2O_2 at 30 °C (Chaturvedi and Verma 2013; Fang et al. 1999). On the other hand, ozonolysis treatment attracts aromatic rings structure of lignin to solubilize it. Furthermore, it has several advantages over other pretreatments methods such as effective removal of lignin without affecting cellulose and hemicelluloses, it does not produce toxic residue, and can conduct the reaction at an ambient temperature and pressure. However, the process is expensive as the amount of ozone needed for it is high. Many researchers have used ozone as a pretreating agent for lignin removal in wheat straw, bagasse, green hay, peanut, pine, cotton straw, and poplar sawdust. Wet oxidation is oxidative pretreatment that operates with water and Oxygen or air at elevated temperature and pressure. During the wet oxidation, organic polymers oxidized into low molecular weight carboxylic acids, or even to CO_2 and H_2O. some researchers have used wet oxidation method to recover cellulose and obtain high yield from wheat straw, corn stoves and spruce (Alvira et al. 2010; Palonen et al. 2004).

4.2.4 Organosolv

Organosolv pretreatment is a process to degrade and solubilize lignin fragments from lignocellulosic material by using organic solvent or mixture of solvents in combination with water. Organic solvents such as ethanol, methanol, acetone and ethylene glycol act as a dissolving agent for lignin under heating condition as high as 200 °C. However, the heating temperatures may vary according to the type of biomass and use of catalyst (organic and inorganic acids). During the organosolve pretreatment, OH-ions from alcohol solvent hydrolyses the internal bonds in lignin and glycosidic bonds in hemicellulose (Lee et al. 2014).

Sun and Chen (2008) and Panagiotopoulos et al. (2012) employed ornaosolve pretreatment, to degrade lignin and hemicellulose from weat straw and poplar wood pulp respectively with 98% of cellulose retention (Sun and Chen 2008; Panagiotopoulos et al. 2013). Furthermore, Ichwan and Son (2011) utilized various combinations of solvent mixtures in order to extract cellulose from oil palm pulp. The analysis of yield shows that ethanol-water mixture pulping resulted in higher crystallinity of cellulose pulp as compared to ethylene glycol-water and acetic acid-water mixture. Besides that, alcohol based organosolv pretreatments was used inorder to improve enzymatic digestibility of Japanese cypress by

Hideno et al. (2013). The major disadvantage of using solvent and catalyst based treatments is that they are expensive. Since, pretreated fibers need an extensive washing with organic solvent to avoid precipitation of dissolved lignin which involves the usage of large amount of solvent. However, the recovery of the solvent through distillation process could reduce the operational cost (Lee et al. 2014).

4.2.5 Ionic Liquids

Ionic liquids are recognized as “green solvents” to replace harmful organic solvents as it is recyclable and environmental friendly. Ionic liquids are organic salts composed of anions and cations. The ionic liquids chemistry makes it highly capable of dissolving wide varieties of biomass types. Ionic liquids are known to possess properties such as high dissolution capacity for lignin, low melting point, good thermal stability, non-volatile, non-toxic, chemically stable, and low cost. Moreover, it possesses widely tunable properties such as polarity, solvent power and hydrophobicity. Ionic liquids that are worth to cite are, 1-alkyl-3-methylimidazolium $[\text{mim}]^+$; 1-alkyl-2,3-dimethylimidazolium $[\text{mmim}]^+$; 1-allyl-3-methylimidazolium $[\text{Amim}]^+$; 1-allyl-2,3-dimethylimidazolium$[\text{Ammim}]^+$; 1-butyl-3-methylpyridinium $[\text{C}_4\text{mP}_\text{y}]^+$; and tetrabutylphosphonium $[\text{Bu4P}]^+$ with = number of carbons in the alkyl chain (Tadesse and Luque 2011; Zavrel et al. 2009). There are several studies that have been conducted on the efficacy of ionic liquids in considering the fact that isolation of nanocellulose from lignocellulosic biomass is a complicated process. Researchers have suggested that alteration of ionic liquids properties plays a major role in solubilization of lignin and hemicelluloses. For instance, 1-ethyl-3-methylimidazolium acetate [Eminm] Ac has high tendency to degrade lignin as compared to cellulose. Apart from being selective toward lignin, an ionic liquid reduces the crystallinity of cellulose to amorphous nature. Since ionic liquids tend to disrupt the hydrogen bonds that exist in cellulose by forming another hydrogen bond between anions of ionic liquids with cellulose, it reduces the compactness of cellulose and therefore the crystallinity decreases (Yinghuai et al. 2013; Moniruzzaman et al. 2013).

4.3 Biological Treatments

Enzymatic pretreatment of lignocellulosic fiber is an attractive approach for delignification process. Biological pretreatment is known to be cost effective, low energy requirement, environmental friendly, higher yields, higher selectivity and can be conducted at mild condition as compared to chemical treatment. Microorganisms such as brown-, white-, and soft-rot fungi and bacteria are used in biological pretreatment to degrade lignin and hemicelluloses from lignocellulosic material. Besides that an enzyme that has been extracted from microbes can be used for biological treatment. Brown rot and soft rot fungi mainly attacks cellulose while a white rot attacks both the cellulose and lignin. However, enzymatic hydrolysis has its own disadvantages as compared to other pretreatments such as longer pretreatment time, and expensive because of the enzymes used (Narayanaswamy et al. 2013).

5 Bionanocomposites

The emerging field in the frontier between material science and nanotechnology has created new generation of hybrid nanostructure materials. Bionanocomposites can be regarded as the new emerging group of nanostructured hybrid materials. Bionanocomposites is defined as a mixture of naturally occurring polymer (biopolymer) and inorganic or organic filler materials that has at least one dimension on the nanometer scale. This new class of composites exhibits significant improvements in mechanical, barrier, and thermal properties, and dimensional stability. Furthermore, it also offers benefits like transparency, low density, better surface properties, good flow properties and recyclability. Figure 8 illustrates the set of composite materials that are classified according to the constituents which determines the structure, properties, functionalities and applications. In order to produce fully renewable and biodegradable nanocomposites, both the polymer matrix and the nano reinforcement have to be derived from renewable resources (Haafiz et al. 2013).

Biopolymer or biodegradable polymer can be disposed by degradation process as a result of the action of microorganism such as bacteria, fungi, or algae with low

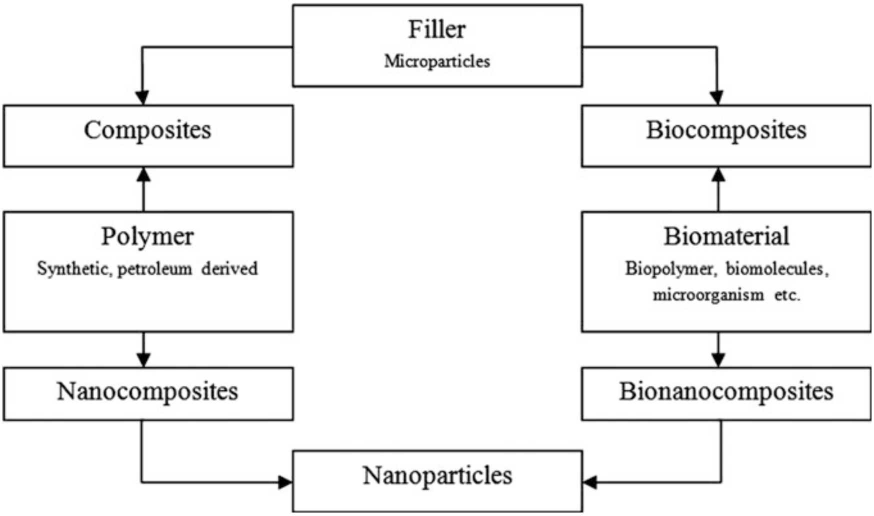

Fig. 8 Main types of composite materials and their constituents (Shchipunov 2012)

environmental impact. The degradation process produces carbon dioxide under aerobic condition or methane under anaerobic condition, in addition to hummus. The properties need to be tuned in order to obtain suitable and competitive materials for vast range of applications. On the other hand, nanocellulose based bionanocomposites combine the advantage of both the guest nanomaterial and the nanocellulose substrate and often exhibit synergetic properties. Nanocellulose is an ideal platform to house a range of guest nanomaterials due to its high specific surface area (Wei et al. 2014).

Various techniques are available for bionanocomposite fabrications. These methods are divided into three types based on the starting materials and processing conditions (Mittal 2015):

(a) Solution casting method—the nanofillers dispersed in the polymer solution for better dispersion. Subsequently the solvents removed by fast evaporation.
(b) Melt extrusion technique—blend of nanofiller and polymer matrix prepared in the molten state preferably in single/twin screw extruder.
(c) In situ polymerization—nanofillers first dispersed in monomers followed by polymerization using solution method in the presence of small amount of catalyst.

5.1 Biopolymers

To comply with the term of green composite, many studies have been conducted to produce 100% eco sustainable biocomposites. These biocomposites are made up of biodegradable polymers and filler materials. Generally, biodegradable polymers can be classified according to their origin, such as polymers that are synthesized from agro based monomers (e.g. poly lactic-acid), agropolymers (e.g. starch and lignin), microbial derived (e.g. polyhydroxyalkanoates) and conventional monomers (e.g. synthetic polyesters). The classification of biopolymers based on their production routes are shown in Fig. 9. The physical, chemical and mechanical properties of biopolymers tabulated in Table 3.

Elaboration of multiphase materials such as blends and composites are most common methods applied in the polymer industry to get tough material. In general, biodegradable polymers are classified according to their origins. The three major categories of biopolymers are (Mittal 2015):

(a) Synthetic polymers, particularly aliphatic polyesters, such as poly (lactic acid) (PLA), poly(butylene succinate) (PBS), poly(ε-caprolactone) (PCL), and poly (*p*-dioxanone) (PPDO).
(b) Polyesters produced by microorganisms, which are various types of poly(hybroxyalkanoate)s, including poly(3-hydroxybutyrate) (P3HB) and poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV).

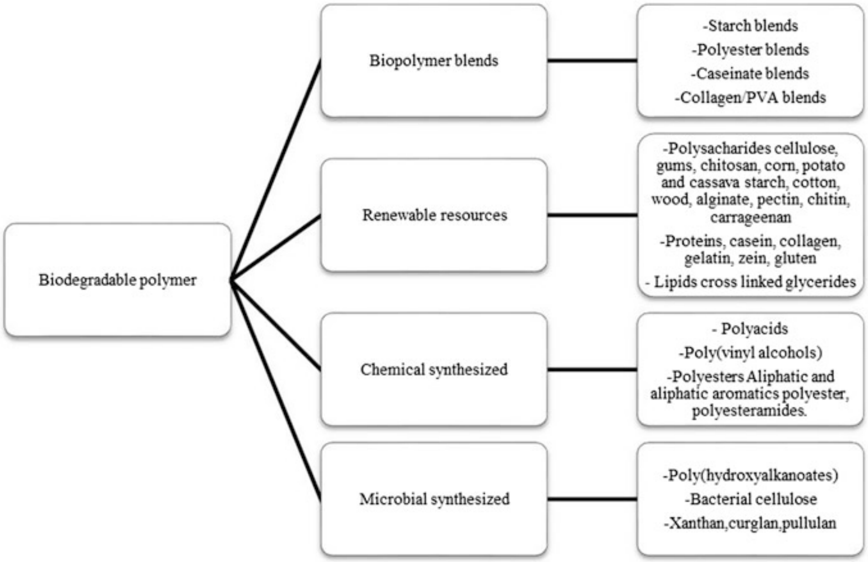

Fig. 9 Classifications of biopolymers and their nomenclature (Satyanarayana et al. 2009)

Table 3 Properties of biodegradable polymers

	PLA Dow–Cargill (nature works)	PHBV Monsanto (Biopol D400G) HV = 7 mol%	PCL Solway (CAPA 680)	PEA Bayer (BAK 1095)	PBSA Showa (Bionolle 3000)	PBAT Eastman (eastar, bio 14,766)
Density	1.25	1.25	1.11	1.07	1.23	1.21
Melting point (°C)	152	153	65	112	114	110–115
Glass transition (°C)	58	5	–61	–29	–45	–30
Crystallinity (%)	0–1	51	67	33	41	20–35
Modulus (MPa) (NFT 51-035)	2050	900	190	262	249	52
Elongation at break (%) (NFT 51-035)	9	15	>500	420	>500	>500
Tensile stress at break (MPa) (NFT 51-035)	–	–	14	17	19	9
Biodegradation (%)	100	100	100	100	90	100
Water permeability WVTR at 25 °C (g/m^2/day)	172	21	177	680	330	550
Surface tension (g) in mN/m	50	–	51	559	56	53

(continued)

Table 3 (continued)

	PLA Dow–Cargill (nature works)	PHBV Monsanto (Biopol D400G) HV = 7 mol%	PCL Solway (CAPA 680)	PEA Bayer (BAK 1095)	PBSA Showa (Bionolle 3000)	PBAT Eastman (eastar, bio 14,766)
gd (Dispersive component)	37	–	41	37	43	43
gp (Polar component)	13	–	11	22	14	11

*Poly lactic acid (PLA); Poly (3-hydroxybutyrate-co-hydroxyvalerate) (PHBV); Polycaprolactone (PCL); Polyesteramide (PEA); Aliphatic copolyester (PBSA); and Aromatic copolyester (PBAT) at break results (Zhao et al. 2013)

(c) Polymers originating from natural sources, including starch, cellulose, chitosan, chitin, lignin, and proteins.

Nanoparticles with at least one dimension in the nanometer range (1–100 nm) are generally used for nanocomposite fabrication in order to improve their mechanical properties. These nanosized fillers are classified according to their aspect ratio and geometry (Siqueira et al. 2010; Avérous and Pollet 2012; Han 2005):

(a) Isodimensional nanoparticles/spherical—silica, metal and metal oxide nanoparticles
(b) Nanoparticles with two dimensions in nanometer range/acicular—carbon nanotubes and cellulose nanowhiskers.
(c) Nanoparticles with one dimension in nanometer range/layered—layered silicate clays or layered crystals

In particular, poly (lactic acid) (PLA) and poly (3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) biopolymers have high significant potential to be used in packaging industry due to their biodegradability, sustainability and biocompatibility. Furthermore, they have comparable mechanical and thermal properties to those of some conventional polymers (Abdelwahab et al. 2012).

5.1.1 Poly(Lactic–Acid) (PLA)

Poly(lactic–acid) (PLA) is a thermoplastic aliphatic polyester, which is highly versatile, biodegradable and biocompatible polymer. Figure 10 shows the chemical structure of PLA. PLA is derived from renewable and biodegradable plant resources such as starch and sugar. Lactic acid is a monomeric building block of PLA which exists in two optical isomers, L- and D-lactic acid due to their chiral nature. The L-isomer rotates clockwise on the plane of polarized light while the D-isomer rotates counterclockwise. The main fraction of PLA derived from renewable resources is made up of L-isomers, which is a biological metabolite Lasprilla et al. 2012). On the

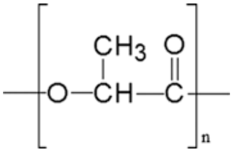

Fig. 10 Chemical structure of PLA

other hand, D-lactic acid isomers can be produced by microorganisms or by racemization. Lactic acid is mainly found in fermented milk products and also can be commercially manufactured by bacterial fermentation process using various source of carbohydrates. PLA can be synthesized by two main synthetic methods which includes, ring opening polymerization, and direct polycondensation (including solution and melt polycondensation) of lactic acid monomers (Ahmed and Varshney 2011; Martin and Averous 2001).

Great interest is given for the application of PLA in packaging industry due to their good optical, physical, mechanical and barrier properties as compared to synthetic polymers. The permeability coefficient of CO_2, O_2, N_2, and H_2O for poly lactic acid (PLA) polymer is lower as compared to polystyrene (PS). Furthermore it has comparable barrier properties as polyethylene terephthalate (PET) against organic permeates (e.g. ethyl acetate and limonene). Oriented PLA has better mechanical performance than oriented PS, but comparable to PET. PLA possesses higher tensile and flexural moduli as compared to PS, polypropylene (PP) and high density polyethylene (HDPE) (Lim et al. 2008). PLA is a promising thermoplastic polymer with unique characteristic to replace conventional polymers like PET, PS and PC for packaging, electronic and automotive applications. The application of PLA and their blends has been tabulated in Table 4. However, neat PLA is a brittle polymer with fracture strain is about 5%, which leads to poor impact and tear resistance. PLA exhibits poor heat stability with low level of heat deflection temperature (HDT) (Zhang et al. 2011, 2012). Furthermore, it is relatively hydrophobic and chemically inert with no reactive side chain group. These drawbacks of PLA have been a major bottleneck for its large scale commercial applications (Rasal et al. 2010).

5.1.2 Polyhydroxyalkanoates (PHA)

Bacterial polyhydroxyalkanoates is another family of biopolymer that is produced as intracellular energy and carbon storage materials by various microorganisms. Poly-3-hydroxybutyrate (PHB) is the most common member of PHA family which belongs to the short chain length PHA (scl-PHA) with its monomers made up of 4–5 carbon atoms. Medium chain length of PHA (mcl-PHA) is made up of 6–12 carbon atoms, such as poly (hydroxyoctanoate-*co*-hydroxydecanoate) or P (HO-*co*-HD). Copolyesters such as 3-hydroxybutyrate (HB) and 3-Hydroxyexanoate (HHx) which are the scl and mcl monomers respectively possesses dramatic improvement in their mechanical properties as compared to PHB (Smith 2005).

Table 4 Application of PLA and their blends in various fields (Babu et al. 2013)

Polymer	Applications	References
PLGA/PGA	Ovine pulmonary valve replacement	Williams et al. (1999); Sodian et al. (2000); Cheng et al. (2009)
PLA/Chitosan PLA/PLGA/Chitosan PLA	Drug carrier/drug release	Jeevita and Kanchana (2013); Jayanth and Vinod (2012); Nagarwal et al. (2010); Chandy et al. (2000); Valatin et al. (2003)
PLGA and copolymers	Degradable sutures	Rajev (2000)
PLA/HA composites	Porous scaffolds for cellulae applications	Jung-Ju et al. (2012)
PLA-CaP and PLGA-CaP	Bone fixation devices,plates, pins, screws, and wires, orthopedic applications	Huan et al. (2012)
PDLLA	Coating on metal implants	Schmidmairer et al. (2001)
PLA/PLGA	Use of cell based gene therapy for cardiovascular diseases, muscle tissues, bone and cartilage regeneration, and other treatments of cardiovascular and neurological conditions	Coutu et al. (2009); Kellomakiet al. (2000); Papenburg et al. (2009)
PLA and PLA blends	Packaging films, commodity containers, electrical appliances, mobile phone housings, floor mats, and automotive spare parts	Rafael et al. (2010)
PLA	Textile applications	Gupta et al. (2007); Avinc and Akbar (2009)

Poly (3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) biopolymer is a copolymer made up of hydroxybutyrate (HB) and hydroxyvalerate (HV) monomer units. Poly (3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) (Fig. 11) is one of the PHA family members with attractive characteristics such as excellent biodegradability, biocompatibility, and some properties similar to those of polypropylene (Zhang et al. 2012). It is a brittle polymer with elongation at break less than 15%, and had modulus and fracture stress value of 1.2 GPa and 25 MPa respectively (Bugnicourt et al. 2014). Furthermore, PHBV possesses high melting temperature (T_m), up to 170 °C for the homopolymer (Gunaratne and Shanks 2005). PHBV demonstrates excellent barrier properties, thus it can be used in packaging industry to replace aluminum as the inner lining of packaging cardboard (Pilla 2011). The thermal and mechanical properties of PHBV can be altered by varying the percentage of hydroxyvalerate (HV) content. The glass transition temperature, impact and tensile strength, melting point and crystallinity decreases as the HV content increases (Ghanbarzadeh and Almasi 2013). However, its brittleness, low impact strength and

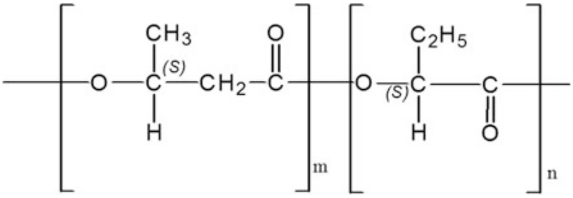

Fig. 11 Chemical structure of PHBV

Table 5 Application of PHA and their blends in various fields (Babu et al. 2013)

Polymer	Applications	References
P(3HB), P (3HB-*co*-3HHX) and blends	Scaffolds, nerve regeneration, soft tissue, artificial esophagus, drug delivery, skin regeneration, food additive.	Yang et al. (2002); Chen and Qiong (2005); Bayram and Denbas (2008); Tang et al. (2008); Clarinval and Helux (2005)
mcl-PHA/scl-PHA	Cardiac tissue engineering, drug delivery, cosmetics, drug molecules	Sodian et al. (2000); Wang et al. (2003); de Roo et al. (2002); Zhao et al. (2003); Ruth et al. (2007)
P(4HB) and P (3HO)	Heart valve scaffold, food additive	Clarinval and Halleux (2005); Valappil et al. (2006)
P93HB-*co*-4HB), P(3HB-*co*-3HV)	Drug delivery, Scaffolds, artificial heart values, patches to repair gastrointestinal tracts, sutures	Turesin et al. (2001); Williams et al. (1999); Chen et al. (2008); Freier et al. (2002); Kunze et al. (2006); Volova et al. (2003)
PHB, Mirel P103	Commodity applications, shampoo and cosmetic bottles, cups and food containers	Philip et al. 2007; Amass et al. 1998; Walle et al. (2001)

high production cost limits the broad range application of PHBV (Ha and Cho 2002) (Table 5).

5.1.3 Polymer Blend

Blending of PLA/PHBV is a practical and economical way to develop new materials with unique properties such as mechanical, thermal, and dynamic mechanical properties. It has been reported by Ma et al. that the blending of PLA/PHBV and an increase in the PHBV content reduces the storage modulus of PLA in the glassy state (Mofokeng and Luyt 2015). The PLA/PHBV blend with 25/75 composition respectively has phase separated particles acting as sites for heterogeneous cell nucleation resulting in high cell density and small cell size. Besides that, another study reported that 15 wt% of PHBV in PLA/PHBV blend is an ideal composition to fully take advantage of the immiscible particle heterogeneous cell nucleation phenomenon due to the maximized interfacial area to volume ratio (Guan and Naguib 2014). According to Zhao and co-workers study the PLA/PHBV mixture ratio of 70/30 wt% was found to be more ductile than the PLA/PHB mixture ratio of 85/25. Besides that, the standard deviation for the elongation to break of PLA/PHBV (70/30) specimens was higher than the other specimens tested for the strain.

6 Application of Bionanocomposites

Cellulose nanoparticles present the potential for diverse applications, and their use in nanocomposites has been extensively studied. By embedding biofibers with renewable resource-based biopolymers such as cellulosic plastics; starch plastics; polyhydroxyalkanoates; polylactides, the so-called green biocomposites could soon be the future. Applications of nanocellulose are mainly considered to be in paper and packaging products, although construction, automotive, furniture, electronics, pharmacy, and cosmetics are also being considered (Fig. 12). For companies

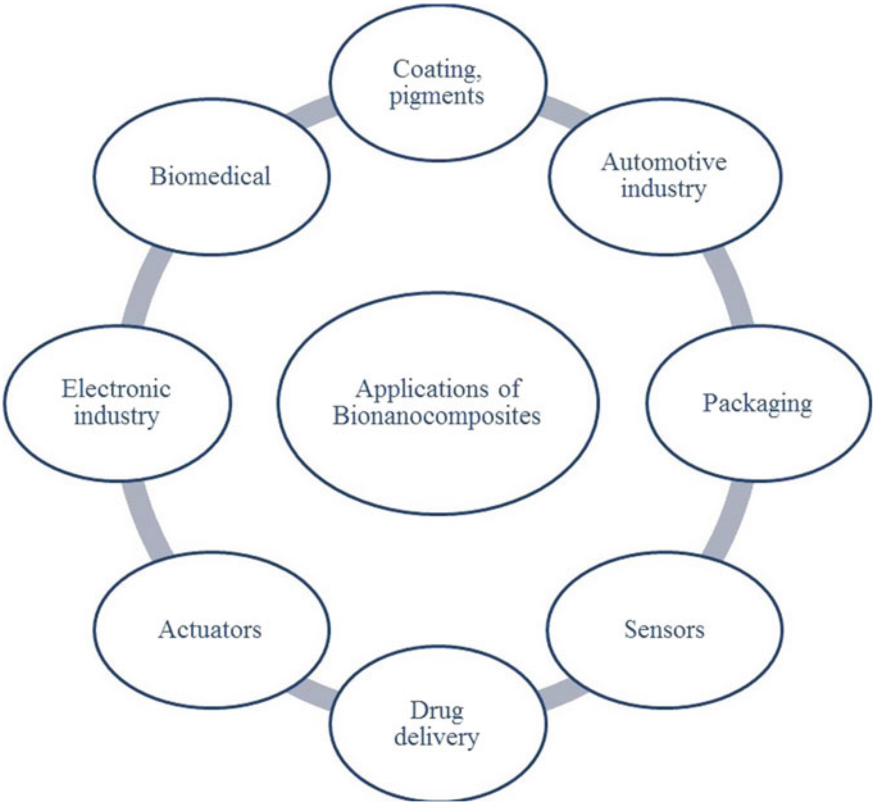

Fig. 12 Applications of bionanocomposites in various fields

producing electroacoustic devices, nanocellulose is used as a membrane for high quality sound. Additionally, nanocellulose is applied in membrane for combustible cells (hydrogen); additives for high quality electronic paper (e-paper); ultrafiltrating membranes (water purification); membranes used to retrieve mineral and oils, and nowadays, nanocellulose has been greatly discussed and researched a huge variety of applications. The high strength and stiffness as well as the small dimensions of nanocellulose may well impart useful properties to composite materials reinforced with these fibers, which could subsequently be used in wide range of applications (Kalia et al. 2011a, b, c).

6.1 Bionanocomposites for Packaging Applications

One future area of application wherein NCC-containing polymer nanocomposites can make an impact is in the field of biodegradable packaging materials. The incorporation of NCC can significantly improve the mechanical performance, thermal stability, and barrier and optical properties due to its improved crystallinity and better interfacial interaction. Biodegradable nanocomposite films with superior properties can also find their applications in food and biomedical packaging areas, in which lower permeability to moisture, gases, aroma, and oil are very much needed (Lange and Wyser 2003).

Packaging is usually classified into two categories including rigid packaging, semirigid packaging, and flexible packaging, based on its ability to change shape. Rigid packaging materials does not change its shape and more reliable in transporting the materials without changing the aesthetic appearance of the product. Generally, the rigid packaging materials has greater impact strength, stiffness and barrier properties as compared to flexible packaging which makes it ideal for more shape sensitive content. The rigid packaging manufactures using injection molding is used for ice cream packaging in the form of cartons made out of plastic. The semi-rigid packaging trays used in frozen food industry can be manufactures from aluminum, fibrous and plastic composite materials. Flexible packaging manufactured from composite materials is almost always from plastic film composites material. There are many different types of flexible packaging depending on its processing and use including shrink wrap, bubble wrap, cling wrap, breathable film packaging, retort packaging, blister packaging, gas flush packaging and vacuum packaging (Alavi et al. 2014).

In one research investigation, PVA-based barrier membranes containing different amounts of NCCs have been reported (Paralikar et al. 2008). These membranes containing up to 10 weight percentage of NCCs have been found to reduce the water vapor transmission rate. The presence of highly crystalline nanocrystals can increase the tortuosity of water vapor within the polymer, leading to a slower diffusion process and, hence, lower permeability. The barrier properties are enhanced if the filler is less permeable and has good dispersion in the matrix along with a high aspect ratio (George and Sabapathi 2015). This improved barrier properties in bionanocomposites is explained on the basis of increased path length due to the presence of cellulose nanofillers which attributes to the increase in tortuosity induced by the presence of the nanofibers (Reddy et al. 2013). NCC also often pressed into thin transparent films referred to as nanopapers and has been identified as potential packaging material (Salas et al. 2014).

However, many scientific and technological challenges have to be addressed in several areas, such as optimizing suitable processing technologies for reducing the production cost, establishing the compatibility between products and packaging materials, and meeting several packaging legislations before achieving a truly biodegradable packaging material that satisfies both industry requirements and consumer expectations (George and Sabapathi 2015).

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Conceptual Design of Biocomposites for Automotive Components

M.L. Sanyang, M.R. Mansor, S.M. Sapuan and B.A. Ahmed Ali

Abstract Recently, biocomposites became highly valuable due to their environmental advantages. The growing environmental awareness of people and the new stringent green policies enacted by governments has intensify the search and development of more environmentally friendly materials to preserve our immediate environment and public health. However, the selection of bio-based materials is quite difficult to perform compared to conventional materials like synthetic fibers and plastics. Hence, the use of computer aided tools for choosing bio-based materials help to minimize material selection errors and accommodates the increasing number of new materials as well as prevents financial and time loss. This review presented a brief insight of biocomposite materials selection using computer aided systems such as expert systems. Multi-criteria decision making models or tools also plays significant role in the evaluation and selection of materials. Numerous factors of various materials such as mechanical properties, material cost, environmental performance, just to name a few, are considered in the material selection process. These factors mostly contradict or even conflict with each other, which further complicates the task. Hence, to alleviate material selection problems and ease out decision making procedures, multi-criteria decision making (MCDM) approach is employed. MCDM is classified into multi attribute decision making (MADM) and multi objective decision making (MODM). MADM is the most

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common approach utilized for composite material selection purposes. This chapter also discusses about life cycle assessment (LCA) of products which is one of the widely used techniques in analyzing and quantifying the effect of biocomposite products on the surrounding environment during their total life time. Finally, a Case study on material selection of Bio-resin for biocomposites using modified digital logic and weighted property method was presented.

Keywords Material selection · Biocomposites · Life cycle assessment · Modified digital logic

1 Material Selection and Its Importance

Material selection is one of the cardinal processes in engineering design to obtain successful products with outstanding properties that best suits their purpose. The task of material selection is normally carried out by design and material engineers (Sapuan 2001). Due to the immense number of materials in the marketplace and trade-offs between material properties pose major challenge for engineering designers to select the best suitable materials for a specific application (Liu et al. 2014).

According to the description of Deng and Edwards (2007), material selection is the process of selecting specific material properties from a group of defined candidates after the physical design structures has been determined. Whereas, Gutteridge and Waterman (1986) described material selection as the identification of materials, which after appropriate manufacturing operations, will possess the dimensions, shapes, and properties desired for the product or component to perform its required function at the lowest cost. Elsewhere, the goal of material selection was enumerated by Thakker et al. (2008) as selecting the best material that fulfills the requirements of the design and offer maximum performance and minimum cost. Anojkumar et al. (2014) considered the selection of best suitable materials in the design and development of any product as one of the most complex and challenging issues, but critically important for the success and to meet the needs of cost reduction and better performance.

Material selection for a specific purpose is not a trivial task because materials play significant role during the entire product design process. They are considered as the main “stuff” of engineering design (Ashby 2001). Materials are responsible for function, shape and interaction with customer/user or with other components of the product (Liu et al. 2014). Making the correct choice of material or combination of materials is a hectic process that consumes a vast amount of time and expert expertise (Jahan and Edwards 2013). Material selection often requires interdisciplinary efforts and involves experts from diverse backgrounds, depending on the product field of application (Jahan et al. 2010).

1.1 Consequences of Improper Material Selection Decision

Material selection has remarkable significance in the design and development of products. It also reflects the expertise and competitiveness of the product producers (Liu et al. 2013). Hence, selection of improper materials for an intended application often results to huge lost in money and time on the redesigning or fabrication of the designed parts (Ipek et al. 2013). Wrong selection of materials can also lead to failure or undesired outcomes of products and dissatisfaction from various parties (see Fig. 1). The overall increase in production cost coupled with pre-mature failure of the product in the field of application as a result of incorrect selection of materials; negatively affect the productivity, profitability and reputation of the concerned manufacturing company (Prasad and Chakraborty 2013; Peng and Xiao 2013). Just as proper selection of materials will provide the product with maximum performance and minimum cost, improper selection of materials may yield early product failure and, thus, significantly decrease the product performance (Jahan et al. 2011; Yang and Ju 2014). Whenever the selection process of materials is done haphazardly, there exist high chances of selecting the wrong material while the best one is overlooked (Farag 2002). There are numerous factors, constraints and limitations to disqualify certain type of materials for a particular application (Fairuz et al. 2012; Cebon and Ashby 1992).

In past years, material and design engineers mostly select materials using trial and error method or on the basis of their previous experiences, which sometimes works. However, the large number of existing materials together with the complicated relationship between the various selection parameters often intensifies the

Fig. 1 Example of arguments inflicted during materials selection (Sapuan and Mujtaba 2010)

complexity of the material selection task (Jahan et al. 2011). Worst of all, recently, there is a rapid growth of so-called ‘new materials’ (i.e. natural fibers and bio-based polymers) both by type and quantity for engineering applications. These new materials are potential alternatives to traditional materials in terms of weight reduction, performance enhancement, environmentally friendliness and so on (Jee and Kang 2000). These vast number of available materials further dense the task of engineers and designers in selecting the most suitable materials. Hence, it is paramount for engineers and designers to adopt systematic material selection procedure to assist in evaluating and selecting the best materials for a precise product component.

1.2 Fundamental Steps in Material Selection

In reality, selecting suitable materials prove to be a difficult task which includes many variables and factors. Try and error method and personal experiences are the most common options utilized by traditional material or design engineers to address this problem (Yazdani and Payama 2015). Nonetheless, such methods cannot always offer the most appropriate solution. For this reason, some accurate methodologies should be at the disposal of material experts to ease the task of choosing the best materials for a specific application. A systematic approach for material selection is essential, due to the numerous factors and parameters involved in the design process of products coupled with the quick increase of materials employed in the fabrication of products (Yazdani and Payama 2015). Table 1 shows the various material selection step suggested by different authors. To crown all, Jahan et al. (2010) presented two main fundamental steps in material selection, namely; screening and ranking.

Table 1 Steps for material selection

Authors	Farag (2002)	Ashby (2004)	Jalham (2006)	Van Kesteren et al. (2006)
Steps for material selections	1. Intinial screening 2. Develope and compare alternative 3. Select the optimum solution	1. Translate design needs into requiemnt for material 2. Screen out those disqualified 3. Rat the surviving ones 4. Search for support information about the top ranked candidates	1. Preselection 2. Selection 3. Post-selection 4. Techno-economic phases	1. Formulate material criteria 2. Make a set of candidate materials 3. Compare candidate materials 4. Choose candidate material

1.3 Multi-Criteria Decision Making (MCDM) Methods for Materials Selection

In the process of selecting the best materials for engineering designs, material or design experts need to consider various significant criteria or attributes simultaneously to achieve acceptable selection results for optimal decision making (Liu et al. 2014). A large variety of factors such as material cost, physical properties, mechanical properties, manufacturing properties, environmental performance, recyclibility, market trends, cultural aspects, availability of supply sources and safety are usually accounted for during the material selection process (Prasad and Chakraborty 2013; Rao 2008; Rao and Patel 2010). These factors contradict and sometimes conflict each other because each material demonstrates dissimilar performance for each property (Matos and Simplicio 2006). Hence, to alleviate material selection problems and ease out decision making procedures, multi-criteria decision making (MCDM) is required. MCDM methods became useful and popular in the field of material selection (Jahan et al. 2011). MCDM is a promising systematic and efficient approach to obtain the optimum material from a large number of potential materials.

MCDM consists of generating alternatives, establishing criteria, evaluation of alternatives, assessment of criteria weights, and application of a ranking system (Jahan et al. 2011; Vincke 1992; Karande et al. 2013). Decision making for choosing the right material in the presence of multiple conflicting criteria (known as MCDM) is divided into two main approaches, multiple attribute decision making (MADM) and multiple objective decision making (MODM) (Jahan et al. 2010; Shanian and Savadogo 2006; Khorshidi and Hassani 2013). MADM is defined as the selection of an optimal material from among two or more alternative materials on the basis of two or more attributes (Jahan et al. 2010; Rao 2008). There are numerous methods in each of the mentioned groups. Interestingly, each of the technique has its own characteristics and the methods can possibly be combined with each other or with fuzzy methods (Jahan et al. 2010).

After a thorough evaluation of the existing decision making methods, Jahan et al. (2010) end-up reporting that the MADM approach has potentiality to further enhance the material selection methodology (Peng and Xiao 2013). The most renounce methods for MADM are Analytic Hierarchy Process (AHP) (Jahan et al. 2010), Elimination and et Choice Translating Reality (ELECTRE) (Shanian and Savadogo 2006), Technique for Order Preference by Similarity to Ideal Solution (TOPSIS) (Rathod and Kanzaria 2011), Vise Kriterijumska Optimizacija Kompromisno Resenje (VIKOR) (Jahan et al. 2010), graph theory and matrix representation approach (GTMA) (Chen 2012) and Preference Selection Index (PSI) (Maniya and Bhatt 2010) method. MADM method is mostly utilized for composite materials selection purposes (Mansor et al. 2014).

2 Materials Selection for Biocomposite Products

Biocomposites are broadly defined as composite materials made from natural fiber and petroleum derived non-biodegradable polymers (i.e. PP, PE) or biodegradable polymers (starch, PLA, PHA). Recently, biocomposites became highly valuable material due to their environmental advantage over counterparts. The growing environmental awareness of people and the new stringent green policies enacted by governments has intensify the search and development of more environmentally friendly materials to preserve our immediate environment and public health. The large number of publications related to the develop, fabrication and characterization of new materials for biocomposites, reflects the growing significant of material selection for biocomposite products. Hence, more and more material experts or

Table 2 Recent publications (2010–2015) on material selection for biocomposites

Authors	Work title
AL-Oqla et al. (2015a)	Decision making model for optimal reinforcement condition of natural fiber composites
AL-Oqla et al. (2015b)	Selecting natural fibers for bio-based materials with conflicting criteria
AL-Oqla et al. (2014a)	A novel evaluation tool for enhancing the selection of natural fibers for polymeric composites based on fiber moisture content criterion
AL-Oqla et al. (2014b)	Combined multi-criteria evaluation stage technique as an agro waste evaluation indicator for polymeric composites: date palm fibers as a case study
Mansor et al. (2014a)	Application of integrated AHP-TOPSIS method in hybrid natural fiber composites materials selection for automotive parking brake lever component
Mansor et al. (2014b)	Materials selection of hybrid bio-composites thermoset matrix for automotive bumper beam application using topsis method
Shah (2014)	Natural fibre composites: comprehensive ashby-type materials selection charts
Sapuan and Mansor (2014)	Concurrent engineering approach in the development of composite products: A review
Ali and BA (2013)	Java based expert system for selection of natural fibre composite materials
Mansor et al. (2013)	Hybrid natural fiber/glass fiber reinforced polymer composites material selection using analytical hierarchy process (ahp) for automotive component design
Fairuz et al. (2012)	A prototype expert system for material selection of polymeric-based composites for small fishing boat components
Sapuan et al. (2011)	Materials selection for natural fiber reinforced polymer composites using analytical hierarchy process.
Sapuan and Mujtaba (2010)	Development of computational framework for material selection of natural fiber-reinforced polymer composite materials using neural network

researchers are looking into this gap. Table 2 presents a number of recently (2010–2015) performed investigation in the field of materials selection for biocomposites product, aimed for specific application.

3 Expert Systems for Materials Selection

Expert systems are subdivision of applied artificial intelligence and it came into being in the mid-1960s by the artificial intelligence community (Liao 2005). An expert system is an interactive computer-based decision making tool that utilizes both facts and heuristics to answer difficult decision problems founded on the knowledge obtained from an expert (Ipek et al. 2013). A wide range of task-specific knowledge is transferred from a human expert to a computer. Such knowledge is kept in the computer and users consult the computer through the user interface for specific advice when necessary. Upon inquire, the computer makes inferences and arrive at a specific answer.

Expert system also called knowledge-based system, are computer program that simulate the reasoning of human expert in a given field of knowledge. Expert systems rely on heuristics, or the rule of thumb, to extract the information from the large knowledge-base. Expert systems are finding many applications in industry including the area of design, manufacturing, trouble shooting, failure analysis material substitution and material selection. An important advantage of expert system is their ability to capture valuable expertise and make it available to a wider circle of users. They also provide impartial recommendation and are able to search large database for optimum solutions (Farag 2006; Weiss 1997).

Nowadays, the use of computers in engineering design has become an acceptable route in most of engineering projects. Expert systems are particularly suitable for the processing of unstructured scattered knowledge for the solution of complex problems. One such problem is the selection of materials for design with novel materials. In all the systems, data about the materials and their properties were processed and stored in database systems. Logical user interfaces between expert systems and database were developed. Then, the design and selection of the optimal materials were solved through experience and expert knowledge. The expert system developed could offer companies sufficient research potential to solve their practical problems (Sapuan 1999).

An expert system is developed by creating a knowledge base that is required for the application. A knowledge base contains facts and data that are specific to a particular problem area and rules that tell how to manipulate the facts or data stored (Yingzhan 2007). Unlike a conventional database, a knowledge base may include facts, assumptions, beliefs, expertise, and heuristic methods, which are exploratory methods for solving problems where an evaluation is made of the progress toward a goal using a series of approximate results.

How to reason result from the phenomena that existed in the system is an important question in using the expert system. According to information of the current problem, the inference engine can distinguish, select and match the rules in knowledge base in order to gain results of problems (Hongwei 2005).

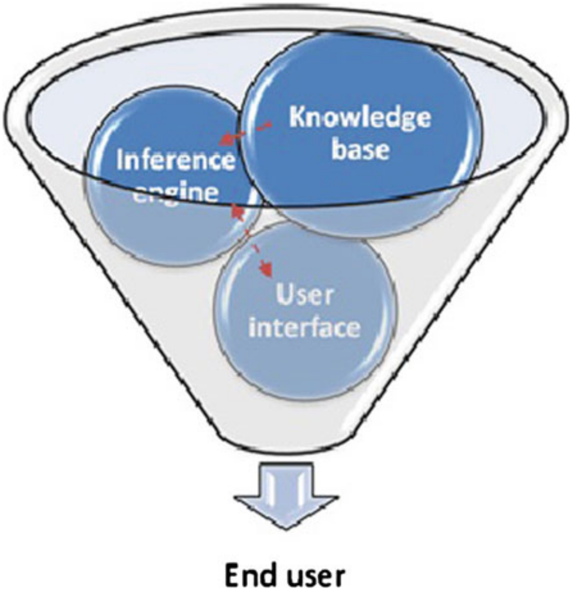
At present, forward and backward reasoning are widely used, forward reasoning is the inference course from premise to conclusion, and on the contrary, backward reasoning is the inference course from conclusion to premise. Applied to the system, forward reasoning is the course from fault feature to fault name, backward reasoning is that first assume fault name, then search for whether prerequisite is satisfied or not, so it can judge whether assumption is right. We utilize forward and backward reasoning in fault diagnosis, and it has got satisfactory effects.

Expert system has been found in many applications especially in diagnosis system, system advisor; web based advisory system, and fuzzy decision making. Guo et al. (2008) have been developed diagnosis system for real time faulty in pneumatic system using expert system approach. The system very effective in improve detection and isolation capabilities of quantitative knowledge based system.

Wang et al. (2010) used expert system approach for heavy machinery fault diagnostic system based on supporting maintenance. Machine design, assembly, processing environment and operation as a factor influence the faulty of the system. Chunming and Dawei (2007) investigated a fault diagnosis expert system includes knowledge base, reasoning machine, explanatory, and interfaced based on transient response testing on the mixed-signal circuit using artificial neural network approach. Yang et al. (2005) proposed an expert system using a decision table based on the cause-symptom matrix as probabilistic method to aid plant operators in diagnosing the cause of abnormal vibration for rotating machinery.

KBS has three main components (Fig. 2) which are typically classified as;

Fig. 2 Expert system components



3.1 Knowledge Base

The knowledge base is the place which contains the rules and techniques that represent human expert knowledge in the system. The domain of a knowledge based system is represented as frames and objects (Sapuan and Abdalla 1998; Sapuan 2001; Sapuan et al. 2002). The connection between the objects is linked together in the form of hierarchy. Information regarding biocomposites and the type of reinforcement are denoted as objects. The manufacturing techniques for biocomposites and its properties such as mechanical and physical properties are kept in the knowledge base. The data for the object are collected from published journals, textbooks, online and other sources. For the frame-based structure, the reinforcement are defined as subclass to the class biocomposite in the object hierarchical tree (Sapuan 2001; Sapuan et al. 2002). In addition, the biocomposite classification is further clarified in depth as the reinforcement-matrix combination and formed as instance.

3.2 Inference Engine

The inference engine is an essential component in a knowledge-based system. It is also known as the 'supervisor' that direct the operation upon the knowledge stored in the expert system. It stands between the user and the knowledge base. The internal operation of the inference engine is transparent to the user. Its fundamental function is inferencing and control. The inference engine consists of program instructions that are required or any expert system to operate. It works depending on rules and arrive at the solution using reasoning method. Forward chaining is the reasoning pattern used by the inference engine. During the operation, the engine will browse through the knowledge base and finds the solution with respect to the rule constraints. The engine continues its act of reasoning until the most suitable results for the constraint defined in the rules is obtained.

3.3 User Interface

This component of the expert system is used for two-way communication between the user and the system. The user interface interconnects and organizes data that have to be evaluated for further evaluation. If the user simply put all the required information, the interface displays all information transaction, which occurs during the consultation. The interface can be in the form of menus, questions, or graphical icons that are displayed on the computer screen. Communication through the user interface is accomplished by using a keyboard, mouse, or trackball. Sapuan et al. (2002) used a session window of Kappa-PC interfaces to create an application interface. They designed a user-friendly interface in such a manner that when an image in the interface is clicked, it invokes the necessary function and start running the interface process.

4 Environmental Life Cycle Assessment of Natural Fiber Composites

The use of various products in daily applications consequently contributed to some portion of environmental damaged throughout the products life time. Due to that reason, understanding the resulting effect of the product as well as differing environmental performance between products are crucial and invokes much interest by various stakeholders in improving the situation towards achieving sustainability. Currently, life cycle assessment (LCA) is among the popular methods applied in analyzing and quantifying the effect of not only products but also services and materials to the surrounding environment during their total life time. LCA is also gaining recognition as among the key factors in environmental management most notably involving corporate and public decision making (Song et al. 2009). The methodology is considered to be young and evolving application, with its roots in research related to energy requirements in the 1960s and pollution prevention, which was formally initiated in the 1970s. Since its establishment, apart from end product assessment objective, the LCA method has expanded into wide range of applications both at the downstream and upstream activities such as eco-labeling, energy systems, product designs, transportations and food productions, which further highlights its functionality and effectiveness (Goedkoop et al. 2013).

In general, LCA is the method available to study the environmental aspects and potential environmental impacts) (e.g. use of resources and the environmental consequences of releases) throughout a product's life cycle from raw material acquisition through production, use, end-of-life treatment, recycling and final disposal, termed as cradle-to-grave approach. The distinguish advantage of LCA lies 42 on its ability to consider the product entire life cycle stages which includes raw material extraction and acquisition, material production and manufacturing, product use, packaging and transportation, end of life treatment and final disposal. The overall overviews of the products help especially to identify the potential environmental burden shifting between individual life cycle stages and minimized its possible occurrence, thus making the whole analysis more comprehensive and consequently enable holistic view of the results to be obtained (Finnveden et al. 2009).

For implementations with regards to the NFC, among the advantages of LCA is the possibility for comparison purpose, such as to determine if from an ecological point of view, the use of natural fibers is more advantageous compared to synthetic fibers as reinforcement in composites. In addition, LCA also enable the identification of key environmental parameters and phases in the whole life cycle of products as well as permitting study on disposal scenarios of the NFC in order to improve the environmental performance for the specific life cycle phase. Furthermore, through the implementation of LCA, the investigation on the effect of different factors to the sensitivity of the LCA results such as resin fiber content, product lifetime and total transport distance can also be performed (Corbière-Nicollier et al. 2001; Luz et al. 2010). Apart from that, LCA also enables specific view to focused stage in the whole product life cycle and subsequently their relation in term of environmental performance to the whole product life cycle such as the analyzing the significance of the disposal phase relative to other life cycle phases and identifying various disposal technology impacts to the overall environmental profile (Schmidt et al. 2004). Business related to NFC applications also may benefit from LCA implementation in 43 reducing the product cost in several ways such as reducing operating costs via supply chain coordination of transports to reduce the fraction of vehicles travelling with light or empty loads, new product introduction by considering unused raw materials as a marketable asset rather than a cost-centered waste stream, reducing disposal cost and improved relations with authorities, linked with the installation of near-zero discharge facilities, which are much easier to implement for small scales if planned from the outset, reducing cost to certify to ISO 9001 and ISO 14001, which also brings indirect benefits via stakeholder coordination (requirements from industrial customers) and reducing overhead by having in place an environmental management system, which permits the SME in question to correspond to clients and suppliers programs. Besides that, LCA can also act as to support NFC related businesses by creating favorable image to local and regional politicians which can further provide loan guarantees for promising firms without any significant operational or environmental risks and improved credit terms with major financial institutions (Rebitzer et al. 2004). Table 3 shows examples of LCA application involving natural fiber composites.

5 Case Study on Materials Selection of Bio-Resin for Natural Fiber Composites Using Modified Digital Logic and Weighted Property Method

Natural fibre composites (NFC) which is made from the combination of natural based reinforcement material and polymer matrix has been extensively explored in recent years as the potential replacement of conventional engineering materials especially synthetic polymer composites for various applications (Faruk et al. 2014). Among the notable advantages of NFC over synthetic composites are improved sustainability performance in term of renewability and biodegradability of the natural based fibres compared to petroleum based synthetic fibres such as glass, aramid and carbon fibres (Mansor et al. 2015; Razali et al. 2015). The renewability advantage also provide the opportunity to gain lower raw material cost and consequently lowers the overall product cost as compared to synthetic fibres (Dungani et al. 2014). The cost saving advantage by using NFC is also made

Table 3 Examples of LCA applications involving natural fiber composites

Natural fiber composites	Application	Life cycle approach	Impact assessment method use	References
Hemp/epoxy versus ABS	Side panel component for passenger car (Audi A3)	Cradle-to-grave	Eco-indicator 95	Wötzel et al. (1999)
Coconut, wood, flax and cotton fiber	Interior components	Cradle-to-grave	Not specified	Finkbeiner and Hoffmann (2006)
PTP vegetable resin versus polyester resin, hemp as the reinforcement material	Bus body component	Cradle-to-grave	Not specified	Müssig et al. (2006)
Hemp/PTP versus glass fiber/polyester	Bus body component	Cradle-to-grave	Eco indicator 99 and cumulative energy demand	Schmehl et al. (2008)
Curaua/PP versus glass fiber/PP	Automotive interior component	Cradle-to-grave	CML	Zah et al. (2007)
Jute fibers (untreated, dried and bleached/dried) versus glass fiber reinforced plastics	Buggy vehicle enclosure component	Cradle-to-grave	Eco-indicator 99	Alves et al. (2010)
Sugarcane bagasse/PP versus talc/PP	Vehicle interior aesthetic coverings component	Cradle-to-grave	Not specified	Luz et al. (2010)
Flax mat/PLLA versus glass fiber/polyester and .flax mat/balsa/PLLA versus glass fiber/balsa/polyester	Packaging for transportation	Cradle-to-gate	Eco-indicator 99 and cumulative energy demand	(Duigou et al. 2011)
Hemp fiber versus flax fiber	Paper pulp product	Cradle-to-gate	CML baseline 2000	González-García et al. (2010)
Kenaf/PP versus polyurethane. glass wool, flax rolls, stone wool, mineral wool and paper wool	Building thermal insulation board material	Cradle-tn-grave	Not specified	Ardente et al. (2008)

applicable due to the lower abrasion property of the fibres compared to synthetic fibres which helps to reduce mould wear during manufacturing hence reducing the manufacturing cost of the product (Yahaya et al. 2015). Apart from that, natural fibres also inherent lower density compared to synthetic fibres which enables higher specific strength and stiffness to be achieve especially for lightweight product design requirements (Mansor et al. 2013). The lightweight performance is currently one of the major focus especially in automotive product development in order to reduce the kerb weight of vehicles hence reducing the overall vehicle fuel consumption (Holbery and Houston 2006).

Another recent trend in the application of NFC is the development of fully biodegradable NFC which comprised of natural fibres as the composite reinforcement material and bio-based resin as the composite matrix. This new class of composites offers improved sustainable advantage in term of sustainability such as fully renewable, recyclable and biodegradable at the end of its life cycle phase compared to NFC made from synthetic matrix. However, natural fibre reinforced bio-resin composites also suffer several disadvantages such as low mechanical properties and higher raw material cost (due to less availability of the bio-resin in the market) compared to natural fibre reinforced synthetic composites.

Koronis et al. (2013) listed several most popular bio-resin for NFC formulation which includes thermoplastic starch, polylactic acid (PLA), poly-L-lactide (PLLA), polyhydroxybutyrate (PHB) and poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) as shown in Table 4. They also compared the bio-resin material properties with polypropylene thermoplastic resin, which is one of the most applied commodity type of matrix for natural fibre composite application. In general, starch is among the most widely used bio-resin due to their main advantages in term of high availability, fully renewable and biodegradable as well as low raw material cost. Thermoplastic starch is categorized as polysaccharides (Gurunathan et al. 2015) and is composed of a mixture of two polymers of α-glucose i.e. linear amylose and a

Table 4 Summary of mechanical properties for bio-resins (Koronis et al. 2013)

Bio-resin	Density (g/cm^3)	Melting point (Tm °C)	Tensile strength (MPa)	Young modulus (GPa)	Elongation at break (%)	Price (USD/kg)
Thermoplastic starch	1–1.39	110–115	5–6	0.125–0.85	31–44	5.5
PLA	1.21–1.25	150–162	21–60	0.35–3.5	2.5–6	2.42
PLLA	1.25–1.29	170–190	15.5–65.5	0.83–2.7	3–4	4.5
PHB	1.18–1.26	168–182	24–40	3.5–4	5–8	4
PHBV	1.23–1.25	144–172	20–25	0.5–1.5	17.5–25	3.5
PP	**0.9–1.16**	**161–170**	**30–40**	**1.1–1.6**	**20–400**	**1.65**

highly branched amylopectin. It is developed using stored carbohydrate from plants such as corn, wheat, rice, and potatoes. In the other hand, polylactide is a thermoplastic biopolymer derived from renewable resources such as corn starch, tapioca and sugarcane. Its basic monomer is lactic acid, which is derived from starch by fermentation and it is a sustainable alternative to petrochemical-derived products, since the lactides produced from agricultural by-products mainly the carbohydrate rich substances (Sahari and Salit 2012). Polylactide is categorized as thermoplastic aliphatic polyester, which can be further divided into several major types which are polylactic acid (PLA) and poly-L-lactide (PLLA), polyhydroxybutyrate(PHB) and copolymer poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Koronis et al. 2013).

There are many reported studies on the development of the aforementioned bio-resins for NFC application. Surin et al. (2015) reported the development of coconut coir reinforced composites using the combination of thermoplastic starch and PLA bio-resins, with and without chemical modifications. In their study, the highest mechanical strength and modulus of the coconut coir reinforced thermoplastic starch/PLA composites were found at the use of between 20 and 30wt% fibre loadings, and higher mechanical properties were also found for coconut coir reinforced thermoplastic starch/PLA composites prepared with chemical modifications (addition of maleic anhydride with thermoplastic starch) compared to similar composites without chemical modification. Apart from that, Espinach et al. (2015) also reported on the application of thermoplastic starch for the development of alpha-grass reinforced starch biocomposites. In their study, alpha-grass was reinforced with thermoplastic starch at fibre loading between 5 and 35wt% and subjected to flexural tests. Results from their test revealed that the alpha-grass reinforced thermoplastic starch composites showed comparable flexural strength and modulus properties with glass fire reinforced polypropylene composites at similar fibre loading conditions.

Furthermore, development of fully biodegradable composites was also reported by Duiguo et al. (2011) using hybrid flax mat and balsa as the reinforcement materials and PLLA bio-resin as the matrix. In their study, the hybrid flax mat/balsa reinforced PLLA composites showed lower environmental impact performance compared to glass fibre mat reinforced polyester composites and hybrid glass fibre mat/balsa wood reinforced polyester composites. Elsewhere, Berthet et al. (2015) reported the development of wheat straw reinforced PHBV composites and studied the effect of moisture of the final composites mechanical properties. Findings from their study have indicated that the presence of moisture at the initial stage of sample preparation (using dried fibres and moisture affected fibres) did little effect on the final composites tensile properties. However, thy also found that the molecular weight of the PHBV bio-resin decreases as the moisture content with the presence of higher moisture content due to the effect of hydrolysis reactions. Finally, Ren et al. (2015) reported on the use of PHB bio-resin for the development of pulp fibre composites. In their study, the effect of higher fibre loading contents (up to 45 wt%) was shown able to improve the tensile and impact properties of pulp fiber reinforced

PHB composites compared to virgin PHB bio-resin due to the increase of reinforcement agents within the material's structure.

Despite the positive contributions of the bio-resin towards the development of green NFC, there are still challenges that needs to be addressed especially by product designers in fully utilising the materials for practical use such as selecting the most appropriate type of bio-resin for specific application. In this chapter, the materials selection issue faced by product designers are solved using the application of multi criteria decision making (MCDM) method, namely modified Digital Logic Method (DLM) and Weighted Property Method (WPM). The aim of this case study is to select the most appropriate bio-resin for producing a new NFC based automotive interior spare tyre cover which able to grant better sustainability performance compared to current component produced using synthetic plastic. In the materials substitution process, the current structural performance importance is preserved to ensure that the new product able to function effectively and safely as per design requirements. The overall flow of the decision making method for the bio-resin materials selection is shown in Fig. 3.

As shown in Fig. 3, the materials selection process for the NFC is developing the selection criteria for the intended materials application (automotive spare tyre cover). For interior automotive application, Koronis et al. (2013) have several main selection criteria for bio-resin related to NFC composites construction which are lightweight, good mechanical strength and thermal resistance as well as low product cost. Based on the application requirements, the individual criteria was then translated into relevant materials properties such as density (corresponding to lightweight), raw material price (corresponding to low product cost) and Young modulus (corresponding to the component structural stiffness). Figure 4 shows the overall bio-resin selection criteria based on the materials properties while Table 5 explained the relationship between the material properties with the practical design requirements.

Fig. 3 Overall bio-resin materials selection flowchart

Fig. 4 Bio-resin selection criteria for automotive spare tyre cover

5.1 *Weighting of Selection Criteria Using Modified Digital Logic Method*

The next step in bio-resin materials selection is to determine the relative importance of each selection criteria with respect to the overall selection goal. This is important especially in MCDM problems as the designers have to comply with all the selection criteria associated with the design requirements, and in practical most of the selection criteria have varying importance between them. To solve the problem, a criteria weighting method called modified DLM is applied in this case study. The modified DLM was a revised version of the initial DLM whereby a modified rating method was used using one (1) to three (3) importance scale (Dehghan-Manshadi et al. 2007). During comparison between the criteria, the value of three (3) is assigned for the most important criteria, value of two (2) is assigned for the equal important criteria and value of one (1) is assigned for the less important criteria. The final weighting factor for each selection criteria is calculated based on Eq. (1).

Table 5 Descriptions of the selection criteria applied in the case study

Selection criteria	Descriptions
Density	This material property corresponds to the weight of the bio-resin. For selection purpose, lowest density is preferred to achieve low resin weight and subsequently final composites with lightweight performance
Young modulus	This material property indicates the capability of the bio-resin to maintain its shape under given force. Young modulus is also referred to the materials stiffness performance. Higher Young modulus value for bio-resin is preferred for structural application which able to provide stiff component performance
Tensile strength	This material property reflects the capability of the bio-resin to absorb the force subjected without failure. Higher tensile strength is preferred for the bio-resin to attain higher load bearing capability for the final composites especially for structural application
Elongation at break	This material property corresponds to the measure of ductility of the bio-resin. For structural application whereby impact loading is present, higher elongation at break value is preferred for bio-resin to achieve final composites impact energy capability, thus enabling component that can withstand higher impact loading
Melting point	This material property reflects the melting temperature of the bio-resin. Higher melting temperature is preferred for producing composites for structural application whereby it enable the material to withstand high operating temperature
Price	Lower bio-resin price is preferred to enable lower final composites raw material cost and subsequently lower product cost which is crucial for successful product

$$\text{Weighting factor, } w = (\text{total positive decisions}/N') \tag{1}$$

where $N' = [2n(n-1)]$ and n = number of selection criteria

In addition, other notable improvement of the modified DLM compared to the conventional DLM is the introduction of equal important rating (value of 2) for rating the compared criteria. The conventional DLM only permitted two rating value during judgment between the criteria, which is one (1) for greater important and zero (0) for less important. Often, in practical, decision makers also give equal rating between the compared criteria as in their judgment, as both criteria are equally important with respect to each other. Nevertheless, similar to the conventional DLM, the modified DLM will also yield total weighting factor value of one (1). Moreover, the application of the three score rating system was also reported to provide higher final decision accuracy compared to the conventional DLM (Dehghan-Manshadi et al. 2007). The overall results of the weighting analysis performed for the selection criteria in this case study is shown in Table 6 while Fig. 5 summarized the weighting analysis results. From Fig. 5, it can be observed that density, Young modulus, tensile strength and price selection criteria shared similar normalized weighting importance value of 0.2 while elongation at break and melting point both score lower normalized weighting importance value of 0.1. The

Table 6 Weighting results bio-resin for criteria materials selection using modified DLM

No	Material properties	Number of possible decisions [W = n(n−l)/2]															Total positive decisions	Weighting factor, w
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		
		1–2	1–3	1–4	1–5	1–6	2–3	2–4	2–5	2–6	3–4	3–5	3–6	4–5	4–6	5–6		
1	Density (g/cm^3)	2	2	3	3	2											12	0.200
2	Yourig modulus (GPa)	2					2	3	3	2							12	0.200
3	Tensile strength (MPa)		2				2				3	3	2				12	0.200
4	Elongation at break (%)			1				1			1			2	1		6	0.100
5	Melting point (Tm_°C)				1				1			1		2		1	6	0.100
6	Price (USD/kg)					2				2			2		3	3	12	0.200

Note Decision ratings: 1 = less important; 2 = equal important; 3 = more important

Weighting factor, a = (total positive decisions/N′) where $N' = [2n(n-1)]$ and n = number of property = 6 Sample calculation: $\sum$w_density = (2 + 2 + 3 + 3 + 2)/[2 × 6×(6 − 1)] = 12/60 = 0.200

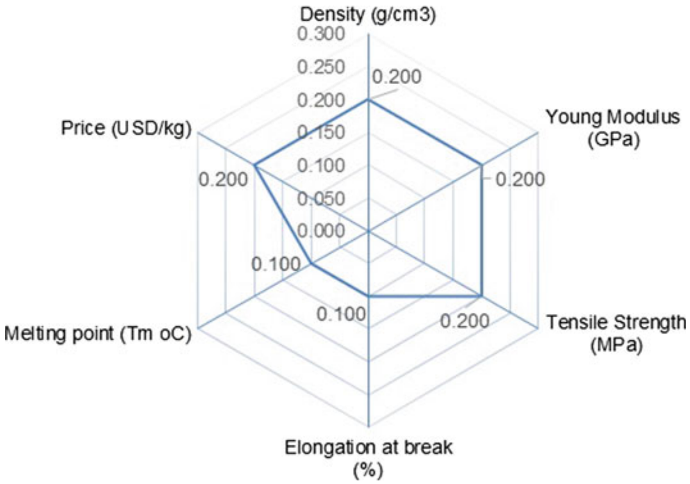


Fig. 5 Result of relative importance between bio-resin selection criteria using modified DLM

results revealed the preference of the product designer (decision maker) in placing the priority for the selection criteria towards achieving the overall project goal.

5.2 Determination of the Candidate Score and Ranking of Candidate Material Using Weighted Property Method

After the selection criteria weightage is obtained, the next stage is to determine the overall score for every bio-resin candidate using the WPM. There are two main steps in calculating the overall score, which are first calculating the scaled property value, β for each bio-resin, followed by determining the final weighted property index, γ also for each bio-resin listed as the selection candidate materials.

The scaled value method allowed the selection process involving selection property with varying attributes and units to be analyzed based on equivalent value simultaneously. For the condition where high value of solution attribute is desired such as material's tensile strength and tensile modulus, the scaled property value, β is calculated using Eq. (2) (Mansor and Sapuan 2014).

$$\begin{aligned}\beta &= \text{scaled property} \\ &= (\text{numerical value of property} \times 100)/\text{largest value}\end{aligned} \tag{2}$$

In contrast, for condition where low value is best such as material's price and density, the scaled property value, β is calculated using Eq. (3).

Table 7 Overall scores of bio-resins materials selection using WPM

Bio-resin	Weighting factors, w												Weighted Property Index, γ
	0.2		0.2		0.2		0.1		0.1		0.2		
	Material properties (average)												
	Density		Young modulus		Tensile strength		Elongation at break		Melting point		Price		
	β	g/cm^3	β	GPa	β	MPa	β	%	β	°C	β	£/kg	
T-starch	100.0	1.195	13.01	0.488	13.58	5.50	100.0	37.50	62.50	112.5	44.00	5.50	50.369
PLA	97.15	1.230	51.33	1.925	100.0	40.50	11.33	4.25	86.67	156.0	100.0	2.42	79.498
PLLA	94.09	1.270	47.07	1.765	100.0	40.50	9.33	3.50	100.0	180.0	53.78	4.50	69.921
PHB	97.95	1.220	100.0	3.750	79.01	32.00	17.33	6.50	97.22	175.0	60.50	4.00	78.948
PHBV	96.37	1.240	26.67	1.000	55.56	22.50	56.67	21.25	87.78	158.0	69.14	3.50	63.992

Sample calculation:

$\Sigma\gamma$_Thermoplastic Starch $= 0.2 \times 100 + 0.12 \times 13.01 + 0.2 \times 13.58 + 0.1 \times 100 + 0.1 \times 62.50 + 0.107 \times 67 + 0.2 \times 5.50 = 50.369$

$$\begin{aligned}\beta &= \text{scaled property} \\ &= (\text{lowest value} \times 100)/\text{numerical value of property}\end{aligned} \tag{3}$$

Determination of the final weighted property index, γ value for each bio-resin is performed using Eq. (4). The final weighted property index, γ is calculated by the addition of the scale property and the weighting factor, w for each of the bio-resin materials property

$$\begin{aligned}\gamma &= \text{weighted property index} \\ &= \sum_{i=1}^{n} \beta_i w_i (n = \text{number of selection criteria})\end{aligned} \tag{4}$$

Table 7 shows the overall scores of bio-resins materials selection calculated using WPM. A sample calculation to describe in detail the calculation process in determining the final weighted property index for thermoplastic starch bio-resin is also included in Table 7. Finally, based on the results, the bio-resins candidate is ranked by their respective weighted property index, γ scores, and the most suitable candidate bio-resin materials which comply to all the selection criteria is selected from the bio-resin with the highest scores and rank. Figure 6 summarized the overall WPM scores obtained at the end of the analysis for each of the bio-resins candidate material.

As indicated in Fig. 6, PLA bio-resin obtained the highest WPM score of 79.498 points, followed by PHB (78.948 points), PLLA (69.921 points), PHBV (63.992

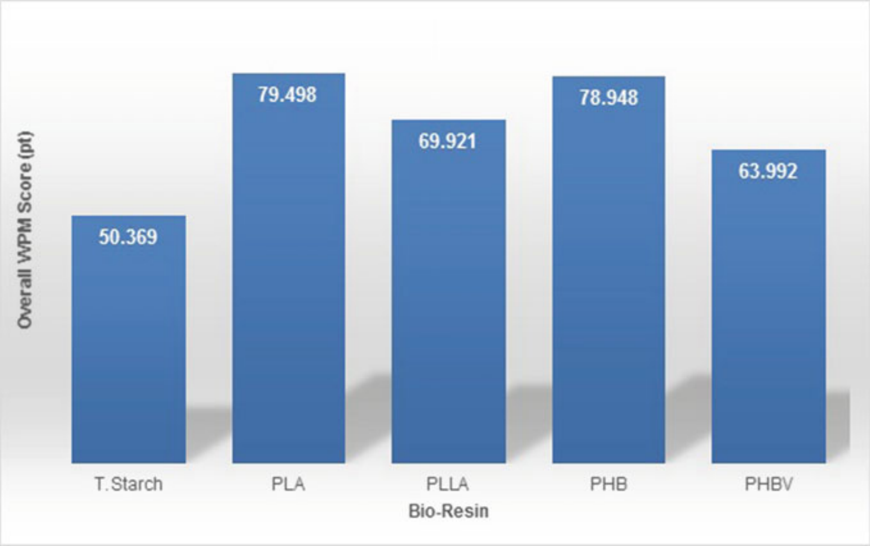


Fig. 6 Overall score of bio-resins for materials selection using WPM

points) and finally thermoplastic starch (50.369 points). The final results revealed that PLA bio-resin is the most suitable candidate materials to be selected as the matrix material for formulating the NFC towards the construction of the new automotive spare tyre cover which able to grant improved sustainable advantages compared to the current synthetic plastic spare tyre component.

6 Conclusion

In this chapter, the significance of material selection in product design are introduced. Material selection challenges faced by product designers are solved using the application of multi criteria decision making (MCDM) method, namely modified Digital Logic Method (DLM) and Weighted Property Method (WPM). The aim of the case study discussed in this chapter is to select the most appropriate bio-resin for producing a new NFC based automotive interior spare tyre cover which able to grant better sustainability performance compared to current component produced using synthetic plastic. The bio-resin candidates were ranked according to their score values using WPM. Hence, PLA bio-resin obtained the highest score and thus, was selected as the most appropriate material compared to the others.

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Design of Prosthetic Leg Socket from Kenaf Fibre Based Composites

M.H. Nurhanisah, N. Saba, Mohammad Jawaid and M.T. Paridah

Abstract Prosthetic socket is one of important part as it involved interface or connecting link between stump and prosthetic components. Besides the functionality of socket itself, it also involved satisfaction on patient due to the force distribution and pressure on stump. Selecting the right liner is essential in order to ensure the prosthesis fits well and is comfortable to wear. The quality and comfort of a prosthetic socket and its design can determine the daily extent of period, as the patients can use their artificial limbs and lead as normal life as possible. Technological advancement has led to wider range of modern orthopedic and prosthetic device. Fibre reinforced composites are most widely used for upper- and lower- limb prostheses due to their superior strength and excellent biocompatibility. In this review, the use of fibre reinforced composite materials for prostheses are viewed. This review article intended to present general information regarding the structure and function of type and application for current prosthetic socket design for the benefit of the reader. This paper also discussed the comfort measurement of residual limb on prosthetic socket.

Keywords Prosthetic socket · Lower limb · Fibre reinforced composites · Comfort measurement

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1 Introduction

In developing countries, amputations are increasing, particularly for the lower limb. The two major causes for amputations are traffic accident, particulary motocycle accident and diabetes. Others reason of amputation are congenital and disease. There are several causes of the amputation such as congenital defect, which related to person who born with missing or damaged limb. Besides that, the leading ailments such as cancer, circulatory disease and infection may lead to the amputation. Likewise in developing countries, the amputation may occur in industrial, vehicular and war related accident. Biomaterials are used in ancient long ago in Egyptian mummy's artificial eyes, ears, teeth, and noses. Today, the medical practice on medical device and medical implant has increase. The application of biomaterial in medical devices and implants has taken a place in largely used to replace and restore the function of traumatized or organ or degenerated tissues, to improve function, assist healing and correct abnormalities all thus improve the quality of life of the patients (Ramakrishna et al. 2001). Today's technological advancement has improved the application on prosthetic devices and modern orthopedic medicine. Prosthetic socket is the essential part that provides the connection between residual limb and the device. Many prosthetics has to face the critical challenge due to discomfort in prosthetic socket. The good quality and comfort of prosthetic socket could determine the daily duration for user and may prevent the soft tissues damage such as blisters and ulcers (Sengeh and Herr 2013). The demands on prosthetics devices are as comforts to the user, high performance, biocompatibility and versatility to enable user to have a quality of a normal life as possible. Current advances in socket technology which focusing on cushioning as contributors to comfort in prosthetic socket have reduced pain in user residual limb. Technologies from gel liner and vacuum-assisted sockets to modern interfaces have covered a large area of products, that rely on residual limb laser scanning and computer aided manufacturing (Martinez-Villalpando et al. 2008).

Presently, fibre reinforced polymer composites are widely used as multiphased materials in orthopaedics particularly for upper and lower-limb prostheses. In developing countries, these materials are difficult to source and it require costly fume extraction equipment due to toxic produced from acrylic resin work. Natural fibre based polymer composites have been reported to possess exceptional strength to weight ratio, high impact resistant and superior biocompatability. However, prosthetic satisfaction is a subjective notion as every person has different sense.

2 Lower Limb Prosthesis

Lower limb prosthetics is a device which designed to replace the appearance and function of the missing limb as the loss can affects an patient's quality of life. The devices are designed to support, supplement, or augment the function of an existing

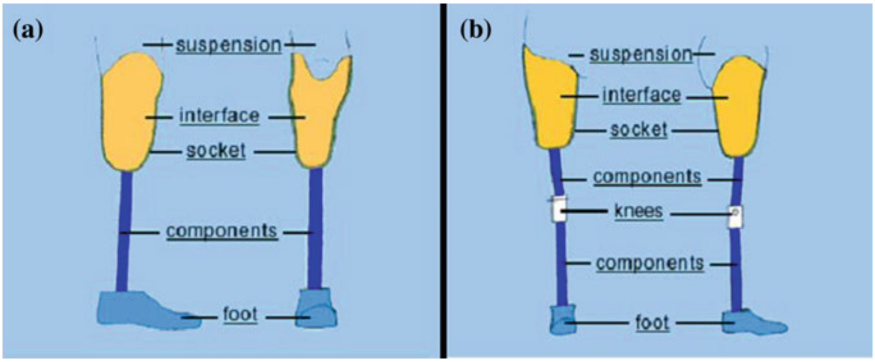

Fig. 1 **a** Trans-Tibial (*below* knee) prosthesis with components part, **b** Trans-femoral (*above* knee) prosthesis with components part. Retrieved from http://www.aalonline.com/about-prosthetics/about-prosthetics

lower limb (Kelly 2009). However, because of discomfort, many amputees use them less than needed or some cases they reject lower limb prostheses. According to (Berke et al. 2010), the poor circulation in the limb leads to arterial disease, with preponderance of the amputations afflict to diabetes mellitus. The types of prosthesis rely on missing limb. There are two types of lower limb prosthetic devices, describe by (Facoetti et al. 2010) and (Rajťúková et al. 2014), which are:

1. Trans-femoral—A trans-femoral prosthesis is an artificial limb that replaces a missing leg on above the knee.
2. Trans-tibial—A trans-tibial prosthesis is an artificial limb that replaces a missing leg on below the knee.

Trans-femoral and Trans tibial and its components are illustrated in Fig. 1. A typical prosthetic lower limb consists of three basic components which are an artificial foot, tube adaptor and socket. For above knee, it also incorporates a knee joint (Strait et al. 2006) and (Rajťúková et al. 2014). Other less prevalent cases for lower extremity beside transtibial and transfemoral which are included (Kapp and Miller 2002):

1. Hip disarticulations—This is refers to the removal of the entire lower extremity through the hip joint.
2. Knee disarticulations—This is refers to knee disarticulating the femur from the tibia bone.
3. Symes—Partial foot and foot amputations.

Researcher in other study reported that the part such as foot, pylon and others components are basically purchased through the catalogues (Colombo et al. 2010). Those components will be delivering and assembled at prosthetic manufacturer following the patient's specific need. However, the socket must be a custom made fabrication based on patient's residual limb and it impossible to manufacture as mass productions. Researchers claimed that, the whole fabrications of the prosthetic limbs are custom made in few facilities (Nair et al. 2008). The prosthetic leg socket is the most individual and custom-made part (Andrysek 2010), and its significance is based on the manufacturing and the functionality. Accordingly, its quality has a major influence on the ability to control the artificial limb and on comfort for prosthetic user. Thus, the socket acts as a joint between prosthesis and stump and determines the comfort of prosthetic leg wearer. Therefore, the design, mechanics and materials aspect must be given consideration to reassurance to the future prosthetic leg devices.

3 Prosthesis Socket Design for Transtibial Prostheses

Sockets are the important part which has a direct interfacing with the stump, which also determines the amputee's comfort and ability to control the artificial limb. Prosthetic design involves making a replacement of a missing body part of the appropriate shape and size (Silver-Thorn 2004). Trans-tibial (BW) prosthesis with liner and components part are displayed in Fig. 2.

In the past decade, the transtibial amputations are among of most regularly major in lower limb amputation with half of it. For every amputee, their challenges are different at different stages of lives. In general, the prosthesis for transtibial amputee consists of socket, adapter to attach the socket to the shank and artificial foot, besides this also includes auxiliary suspension (Silver-Thorn 2004), to attach the residual limb to the socket. In transtibial prostheses, there are varieties of socket

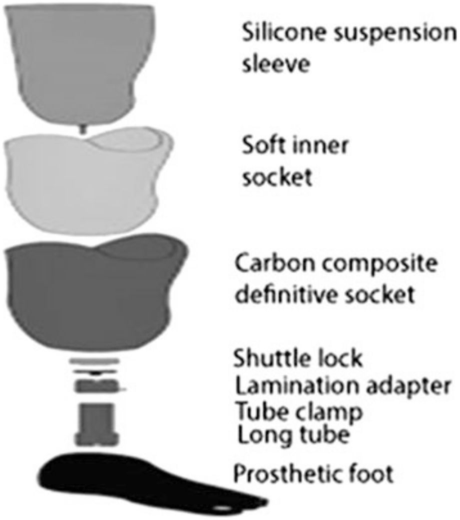

Fig. 2 Trans-Tibial (*below* knee) prosthesis with liner and components part. Retrieved from http://www.propaedics.co.za/Prosthetics

designs available. However, even the mould follow the exact shape of residual limb while fabricating the socket, still does not produce a proper socket and needs to be adjusted. Moreover, the adjustments were made at the region around patellar tendon and at the tibia part to push the bone up in back as a shield in distal tip. There are two areas of sensitive areas where relief regions are added which are at the top end of the fibula and the very distal (lower) tip. Thus, the real art of prosthetics based on discovering in sculpting and fine-tuning on the socket shape (Smith 2003). In providing the comfortable and minor changes in size of the stump, sockets need to incorporate with foam or silicone gel liners. Cotton or wool socks, which are easier to clean than the liner and more durable, need to wear with hard socket. Others type of socket which rigid outside frame was made from soft material inside. This type of socket is flexible and the shape can change to provide contractions of the intrinsic muscles. It is also able to be used for residual limb which are scarred and hard to fit. The historic design (dating back to 1696), which incorporates a thigh corset, side joints, and an open-ended wood socket are not been used in present, unless for those succeed worn it from the past and those who seldom do the maintenance in prosthetic care, reviewed by the researchers (Silver-Thorn 2004) and (Smith 2003).

Many prosthetist clinicians and researcher around the world have discovered the design and materials since 1980s. The improvement of the design for socket can give good connection between the sockets and stump (Marks and Michael 2001). The basic components of prosthetic device remain the same even new materials and technologies have developed since the past century. The presence of the new materials, such as advanced plastic and carbon fibre composites have made the prosthetic more lightly, stronger and more realistic. Despite the development in prosthetics and surgical techniques, many work still needs to be improve to enhance the quality of prosthetic wearer's life.

4 Thermal Comfort on Prosthesis Socket

The thermal stresses has affects many amputee in their daily life, as thermal discomfort in socket could give an adverse effect on prosthetic use, comfort and satisfaction. The prosthetic socket barrier leads many problem including radiation, evaporation convection, and conduction. In some cases skin irritations usually appear on people with amputation due to thermal environment inside prosthetic socket. These also cause skin irritation, unpleasant odor, friction blisters, infection and bacterial invasion to residual limb and lead to discomfort. (Hagberg and Brånemark 2001) reveal that thermal discomfort would give bad influent to prosthetic user. In another study by (Lake and Supan 1997), 60 to 70% of the amputees claimed that high perspiration as major problem within their prosthetic socket.

Interestingly, in hot and humid environment can lead to elevated skin temperature and thermal discomfort on residual limb and both of these symptoms of prosthesis uses are most common reason to reduce the amputee quality life

(Han et al. 2015). The effective heat transfer may reduce the skin temperature involving the process controlled by the thermal conductivity such as liner, socks and socket layers (Klute et al. 2007). Most typically, the amputee will wear 1 to 15 ply of cotton, wool or synthetic socks throughout the day, to absorb perspiration and accommodate residual limb volume fluctuations (Silver-Thorn 2004). However, in hot and humid weather, the perspiration will increase and create less comfortable and unclean environment (Smith 2003) inside the socket. Thus, it is reasonable to assume that decreasing skin temperatures and moisture at the residual limb skin interface can reduce discomfort and incidence of injury (Peery et al. 2006).

In Malaysia, the analysis of temperature records shows a warming trend and the temperature changes from 0.7 to 2.6 °C while precipitation changes ranging from −30 to 30%, reported by Ministry of Science, Technology and the Environment 2000 (Rahman 2009). Since most of the people in this country experience hot-humid weather all the year round, it is particularly important to develop a design for prosthetic leg socket in order to reduce the heat and allowed the air ventilation inside the prosthetic leg socket. The fundamental designs for prosthesis cooling system in prosthesis device are necessary to maintain the standard temperature on skin surface.

To resolve the problem, the current development in prosthetic technologies introduces the advance prosthesis and residual limb interface material. The elastomeric liner material could improve weight bearing and suspension to provide a snug fit by adapting the shape of stump owing to specific viscoelastic properties. However, these liners prevent air circulation and ventilation between prosthetic and stump surface. The heat transfer from residual stump to environment affected by the poor thermal between liner and socket. The closed environment between a residual limb and prosthesis system also caused evaporation or sweating through heat transfer. In fact, the heat generation of the limb, temperature surroundings and thermal resistance of the prosthesis were effected the thermal environment inside the prosthesis (Han et al. 2015). Furthermore, air moisture that gets trapped between residual limb and liner, consisting of silicone, plastic and other inorganic materials and avoids sweat evaporation thus consequently leads to skin irritations. The thermal conductivity also gets influence from the thickness of the material applicable in fabrication and liners. Although it difficult to maintain a comfortable temperature in the socket when the amputees perform different activities and in various environment. However, use of sock ply also could be subject to increased incidence of problems, secondary to a prosthesis that is quite large (Baars and Geertzen 2005).

Researchers reported that the largest areas of elevated temperature were located at the lateral and posterior sides (Peery et al. 2006). Figure 3 show contours of skin temperature generated for prosthetic socket system. In this Figure, although individual muscles were not modeled, but elevated skin temperature were located near muscle tissues as a representative of actual muscles, including tibialis anterior Fig. 3a, peroneus brevis and longus Fig. 3b and the medial and lateral heads of the gastrocnemius Fig. 3c and d. From the Figure below, decreased temperature were located

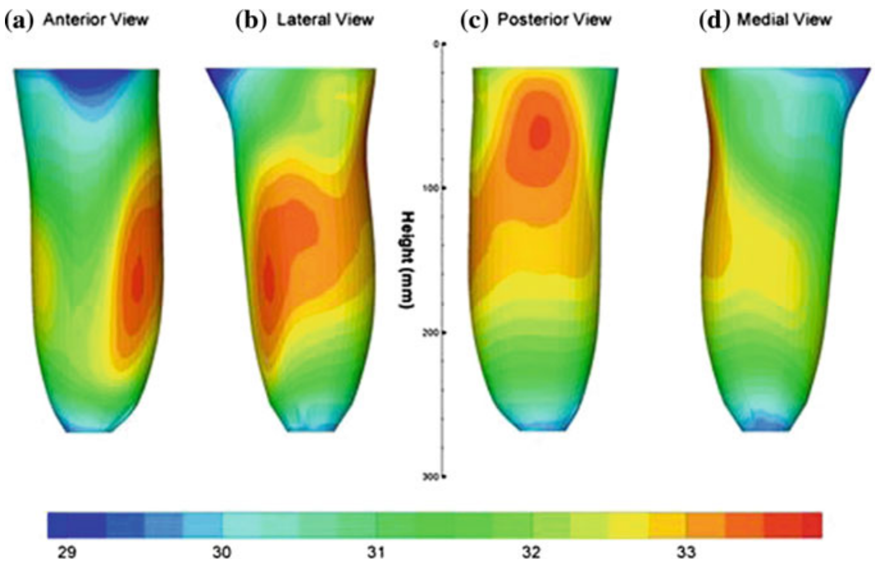

Fig. 3 Skin temperature contours from the numerical model of the left residual limb and prosthetic socket (Peery et al. 2006)

over tibia Fig. 3a and at the distal end of the stump Fig. 3a–d (Peery et al. 2006). Figure clearly showed that, the near muscle tissue were predicted as high skin temperature while in the external to the tibia and at the distal end were predicted as low temperature (Peery et al. 2006). This finding can contribute in order to better understand the area of residual limb skin interface and to develop the new design of prosthetic leg socket that may be used in the future with attention to the thermal properties inside the prosthetic leg socket.

5 Prosthesis Socket Material

The material on prosthetic socket is very important as to meet the requirements in order to make them effectively functional. Prosthetic sockets were fabricated from materials such as leather, wood, latex and metal before the introduction of nowadays advanced resins such as composites and thermoplastics (Me et al. 2012). In the past, certain types of leather or wood were stretched, soaked, carved and stitched into the form of prosthetics. After dried, lacquered or sealed, it found to be more durable. The flowcharts of material for conventional socket fabrication are shown in Fig. 4. Initially leather sockets basically were suspended with the wood frame or structural metal. Certain part such as the foot especially had traditionally been made of rubber and wood. Even at present, the foot now made from urethane foam with a wooden inner keel construction and the polypropylene-based materials such as

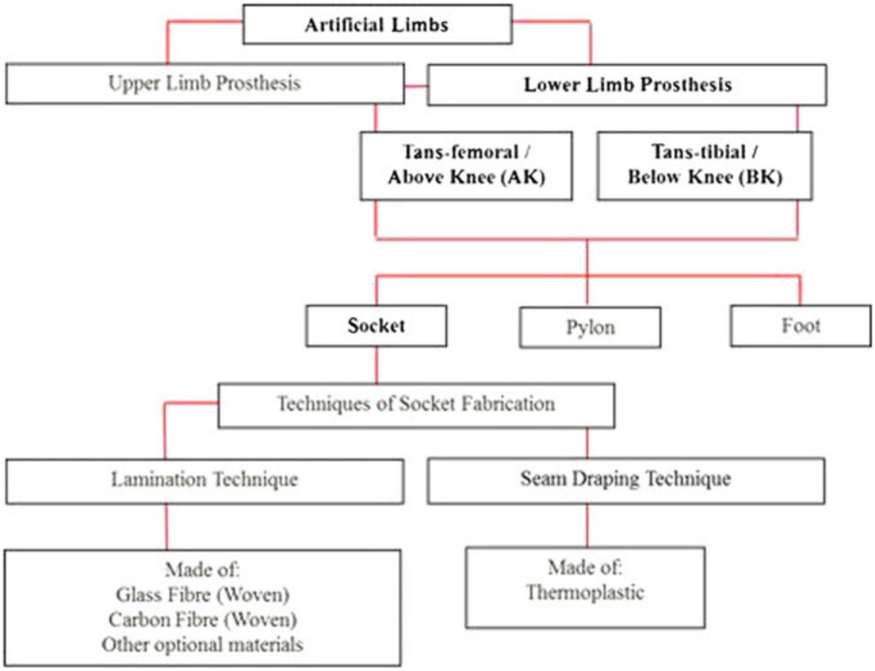

Fig. 4 Flowchart of material for conventional socket fabrication

polyethylene, polypropylene, acrylics, and polyurethane has replaced the previous leather or wood due to uneconomical and hazardous effects on the environment (Me et al. 2012).

Marks and Michael reported that the lightweight pylon which made from carbon fibre was the newest development in prosthesis manufacturing (Marks and Michael 2001). The revolution of carbon fibre reinforced polymer composites (CFRP) in structural design of artificial limb was enabled the amputee to participate in professional sport. (Scholz et al. 2011) claimed that it is able to attach an energy return system within lower limb prostheses by using extremely lightweight and high strength CFRP. However, in developing countries, where the disproportionate number of amputee live with the causes by war and landmines, CFRP prosthetic found to be highly expensive and are not always reliable. Generally, polymers such as polyethylene, high-density polyethylene (HDPE), acrylics, polypropylene, and polyurethane are used for fabrication. Carbon and glass fiber composites, with application of acrylic resins, are largely used due to their superior properties. However, these are expensive and will create harmful gasses in manufacturing (Manohar 2016). Although as glass fibre/high density polyethylene (GF/HDPE) and polypropylene plastic composites offer the less expensive prosthesis for commercial purposes. Currently they are receiving great attention at manufacturing reliability, mechanical performance, and expense of comfort.

5.1 Prosthesis Socket Manufacturing

Prosthetic leg socket is upper most part of a prosthesis that makes contact with the residual limb and transfers the forces of walking to the ground. In socket fabrication, the three dimension (3D) shape of the stump will capture by the prosthetics and wrap a cast around it whether loaded or unloaded, according to prosthetist preference. The negative mold will be acquired from a positive mold of the residual limb. On the positive mould, the anatomical points of interest will be identified. Therefore the material will be added to relieve pressure at sensitive regions or removed to increase pressure at specify loading bearing locations (Muller et al. 2007). The type of material used for construction is main important part to consider in the designing and fabrication of limb prosthetic. The comfort of the socket will be influenced by interface materials. The strength and weight will be affect structural materials of the overall prosthesis (Uellendahl 1998).

In general, the process in fabricate the prosthetic legs socket is begin with constructing the positive cast of patient's stump. Basically, this can be made by manually which is filling the negative impression of patient's stump with a plaster of paris (POP). However, with the advancement technology, it also can create by software such as computer aided design and manufacturing (CAD/CAM) (Faustini et al. 2006). The lamination process basically initiated by sandwiching the selected materials over a cast then the selected resin will injected through the polyvinyl alcohol (PVA), polyvinyl chloride (PVC) or optional advanced materials. The injected process need to be conjunction with the vacuum assistance to avoid trapped moisture. However, the improvement of fabrication process will be readily available when the industry standard resins are using (Me et al. 2012). Due to mechanical strength, commonly the epoxy resins will use together with advanced laminating materials such as carbon fibre, stockinette, hybrid matt and so on (Rogers et al. 2008). In composite material, the fibre orientation and resin as matrix are the most important thing need to be considered to ensure the optimum strength of resin capability. Lamination method of socket fabrication is suitable for natural-based biocomposites, since the proposed materials can be woven into a layer form (Me et al. 2012). In lamination socket, the used of glass fiber in woven or in layer form refereed as glass fibre stockinette (tubular glass cloth), gives the premium strength. Thus, the use of natural fibre materials as particular layer actually have potential to be replaced the common synthetic fibres in the existing laminated socket structure. Indirectly, the use of natural fibre can be as alternative materials in laminating prosthetic socket fabrication, thus it will lessen the cost while improving the socket's strength.

Seam drapping is the other promising fabrication process for sockets fabrication which involves the vacuum casting (Me et al. 2012). This type fabrication process engages several steps, including, (i) making a positive cast of patient's stump; (ii) locating mechanical press on distal end of positive cast; (iii) moulding a component of prosthetic socket over a positive cast and mechanical press; (iv) the prosthetic socket is pushed apart by activating the mechanical press from the distal end of the positive cast (Faustini et al. 2006). Accordingly, a sheet of thermoplastic will heated in the oven and later will be form around the mould by using a vacuum. Within this process, the sheet will lie over the top of the mould in a vacuum chamber, however, to ensure zero air tolerance space the sheet need to reheated, if necessary. This step requires air in between the mould and the sheet which it sucked out of the chamber as well as collapsing the sheet on the mould then forcing it to follow the exact shape of the mould (Faustini et al. 2006). For this technique, the other material available includes a polypropylene polymer material, flexible thermoplastic material and clear thermoplastic material (Zheng et al. 2001). This second technique involves higher technology as using the equipment such as oven to soften the very high melting of materials.

6 Natural Based Materials for Manufacturing of Prosthesis Leg Socket

Natural fibers are the material that is environmentally friendly, recyclable, potentially abundant and cost effective as compared with synthetic fibers. These can be support concept back to nature and go green (Irawan et al. 2011). The use of natural fiber reinforced composites (NFRCs) in orthopedic and prosthetic would result in lighter weight, cost effective, sustainable, and widely available materials for use in these critical biomedical devices (Kramer et al. 2015).

The low cost of prosthetic devices manufacturing may allow the less financially of disabled wearers to have a chance to get affordable prosthetic legs particularly in third world countries and most developing (Jensen and Raab 2007). There are many studies carried out throughout the world to develop the cheap yet eco-friendly prosthesis product. For example, based on previous studies shown that kenaf can be processed into yarn and converted into composites of high impact strength to replace the fibre-glass as one of the layer in prosthetic socket fabrication (Me et al. 2012). Similar results studies indicate that the ramie composite material substitute with fiberglass polyester composite (FGP) have a potential to be an alternative material to replace a current prosthetic socket material and its lightweight, locally available, comfort, good strength, and appearance acceptable (Irawan et al. 2011). Bamboo fibre reinforced composite can be replace the cotton and nylon composite that are currently used in orthopedic and prosthetic due to their superior strength and ductility (Kramer et al. 2015). The previous findings of natural based materials on prosthetic field could have potential to serve as a cost effective, practical, and environmentally sustainable material choice in both orthopedic and prosthetic fields. All the positive findings could lead the present study to produce and fabricate eco-friendly and low cost manufacturing of prostheses made from the proposed natural fibres based composites.

7 Kenaf Fibres Polymer Composites as Potential for Manufacturing of Prosthesis Leg Socket

Composites are hybrid materials made of a polymer resin reinforced by fibers, combining the high mechanical and physical characters of the fibers (Abilash and Sivapragash 2013). Mechanical and physical properties of natural fibers are highly variable and are solely depend on environmental conditions of growth (Wambua et al. 2003). The use of natural fibre as a reinforcement agent offers many benefits for environment. These can reduce the reliance on non-renewable sources of energy and material, allowing lower greenhouse gas emission, pollutant emissions, thus its enhance energy recovery and end life of biodegradability of components as well (Joshi et al. 2004). The advantages of natural fibre reinforced thermoplastic as recyclability have attracted greater attention compared to thermoset reinforced polymer composites (Ku et al. 2011) Furthermore, these significant qualities of natural fibre in environment and cost effectiveness aspects led to alternative material for glass fibre.

Kenaf fiber (Hibiscus Cannabinus) is produced from the bast. It contents of lignin (8–14 wt%), hemicellulose (21–35 wt%), cellulose (56–64 wt%), and small amounts of extractives and ash (Mahjoub et al. 2014). Dense cultivation of kenaf and fibers of kenaf are illustrated in Fig. 5 (Saba et al. 2016) and Fig. 6 (Hasan et al. 2015). Density and mechanical properties of kenaf fibre are tabulated in Table 1 (Saba et al. 2015). This plant can grow higher than 3 m within three months and the stem diameter of 25–51 mm. The long stem provides long fiber which is a particular and fascinating character of kenaf plant. Kenaf possess remarkable physical and mechanical properties like other natural fibres, and are still

Fig. 5 The dense kenaf plantation in Malaysia (Saba et al. 2016)

Fig. 6 Fibers of kenaf (*Sources* from Hasan et al. 2015)

Table 1 Density and mechanical properties of kenaf fibre adopted from (Saba et al. 2015)

Density (g/cm^3)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
–	692	10.94	4.3
–	930	53	1.6
1.45	930	53	1.6
1.4	284–800	21–60	1.6
1.5	350–600	40	2.5–3.5
0.75	400–550	–	–
0.6	–	–	–
0.749	223–624	11–14.5	2.7–5.7
1.2	295	–	3–10

enormously potential replacement for synthetic fibres, as a lighter, cheaper and safer with compared to glass fibres.

Properties of kenaf fibres based polymer composites mostly depends on the fibre arrangements and directions, fibre length and compositions characteristics. The fibre-matrix adhesion identified as the most drawbacks in natural fibre composites. At the interface, the matrix acts as the load to the stiff fibre through shear stresses. This requires an excellent bond between the reinforced fibres and polymeric matrix, thus poor mechanical properties results due to insufficient adhesion (Wambua et al. 2003). Nevertheless, by many modifications like physical and chemical treatments these natural properties actually can be improved, such as silane and alkali. Literature reviewed that fibres treatment with silane improves the tensile, flexural strength and stiffness (Bledzki and Gassan 1999). Moreover, the use of coupling agents such as maleic anhydride through hydrophilization to embodied hydroxyl groups on matrix may also improve the adhesion. Consequently, it enhance the effect of wetting in fibre resins (Wambua et al. 2003).

Use of kenaf fibres polymer composites in manufacturing prosthetic socket, will reduced the materials procuring and manufacturing cost, as many of prostheses components are locally produced, consequently lessen the dependency on imported parts and the quality of products can be easily controlled or maintained. Moreover, it is anticipated to contribute to the poor and developing countries and those who unable to afford an expensive artificial limbs.

8 Conclusions

Present review article intended to present the analysis of the socket design associated with the thermal comfort on prosthetic socket and the fabrication of the prosthetic leg socket made from woven kenaf-glass fibre composite. This study also proposes the development on the design of prosthetic socket with the natural fibre based biocomposite materials. The hot and humid environment surroundings lead to thermal discomfort and elevated residual limb skin temperature due to the resistance between skin and the prosthetics socket and thus the skin not freely breathable. The poor environment results perspiration and sweating on prosthetic socket and finally results many skin problem such as blister, ulcerations and others. Utilization of natural fibre as main prosthetic socket materials, by replacing the existing material however can minimize the problems, especially in prosthetic and orthopedics field. Introduction of natural fibre based polymer composites associated with the development of prosthetic socket design will reduce the problem regarding the thermal discomfort and will provide the eco-friendly product alternative to plastic based materials that are being used worldwide.

However, the commercial applications and the complexity related to this issue, requires the cooperation from various fields such as industrial designers, medical experts and engineering. Additionally, the consideration on aesthetic parameter should be preferred as satisfaction and appeal to the patient. Present article will guide the designer to improve the current prosthetic socket design with regard to the environment and amputee’s condition to enhance the quality of the amputee’s life to lead them a normal life as possible.

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Synthesis of Soy Protein Based Biocomposites for Packaging Applications

Sarat K. Swain, Pramod K. Sethy and Adrushya J. Pattanayak

Abstract Introduction of Soy Protein based bionanocomposites in the present era has made a significant contribution to extent the shelf-life of human being. It increases the food quality as well as put a huge impact on reducing the packaging waste. Bionanocomposites are high performing, light weighted green materials as compare to conventional non-biodegradable petroleum based plastic packaging materials. Most of the bionanocomposites used so far for packaging application are starch and cellulose derivatives such as polylactic acid (PLA), polycaprolactone (PCL), poly(butylenes succinate) (PBS) and polyhydroxybutyrate (PHB). In the present chapter, incorporation of different inorganic nano-fillers in soft network of bio-based soy protein was obtained by green technique. The characterisation of prepared bionanocomposites, bonding pattern and their behaviour have been presented through morphological analysis, UV-visible spectroscopy, FTIR (Fourier Transform Infrared) Spectroscopy, XRD (X-ray Diffraction) Spectroscopy. The thermal, mechanical biodegradability, chemical resistance and gas barrier properties of soy based nanocomposites are measured and compared. Finally a detail discussion on its packaging application and future aspect is presented.

Keywords Biocomposites · Bionanocomposites · Green technique · Gas barrier properties · Packaging

1 Introduction

The word Composite means a combination of two or more materials having distinct constituents and phases. Polymer composites are the homogeneous polymer based material with specific properties. Polymer composites are comprised of two phases (i) Matrix Phase with the properties of lower modulus and high elasticity

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(ii) Reinforcing Phase characterized with high load capacity. Due to lower modulus and high elasticity polymers are highly chosen as matrix component. In nature there are three types of composites (a) Particle reinforcement composites formed by suspending one material to another to form a strong matrix (b) Structural composites or sandwich composites are two or different materials bonded one layer to another to form strong layers (c) Fibre reinforcement composites one material embedded to other material and form long fiber of extremely strong matrix. Now a day, environmental pollution in particular due to deposition of non-degradable, non- recyclable, unitary used plastic as packaging material is a serious major issue. Biopolymer composites are the appropriate replacement to overcome this threat. The reason for selecting polymer bio-composites as replacement being these are cheaper, recyclable, biodegradable and most importantly of their eco-friendly nature (Guerrero et al. 2010). In all most all packaging related literatures keywords like "biodegradable", "biocompatible", "environmentally-friendly," "recyclable", "green" and "biopolymers" are the frequently used. This reflects the impact of non-biodegradable solid wastes on nature which enhances the environmental pollution and diminishing the natural resources. Day by day there is an increasing demand for the production of high quality food materials from limited natural resources and their preservation for longer duration is a matter of concern. The population growth becomes alarming as a result there is huge depleting of natural resources that is why the use of natural renewable recourses for the production of edible or biodegradable packaging material is considered. The packaging material should maintain quality of food or the products in general as well as it should minimize the environmental waste disposal problems. Among the wide range of biopolymers such as proteins, polysaccharides, lipids and their composites which are from nature and are renewable, processed for preparation of biodegradable packaging materials. These improved processed packaging materials replaced their bionondegradable petrochemical based counterparts (Debeaufort et al. 1998; Kester and Fennema 1986). These provide a suitable physicochemical environment and enhance the shelf-life of the product. The packaging system consists of products and processed packaging materials with suitable mechanical, gas and water vapour barrier properties. The challenges for the packaging system are to protect the products and increase their longevity especially food products from contamination of microorganisms and the overall quality during storage and handling. The main aim of the newly synthesized packaging material is that after a useful life it should biodegrade in appropriate time frame without harming the environment. In this regard bio-based composite materials have some advanced beneficial properties as packaging material which edge over the traditional nonconventional plastic products. The biopolymer composites help in improving the quality of food, extends the shelf-life, minimizes the microbial growth etc. These not only serve as barrier to gas, water vapor, moisture and solid waste but also act as carrier to few active substances which are beneficial to the products. Among the various biopolymers used for synthesis of biocomposites such as derivatives of plant materials (e.g. starch, cellulose, chitin, chitosan, other polysaccharides and proteins) animal products (proteins like casein, collagen and polysaccharides) products from microorganisms (e.g.

polyhydroxy alkanoate such as polyhydroxyl butyrate) are significant. Few synthetic polymers are also used for preparation of biocomposites (e.g. Polyamide, Poly-anhydride, Poly vinyl alcohol, Poly vinyl acetate etc.). Among the biopolymers soy protein is considered as potential alternate for petroleum and synthetic based biopolymers due to its large availability and biodegradable nature. (Gennadios et al. 1997; Kumar et al. 2002; Rudnik 2008). The major contributions of biocomposites are that these are truly green in every sense; these are biodegradable, eco-friendly, compatible and sustainable too, after their use and reuse these can be dumped or disposed without causing environmental pollution. Biopolymers with poor mechanical and barrier strength are less selective for packaging application in industry. When we consider nano sized particles instead of micro or macro particles in biocomposites a majority of physical properties changes. It is mainly due to increase in surface area to volume ratio i.e. aspect ratio, with decrease in size further the aspect ratio increases. High aspect ratio is an important factor for synthesis and isolation bionanocomposites and ultimately it enhances the physical properties in a constructive way. It increases the efficiency of catalysts in catalysis, improves the performance of structures like electrodes, fuel cells and batteries. With increase in surface area the interaction between the components in biocomposites increases, as a results there is increase in tensile strength, heat and chemical resistance. These are the major requirements of biocomposites used in packaging sectors. As explained earlier the nanofillers used in bionanocomposites have properties like low density, high flexibility, high tensile strength, rigidity and heat resistance. As a result there is increase in mechanical properties, thermal stability, electric properties, gas barrier properties and rates of biodegradation (Jordan et al. 2005). Due to all these improvements biocomposites are suitably applied for packaging applications. Among the protein resources soy protein is unanimously selected for food and packaging industries because it is worldwide available and is readily renewable. Soy protein is largely used in food industry such as salad dressings, soups, meat analogues, beverage powders, cheeses, non-dairy creamer, frozen desserts, whipped topping, infant formulas, breads, breakfast cereals, pastas, and pet foods. It is also used for emulsification and texturizing. Specific application include adhesives, asphalts, resins, cleaning materials, cosmetics, inks, pleather, paints, paper coatings, pesticides/fungicides, plastics, polyesters and textile fibres. Dehulled and defatted soybeans are processed into three form of commercial food products soy flour, soy concentrates, and soy isolates. In the current era most of the countries allow health claims for foods rich in soy protein, so it is used globally as normal food substitute. Many scientist showed great interest to work on soy protein, few are illustrated here, Soy protein used as biodegradable plastics (Lu et al. 2004), textile fibers (Liu and Li 2004), biodegradable membranes (Paetau et al. 1994), adhesives, binders (Zhong and Sun 2001) and packaging materials (Foulk and Bunn 2001), blended with organic and inorganic nanoparticles (Jiang et al. 2007) by solution mixing and melting-compression (Ai et al. 2007), biodegradable with feebly flexible (Wang et al. 2007). Huang and Netravali used nanoclay to reinforce the phytagel-modified soy protein concentrate and observed improvement in mechanical and thermal properties (Huang and Netravali 2006), Xiang and his co-workers prepared and characterised soy protein isolate/montmorillonite bionanocomposites and reported the improved mechanical strength and thermal stability (Xiang et al. 2009), gas barrier property (Kisku and Swain 2012).

There are different types of soy proteins according to their methods of production and protein content. (i) Soy protein isolate contains about 90% of the protein is the most refined form of soy protein, it is mixed with meat products to improve its quality and texture (ii) Soy protein concentrate contains about 70% of the protein is basically soybean without the water soluble carbohydrates (iii) Textured soy protein, often called TSP contains about 70% of the protein is made from soy protein concentrate by giving it some texture. It may be dry flakes or chunks. It keeps its structure when hydrated and used as a meat substitute or an additive to meat. The structure of soy protein mainly consists of around 90% storage globular proteins such as albumin, globulin etc., mainly consists of 7s (β-conglycinin) and 11s (glycinin) (Thanh and Shibasaki 1976). Globulins are protein fractions in which the subunits are associated via hydrophobic and hydrogen bonding (Chabba et al. 2005). Soy protein is globular, reactive and often water soluble as compared to helical or planar, non reactive and water resistant synthetic polymers. The improved tensile and thermal properties of soy protein implimented in packaging are due to presence of polar reactive amino acids like cystine, arginine, lysine and histidine in a crossed linked manner (Pavlidou and Papaspyrides 2008).

This chapter briefly discussed the synthesis of soy protein based biocomposites by green technique solution casting method (Swain et al. 2012; Dash and Swain 2013). The fabrication method, interaction of components through characterisation and the improved properties of soy protein were presented in detail. Soy protein bionanocomposites with incorporation of various weight percents of clay via solution blending without any plasticizer were reported., this work aims at improvisation of the oxygen barrier property in addition to thermal resistance of soy protein by employing an organically modified clay i.e. Cloisite®30B having –OH groups attached to the organic modifier, which would possibly increase clay-protein interaction through hydrogen bonding for enhancement in material properties. The next bionanocomposites i.e. soy/BN and soy/SiC biomaterials were prepared via the same technique with the aim of improving the properties of the polymeric materials by the incorporation of thermally stable boron nitride or silicon carbide nanoparticles. The prepared bionanocomposites are having superior thermal stability and mechanical properties along with improved chemical resistivity which are the essential for a substance to be used as packaging material.

2 Preparation/Synthesis Technique

Soy protein based bionanocomposites are mostly synthesized by solution casting method. The solution casting means polymer and pre-polymer are equally soluble. In the suitable solution the polymer dissolved easily while nanoparticles are

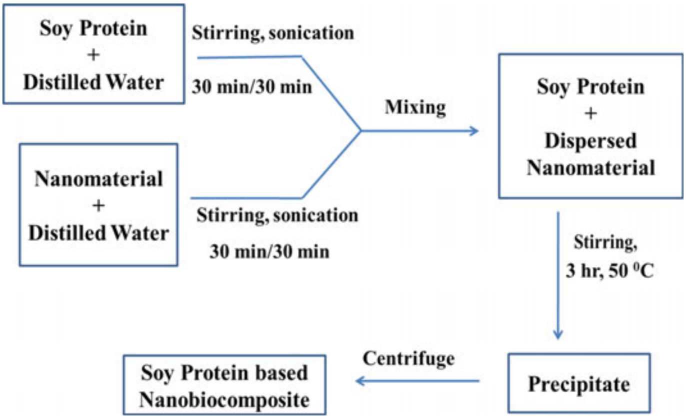


Fig. 1 Schematic representation of the synthesis of soy protein based bionanocomposites

dispersed in same or different solution before two mixed. For example to prepare bionanocomposite the solution must be swelling to clay (Ray and Okamoto 2003). The clay is dispersed by weak force and the layers are filled one by one. Once the solution swelling then mixed in clay dispersion. The polymer chain break when put into a solvent. In this manner solvent adsorbs on to silicate surface. In biopolymer clay solution, entropy gained from desorption of solvent. As a result there is decrease in entropy of confine intercalated chain. The solvent get evaporated to get nano composite structure (Pavlidou and Papaspyrides 2008) (Fig. 1).

3 Synthesis of Soy Based Bionanocomposites

A large number of soy based bionanocomposites are synthesized by keeping soy protein as common with different nanofillers such as boron nitride or Silicon carbide nanopowder with characteristics particle diameter of 70 nm or Cloisite®30B which is a natural MMT modified with a quaternary ammonium salt. The other chemicals used such as $CuSO_4$ and glycine are of analytical grade and the used solutions were synthesized using double distilled water.

3.1 Synthesis of Soy Protein Bionanocomposites

Soy protein based bionanocomposites were synthesized by green solution casting method. According to this method, different nanomaterials such as boron nitride/cloisite®30B or SiC is incorporated into the soy protein network though aqueous phase interactions.

3.2 Synthesis of Soy/Boron Nitride Bionanocomposite

Boron nitride reinforced soy protein nanobiocomposites were synthesized by the same technique. To prepare soy protein solution, soy protein was dispersed in double distilled water by stirring at 50 °C for 1 h followed by treatment of ultrasound sonicater (120 W/80 kHz) for 30 min. At the same time a calculated amount of boron nitride nano power was dispersed in distilled water using same procedure. The boron nitride solution was added into soy protein solution followed by addition of prepared copper sulphate and glycine (3:1) and then stirring at 50 °C for 3 h. The obtained viscous liquid was centrifused with a speed of 9300 rpm at 25 °C for 15 min. After centrifugation the obtained precipitate was suspended in 10 ml of acetone and then filtered. Subsequently the ensuing product was dried at room temperature for 2 days to obtain nanocomposite powder.

3.3 Preparation of Soy/Cloisite®30B Bionanocomposite

Soy protein/Cloisite®30B bionanocomposites of different clay contents were synthesized by solution blending method. 4 gm of soy protein was dissolved in 40 ml of double distilled water at ambient temperature with stirring. At the same time a calculated amount of Cloisite®30B was dispersed in 10 ml of distilled water. Both the solutions were stirred separately for 30 min. The Cloisite30B suspension was then added into soy protein solution with stirring at 60 °C for 3 h. The obtained light yellow viscous liquid was centrifuged with a speed of 9300 rpm at 25 °C for 15 min. After centrifugation the obtained precipitate was suspended in 10 ml of acetone and then filtered. Subsequently the ensuing product was dried at room temperature for 2 days to obtain a light yellowish grey-colored nanocomposite powder.

3.4 Preparation of Soy/SiC Bionanocomposites

The green technique was used for synthesis soy/SiC bionanocomposites by taking different weight percentage of nano SiC (Sarkar et al. 2016). To prepare soy protein solution, soy protein was dispersed in double distilled water by stirring at 50 °C for 1 h followed by treatment of ultrasound (120 W/80 kHz) for 30 min. At the same time a calculated amount of silicon carbide nano power was dispersed in distilled water using same procedure. The silicon carbide solution was added into soy protein solution followed by addition of prepared copper sulphate and glycine (3:1) and then stirring at 50 °C for 3 h. The obtained viscous liquid was centrifuged with a speed of 9300 rpm at 25 °C for 15 min. After centrifugation the obtained precipitate was suspended in 10 ml of acetone and then filtered. Subsequently the ensuing product was dried at room temperature for 2 days to obtain nanocomposite powder. The significance of $CuSO_4$ and glycine mixture used as catalyst during synthesis of the bionanocomposite can be illustrated as follows:

$$\begin{gathered}\mathrm{CuSO_4 + Glycine \rightarrow Complex - I}\\ \mathrm{Soy\,protein + Complex - I \rightarrow Transient\,complex}\\ \mathrm{Transient\,complex + SiC \rightarrow soy/SiC\,complex}\end{gathered}$$

4 Characterization of Bionanocomposites

4.1 UV-Visible Spectrum Analysis

The UV-Visible characterization was only carried out for nanoclay reinforced soy protein bionanocomposites. UV–visible spectra of soy protein, Cloisite®30B and soy protein/Cloisite®30B composite (BNC_5) were compared in Fig. 2. The absorption peak for Cloisite®30B was observed at λ_{max} of 249 nm. The absorption peak at 267 nm of soy protein was due to conjugation of lone pair of electrons on nitrogen atom of amide group present in the backbone of the soy protein. The lowering of absorption wavelength to 225 nm in case of the bionanocomposite may be due to removal of the conjugation by the hydrogen bonding of –OH group of Cloisites®30B with the available lone pair of electrons on the nitrogen atom of the peptide linkage of the soy protein. Thus the blue shift of absorption peak in the bionanocomposite can be regarded as an evidence for the chemical interaction of clay with soy protein.

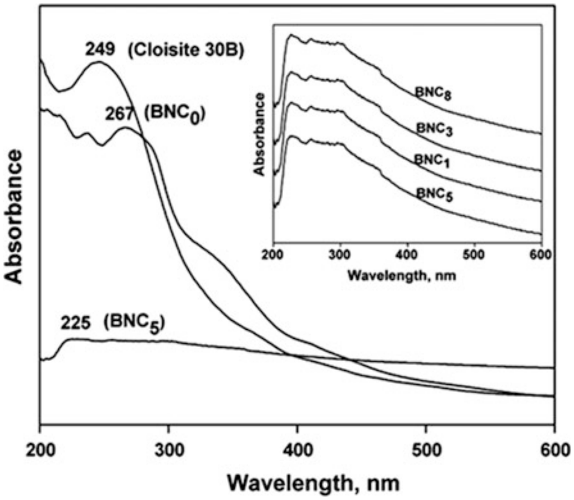


Fig. 2 UV-Visible spectra of Cloisite®30B, soy protein and (bionanocomposite with 5% clay content (*Inset* shows the UV-Visible spectra of the bionanocomposites with 1, 3, 5 and 8% clay content) (Swain et al. 2012)

4.2 FTIR Analysis

Figure 3a shows the FTIR spectra of soy protein, Cloisite®30B and soy protein/Cloisite®30B composite. In the spectrum of clay (Cloisite®30B), the absorption peak at 3645 cm^{-1}corresponds to O-H stretching, the peaks at 1032, 1440 and 2927 cm^{-1} are due to Si-O stretching, C-C stretching and C-H stretching respectively. In the spectrum of the virgin soy protein, the absorption peak at 1650 cm^{-1}corresponds to C=O stretching, whereas the peak at 1540 cm^{-1}corresponds to N-H bending of the peptide linkage. The appearance of Si-O stretching peak at 1045 cm^{-1} in the spectrum of the bionanocomposite indicates the incorporation of organoclay into soy protein. Further the broad bands of very low intensity observed in the region of 3600–3750 cm^{-1} can be attributed to free and bound –OH and –NH groups, which are interacted via hydrogen bonding with the –OH group of Cloisite®30B and this result is supported by the observation made from the UV-visible spectral analysis. In case of soy/BN nanocomposites (shown in Fig. 3b), a sharp characteristic peak at 812 cm^{-1} was due to the B-N stretching vibration mode. The soy protein spectrum of Fig. 3b is similar to that of the soy protein spectra of Fig. 3a. The soy/BN nanocomposites spectrum shows the characteristic peaks of soy protein and boron nitride at the same position with different intensity which indicates the composites formation. The similar spectra were obtained for soy/BN nanocomposites having different wt% of BN loading. In case of soy/SiC nanocomposites [shown in Fig. 3c], the FTIR curve of 5 wt% of SiC indicates that SiC peaks appear at 1,389 cm^{-1} and 876 cm^{-1} along with the shifting of peaks at 2,918 and 3,500–3,000 cm^{-1} (broad peak). Another peak for bionanocomposites appears at 839 cm^{-1} signifies the presence of Si-N coordinate bond in expense of free and bound –NH_2 groups which proves the formation of soy/Sic bionanocomposites through chemical interaction. The possible reason is that chemical interaction between free and bound –NH_2 groups and SiC occur due to the delocalization of lone pair electron of N atom to the vacant d-orbital of Si atom of SiC nanoparticles.

4.3 XRD Analysis

The structure of soy protein/Cloisite®30B nanocomposites synthesized through solution technique were investigated by X-ray diffraction (XRD). The XRD patterns for soy protein and protein/clay nanocomposites were compared in Fig. 4a, b with 2θ range of 3°–10°. The clay-free soy protein does not show any diffraction peak in this region. The characteristic crystalline peak of the clay was observed at 2θ value of 4.8° which shifted towards left to the 2θ value of 3.92° with low intensity in case of the composite of 8% clay loading (BNC_8). This gave the evidence of the expansion of clay layers from 1.84 nm to 2.25 nm, as calculated from Bragg's equation. However in case of the composites of 3% (BNC_3) and 5%

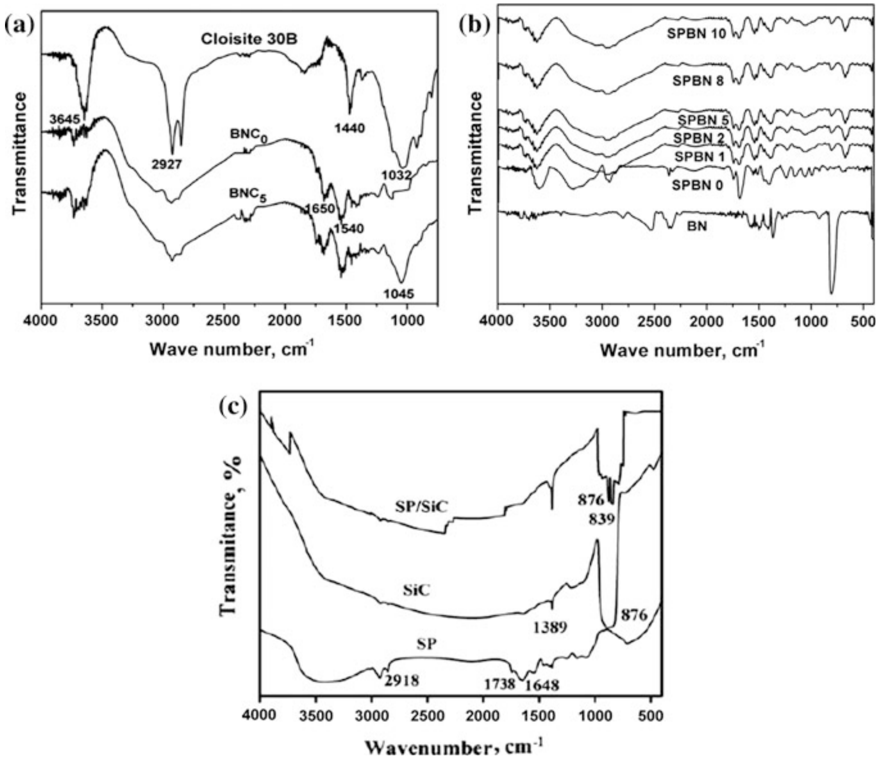


Fig. 3 FTIR spectra of Cloisite®30B, BNC$_0$ (neat soy protein) and BNC$_5$ (bionanocomposites with 5% clay content) (**a**) and soy protein, boron nitride and soy/BN nanocomposites at different wt% of BN (**b**). FTIR spectra of soy protein, nano Sic, and soy/Sic bionanocomposites (5 wt%) (**c**) (Swain et al. 2012; Dash and Swain 2013; Sarkar et al. 2016)

(BNC$_5$) clay loadings the peak vanished indicating achievement of exfoliated structure due to complete delamination of the layer structure of Cloisite®30B in aqueous medium by soy protein macromolecules. The low dispersion at the high concentration of clay may be due to agglomeration. The reason is in accordance with conclusion made by Ray and Okamoto that the exfoliated structure at lower and intercalated structure at higher clay loading. Further the XRD patterns of soy protein and its composites were compared in Fig. 4b with 2θ up to 30°. It was noted that the single broad peak of the diffraction pattern of soy protein was converted to multiple peaks in the diffraction patterns of the composites as shown in the encircled part and notified to the change in crystallinity of soy protein in bionanocomposites due to dispersion of clay layers. The structural analysis of the soy protein, boron nitride nanopowder and soy/BN nanocomposites were investigated by X-ray diffraction (Fig. 4c). High crystalline peak of Boron nitride was appeared

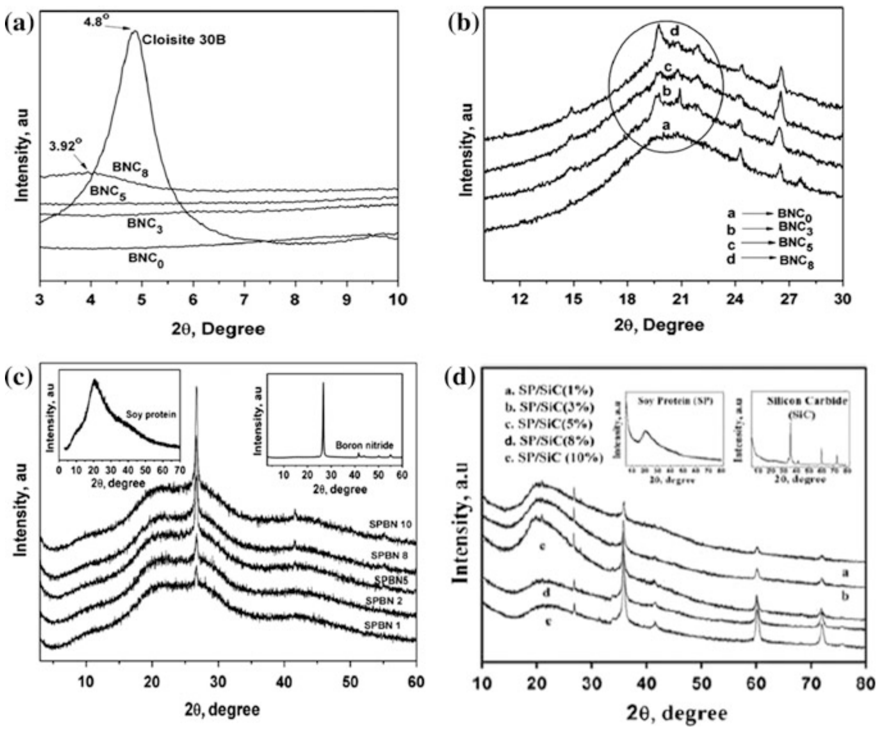


Fig. 4 XRD patterns of the Cloisite®30B, soy protein (BNC_0) and the bionanocomposites with clay loadings of 3% (BNC_3), 5% (BNC_5) and 8% (BNC_8) in the 2θ range of 3° to 10° (**a**) and 10° to 30° (**b**), XRD patterns of soy/BN nanocomposites (**c**) and XRD patterns of soy/SiC nanocomposites (**d**) (Swain et al. 2012; Dash and Swain 2013; Sarkar et al. 2016)

at 2θ value of 26.7° along with other two less intense peaks at 2θ values of 41.66° and 55.36° (Inset, Fig. 2). XRD pattern of Soy protein (Inset, Fig. 2) showed a broad peak at 2θ value of 20°. In XRD pattern of nanobiocomposites, the peaks were more intense due to BN but less intense for soy protein at 2θ value of 20°. This was due to the decreasing crystalline structure of soy protein during the formation of nanocomposites. The structural properties of the soy protein, SiC nanopowder and soy/SiC nanobiocomposites were studied by XRD (Fig. 4d). Silicon carbide showed a high crystalline peak at 2θ value of 35.99° and two small peaks at 2θ values of 59.89° and 72.20° (Inset, Fig. 2). Soy protein XRD pattern (Inset, Fig. 2) showed a broad peak at 2θ value of 20.38°. In the composites, the peaks due to Silicon carbide were prominent but the peak at 2θ value of 20.38° for soy protein was less intense. This was happened due to the decreasing crystalline structure of soy protein during the formation of bionanocomposites. The similar result was obtained as that of soy/BN bionanocomposites.

4.4 Morphological Analysis

TEM study is essential to verify the extent of exfoliation in the composite as a support to the results obtained from XRD study. Figure 5a represents the TEM image of the bionanocomposite with 5% clay loading, in which the clay layers are seen to be delaminated into some thin lamellas by soy protein with about 2 nm thickness in dimension. The black patch in the TEM micrograph may be due to local agglomeration of clay within the soy protein matrix. In case of soy/BN bionanocomposites, HRTEM is used to detect the distribution of BN nanoparticles and from its image, it was noticed that BN nanolayers were distributed uniformly within soy protein matrix and were arranged in an orderly manner to create a torturous path to check the oxygen penetration. The structural dispersion of BN nanolayers was in accordance with the result of XRD. In case of soy/SiC nanobiocomposites, distribution of SiC nanolayers can be studied by FESEM (Fig. 6a–e) and its image noticed that SiC nanoparticles are seen to be distributed and implanted uniformly within soy protein matrix. Within the image white spots characterize the SiC NPs, whereas, the black spots are rare to be observed and may be the reflection of local agglomeration of SiC nanoparticles. The mobility of soy protein chain is restricted at the higher percentage of nano SiC which is a reason for agglomeration. The internal dispersion of SiC nanoparticles within soy protein matrix was noticed from HRTEM images of the synthesized soy/SiC bionanocomposite with 5 wt% of SiC loading (Fig. 6f). In the TEM image (Fig. 6g), SiC NPs (average diameter ~70 nm) were distributed with high inter-connecting network; with local agglomerating nature of SiC NPs within the bionanocomposite.

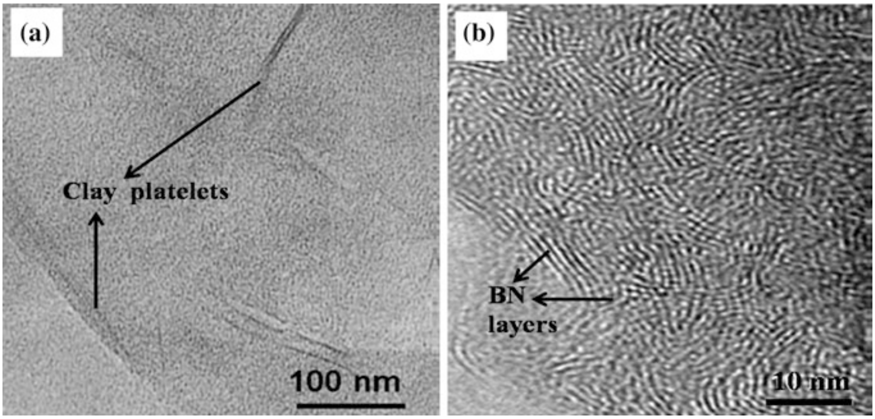
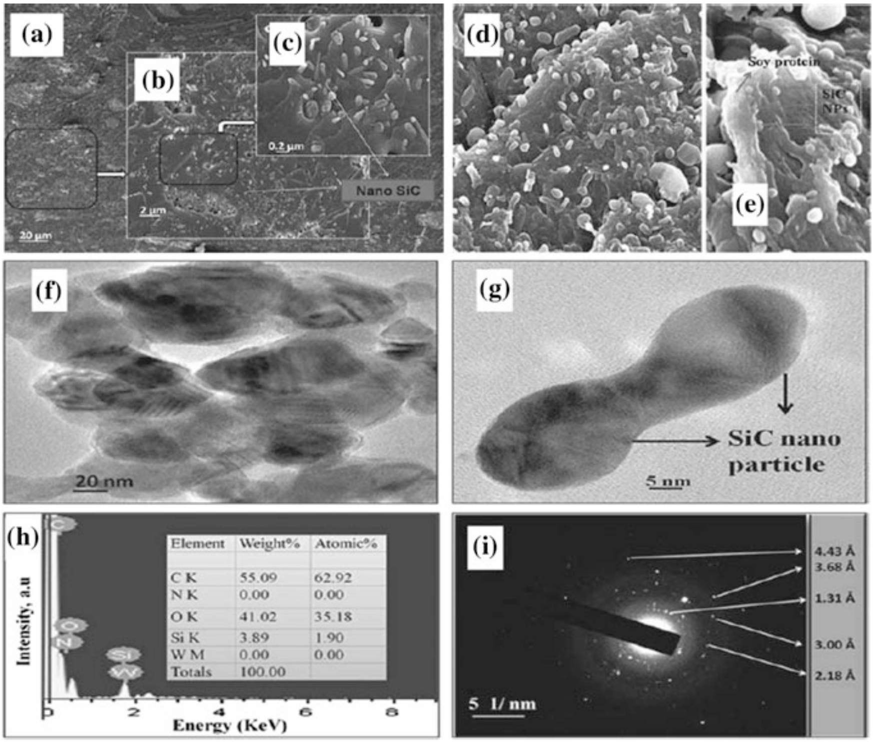


Fig. 5 TEM images of the bionanocomposite with 5 wt% clay (BNC_5) (**a**) and soy/BN bionanocomposites (**b**) (Swain et al. 2012; Dash and Swain 2013)



Element	Weight%	Atomic%
C K	55.09	62.92
N K	0.00	0.00
O K	41.02	35.18
Si K	3.89	1.90
W M	0.00	0.00
Totals	100.00	

Fig. 6 FESEM micrographs of nano SiC reinforced soy protein bionanocomposites (5 wt% SiC) (**a–c**); cross-sectional view of bionanocomposite (**d** and **e**); HRTEM images of soy bionanocomposite (**f** and **g**); energy dispersive spectra (**h**); and SAED pattern (**i**) of soy/SiC bionanocomposite (Sarkar et al. 2016)

The crystalline nature of SiC (5 wt%) were identified by selected area electron diffraction (SAED) pattern as show in Fig. 6i.

5 Properties of Soy Based Bionanocomposites

5.1 Thermal Properties

The Fig. 7a displays the thermo gravimetric analysis of soy protein, Cloisite®30B and soy protein/Cloisite®30B bionanocomposites with 5 and 8% clay loading in the temperature range of 25–600 °C. The thermal decomposition temperature of soy protein was 250 °C which was occurred with a maximum decomposition to water loss from 30 to 120 °C, the second step from 120 to 250 °C due to degradation of soy protein and third due to the oxidation of partially degraded soy protein and then

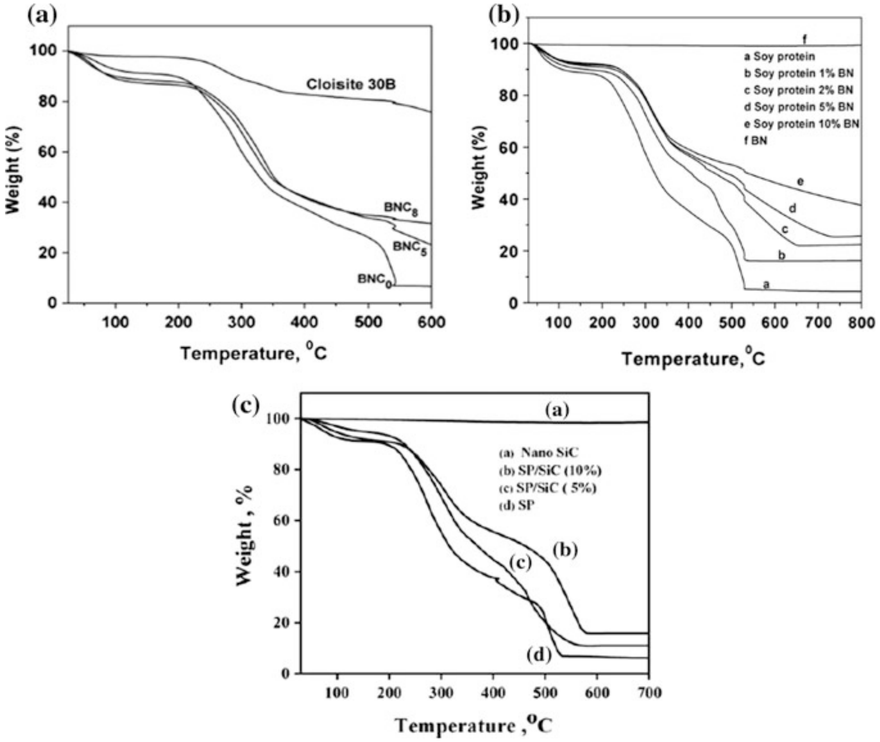


Fig. 7 Thermo gravimetric analysis (TGA) of Cloisite®30B, soy protein (BNC_0) and their bionanocomposites with 5% clay loadings (**a**), soy/BN nanocomposites (**b**) and soy/SiC bionanocomposites (**c**) (Swain et al. 2012; Dash and Swain 2013; Sarkar et al. 2016)

charring. It can be observed that in comparison to soy protein the thermal decomposition of soy protein/Cloisite®30B bionanocomposites were delayed as the onset decomposition temperature (T_{onset}) and the temperature of 50% degradation (T_{50}) shifted towards a higher temperature. In addition the weights of residual char (Wr) at 600 °C were found to be remarkably higher for the bionanocomposites compared to the virgin soy protein which underwent decomposition almost completely. The significantly enhancement in thermal resistance of the bionanocomposites can be attributed to the delamination of silicate layers in the protein matrix preventing out diffusion of the volatile decomposition products. Moreover the clay is highly resistant to weight loss by heating as evident from TGA plot, which shows a much higher onset decomposition temperature and a very small weight loss. The glass transition temperatures (Tg) as a function of clay content for soy protein and its bionanocomposites were presented in Fig. 7a. It was observed that glass transition temperature was increased proportionately with increase in clay content. With 8% of clay loading the Tg was enhanced almost by 30% to that of soy protein. The mechanism of improvement of thermal resistance may be attributed to the thermal insulation behaviour of nanoclay and change in the dynamics of molecular motion in soy protein/clay nanocomposites. Figure 7b shows the thermo gravimetric analysis graph of soy protein, boron nitride and soy/BN bionanocomposites in the temperature range from 30 °C to 800 °C. Decomposition report of soy protein is discussed in above. The degradation temperature of soy/BN nanocomposites is higher than corresponding virgin soy protein and the degradations start at the temperature range of 200–235 °C in both soy protein and soy/BN nanocomposites. From TGA data, it was found that at about 535 °C temperature soy protein degraded fully where as more amount of residue was obtained in case of bionanocomposites and about 40% more residue was left after weight loss of soy/BN (10 wt%) bionanocomposite when heated at 800 °C. Hence the thermal stability of soy/BN nanocomposite was more than that of soy protein due to inclusion of thermally stable BN nano particles. Thermo gravimetric analysis (TGA) was carried out in the temperature range 30–700 °C under nitrogen atmosphere to compare the thermal properties of soy protein, nano SiC and soy/SiC bionanocomposites as shown in Fig. 7c. The thermal decomposition of soy protein involved in three steps, in first step weight loss is due to loss of moisture from the surface of soy protein at 113 °C, second step due to decomposition of soy protein in the temperature range of 200–477 °C and third step is due to oxidation of partially decomposed soy protein in the temperature range of 477–535 °C followed by charring. Whereas nano silicon carbide is found extremely thermal stable in the temperature range of 30–700 °C and its weight remains as in initial form. The initial step for thermal decomposition of soy/SiC nanocomposites (5 and 10 wt% of SiC loading) occurs at higher temperature (216 and 233 °C respectively) as compared to the virgin soy protein. Hence the thermal stability soy/SiC nanocomposite was more than that of virgin matrix due to inclusion of thermally stable nano silicon carbide.

5.2 Gas Barrier Properties

The oxygen flow rate of the bionanocomposites was found to be decreased in proportion to clay loading (Fig. 8a). At 8% clay concentration, the oxygen flow rate (permeability) was reduced by 6 times as compared to the virgin soy protein. This is because the clay platelets act as physical obstacle retarding the movement of the gas. Further the nanocomposites have ordered nanostructure which creates a tortuous path in an exfoliated polymer/clay nanocomposite as shown in Fig. 8a that provides more barriers to oxygen penetration compared to that in a conventional composite as represented by Fig. 8b. The oxygen permeability of the soy/BN nanocomposites at constant pressure was analysed in Fig. 8c and found that the oxygen flow rate was decreased with increase in wt% of boron nitride. The oxygen barrier property at different pressure was measured in Fig. 8d and found that oxygen permeability was significantly decreased due to dispersion of boron nitride nanoparticles within the soy protein matrix and may block the voids for oxygen

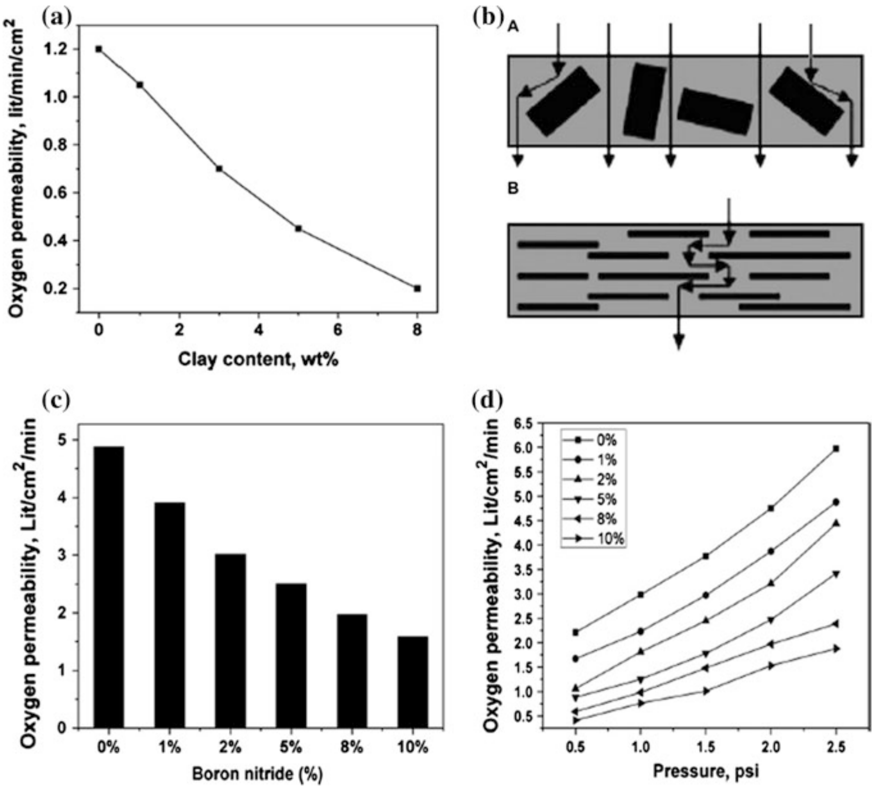


Fig. 8 Oxygen permeability values of the bionanocomposites as a function of clay weight percent at a pressure of 5 psi. Schematic representation for oxygen penetration through an easy path in a conventional composite and a tortuous path in an exfoliated polymer/clay nanocomposite (**b**) Oxygen permeability of soy protein and soy/BN nanocomposites at (**c**) constant pressure and (**d**) different pressure (Swain et al. 2012; Dash and Swain 2013)

penetration. In soy/BN nanocomposite with 10 wt% BN, the oxygen flow rate was reduced by more than six times as compared to the soy protein (virgin).

5.3 Biodegradable Properties

Figure 9 displays the biodegradability study of soy/BN and soy/SiC bionanocomposites as compared with virgin soy protein for 6 months with an interval of one month. The degration of soy/BN bionanocomposites was studied by calculating the percentage weight loss in activated sludge water (Fig. 9a). It was found that the percentage weight loss of composites was increased with increase in percentage of soy protein. Biodegradation of composites as well as virgin soy protein was further

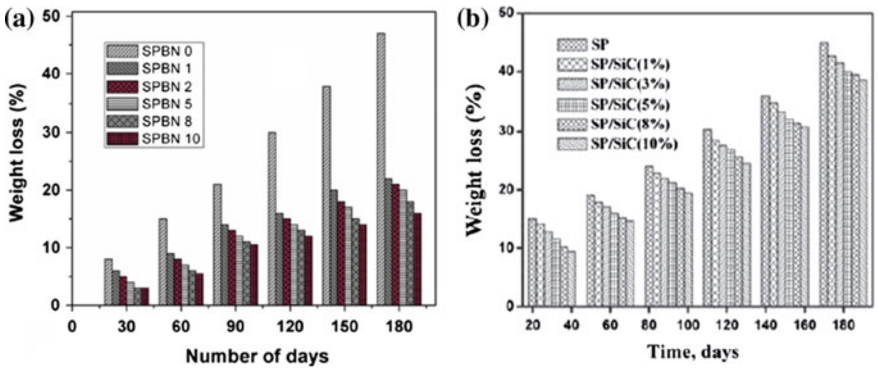


Fig. 9 The weight loss (%) of soy protein and soy/BN nanocomposites (**a**) and soy protein and soy/SiC nanocomposites (**b**) due to biodegradation in activated sludge water at different interval of time (Das and Swain 2013; Sarkar et al.2016)

increased with increase in duration time in the active sludge water. The similar results were found in case of soy/SiC nanocomposites as shown in Fig. 9b. The chemical interactions of soy protein with boron nitride or silicon carbide matrix may be the cause for improvement of biodegradation properties. Further the enhancement of biodegradable properties of composite may be due to the well dispersion of soy protein within BN or SiC matrix in the composites.

5.4 Chemical Resistance Properties

The chemical resistivity of soy/BN and soy/SiC bionanocomposites towards acid and alkali solution having 1 N concentration for 60 days with an interval of 10 days was illustrated in Fig. 10. The percentage weight loss of soy/BN nanocomposites due to treatment of acid and base with time was studied as in Fig. 10a, b. The synthesized bionanocomposites show significant resistance towards acid and base as chemical inertness of BN present in the soy protein matrix (Das and Swain 2013). The resistance capacity of soy/SiC bionanocomposites towards acid as well as alkali (shown in Fig. 10c, d) was found to increase extensively as compared to virgin soy protein. In case of acid the resistance power towards acid was pronounced more as compared to the basic phase. The solubility of SiC is more in base as compared to acid because of its acidic character and due to this reason the synthesized material is more resistant towards acid than base. Further the chemical resistivity is improved with increase in weight percentage of SiC and in the bionanocomposites the percentage of weight loss is increased with progress of time period due to the loss of chemical resistance of SiC nano particles within soy protein matrix. As the chemical resistivity of the bionanocomposites with higher

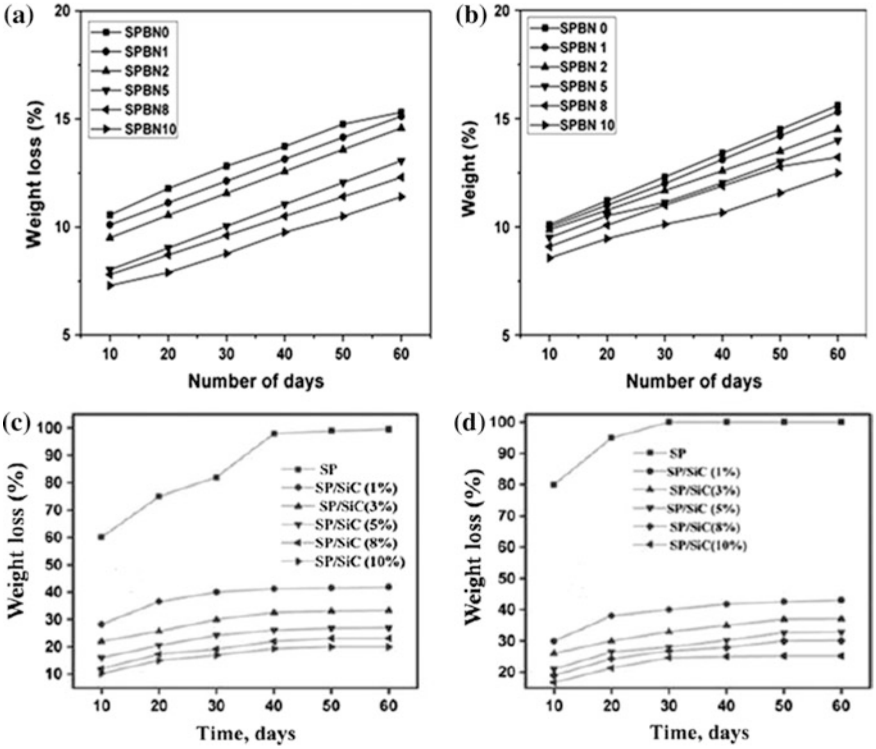


Fig. 10 **a, b** The weight loss (%) of soy protein and soy/BN nanocomposites due to treatment in dilute HCl (**a**) and dilute NaOH (**b**) and Percent weight losses of soy protein and soy/SiC bionanocomposites in dilute HCl (**c**) and dilute NaOH (**d**) at different interval of time respectively (Dash and Swain 2013; Sarkar et al. 2016)

percentage of SiC loading is more pronounced as compared to the lower SiC loading due to the interfacial adhesion with the polymer matrix.

5.5 Mechanical Properties

The following given Table 1 summarized the mechanical properties such as Young’s modulus, breaking stress, elongation at break, toughness, yield stress and yield strain of virgin soy protein and soy/BN nanocomposites of different wt% of boron nitride content. From the table it was noticed that breaking stress of nanocomposites with 10 wt% of BN loading was reduced to half of its value but the elongation at break and toughness of nanocomposites were increased with increasing BN content. However the toughness of nanocomposites with 10 wt% of BN was doubled as compared to that of the virgin soy protein and also found that

Table 1 Mechanical property of soy protein and soy/BN nanocomposites. Reproduced with permission from (Dash and Swain 2013)

Sample name	Young's modulus (MPa)	Breaking stress (Mpa)	Elongation at break (%)	Toughness (Mpa)	Yield stress (Mpa)	Yield strain (Mpa)
SP	285 ± 13	19.27 ± 1.5	702 ± 36	112.8 ± 12	18.02 ± 1.2	0.2282 ± 0.018
SPBN1	296 ± 15	15.28 ± 0.9	848 ± 48	128.6 ± 7	18.36 ± 1.4	0.2144 ± 0.022
SPBN2	304 ± 19	12.62 ± 0.8	862 ± 55	134.2 ± 9	19.02 ± 0.8	0.2085 ± 0.016
SPBN5	312 ± 18	10.09 ± 0.8	878 ± 32	136.4 ± 6	19.94 ± 1.1	0.2037 ± 0.019
SPBN8	316 ± 21	9.72 ± 0.6	906 ± 62	248.6 ± 14	19.83 ± 0.9	0.1907 ± 0.008
SPBN10	322 ± 12	9.48 ± 0.5	948 ± 58	256.1 ± 13	19.99 ± 1.5	0.1898.01

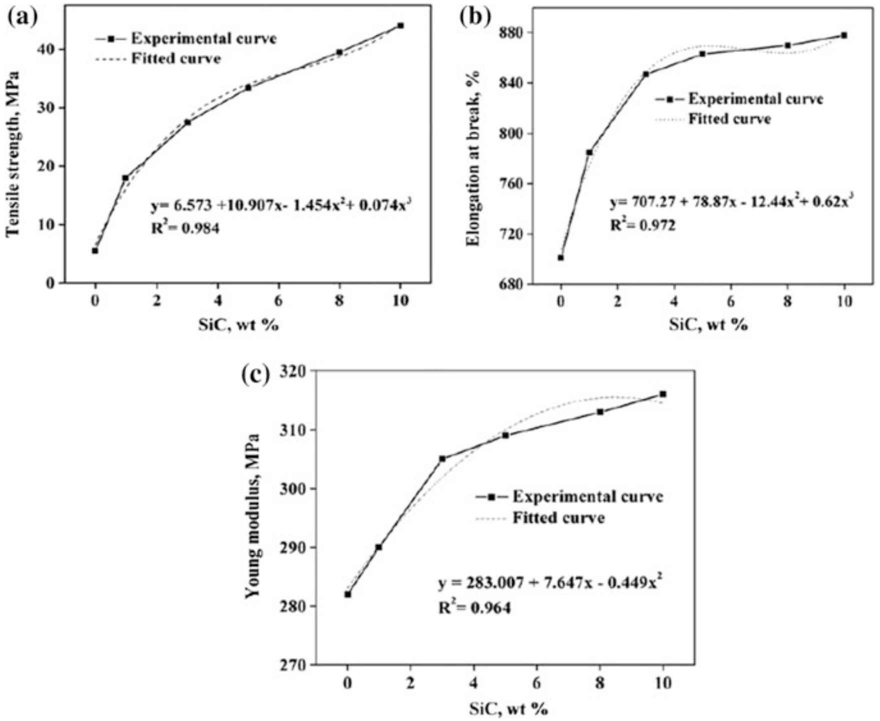


Fig. 11 Tensile strength (**a**), elongation at break (**b**), and Young's modulus (**c**) of soy/SiC bionanocomposites with different wt% of SiC loading (Sarkar et al. 2016)

the yield stress was increased but the yield strain was decreased with increase in BN wt%. Hence mechanical properties of nanocomposites with increase in BN content were improved and that may be due to the strong interfacial adhesion of stable BN nano particles within soy matrix in bionanocomposites. From Fig. 11 it was noticed that the tensile strength of soy protein is increased with increasing SiC concentration as it is a function of nano SiC concentration. Furthermore the tensile strength of soy protein was improved by four times even with incorporation of small amount (1 wt%) of nano SiC. The reason may be due to strong interfacial adhesion between soy proteins with uniformly dispersed nano SiC particles.

6 Packaging Applications

Compounds used as potential food packaging materials should have some unique properties. Soy protein is globally used as component of bionanocomposites in the food packaging sector A few properties along with their application are mentioned below.

- Soy protein has good packaging property due to its inherent properties like mechanical (tensile strength), thermal and gas barrier properties.
- It is prone to biodegradation.
- Due to its antimicrobial property as well as oxygen barrier property it is used as potential packaging material
- It interacts with environment so undergoes spoilage after use.
- It is a bio based or bioactive compound. So it can be used in delivery and control release.
- Soy based bionanocomposites can be used as nanosensor to indicate the quality of food and growth of microorganisms.
- Soy based biocomposites are used for monitoring product conditions like time temperature indicator (TTI), leakage of products, detection of gases.
- Soy based bionanocomposites are antimicrobial in nature and used for nanocoating.

6.1 Food Packaging Applications

Food packaging is the industrial method by which the food products are properly packed to minimise the food loss, supply the fully safe and wholesome food products to the costumer. Nanocomposites are better option for food packaging as compared to frequently used conventional non-biodegradable plastic materials. The reason for selecting nanocomposites in food packaging sector is due to their (i) gas barrier (for oxygen, carbon dioxide) (ii) water vapour barrier (iii) high tensile strength (iv) heat resistance (v) chemical stability (vi) thermal stability (vii) recyclability (viii) biodegradability (ix) configuration stability (x) good optical clarity (xi) developing antimicrobial and antifungal active surfaces, and most importantly (xii) sensing and signalling the change in microbiological and biochemical activities. Due to all these unique unmatchable properties several innovations with potential food packaging applications in industry are encouraged for development of nanocomposites technology. The main purpose of using nanocomposites in food packaging industry is to increase the shelf-life of various food products like processed meats, cheese, cereals, corns, mushrooms, confectionery, boil-in-bag foods, extrusion-coating applications in association with paperboard for fruit juice and dairy products, beer and carbonated drink bottles. In this case there is utilisation of low weight packages, less materials required which are biodegradable having better barrier properties and most importantly cost effective for consumers of all categories. The food packaging applications of nanocomposites are presented in various review articles (Sorrentino et al. 2007; Rhim and Ng 2007; Akbari et al. 2007; Arora and Padua 2010). Bionanocomposites such as polymer/clay use in a variety of food packaging applications such as processed meats, cheese, confectionery, cereals, boil-in-bag foods as well as in extrusion coating applications for fruit juices and dairy products or coextrusion processes for the manufacture of bottles for beer and carbonated beverages (Smolandar and Chaudhry 2010; Johansson 2011; Hatzigrigoriou and Papaspyrides 2011; de Azeredo 2009; Duncan 2011). Polymer/clay and polymer/SiC nanocomposites have improved barrier properties and are generally used as a multilayer packaging material with more than one other structural layers. In case of multilayered nanocomposites for rigid food packaging applications include beer bottles, carbonated beverages, and thermoformed containers. (i) The very first type of multilayer biocomposites traditionally used is composed of a barrier layer at the middle which is sandwich between outside structural layers (ii) The second type is a passive barrier type bionanocomposites in which the middle layer is reinforced with nanocomposite film with improved barrier property (iii) The third one is an active barrier composed of gas (O_2) scavenger incorporated film layer. (iv) The last one is the combination of passive and active barrier layers. Hence now a day nanocomposites are used globally as a replacement of un-cyclable packaging material because recycling is a major issue in the current era which reduce the packaging waste. It also protect the food materials from deteriorative oxidation process, prevents colour change, microbial growth and change in flavour due to the oxygen scavenging properties of nanocomposites.

6.2 *Antimicrobial Food Packaging Application*

Nanocomposites due to their oxygen scavenging and oxygen barrier properties widely are used to remove the residual or extra pace of oxygen in the package. Antimicrobial packaging of food materials by applying bionanocomposites is another important prospect to control the undesirable microorganisms like bacteria, fungus etc. During antimicrobial food packaging a layer of antimicrobial compounds is coated onto the packaging material (Suppakul et al. 2003; Appendini and Hotchkiss 2002; Nigmatullin et al. 2008; Persico et al. 2009).

Many of the synthesized bionanocomposites have antimicrobial property like antibacterial and antifungal activities. These prevent the growth of microorganisms during post processing. By doing so these enhance safety measures and increase shelf-life of food products. Due to high aspect ratio (surface to volume ratio) bionanocomposites are very much effective in antimicrobial system as it enhances the catalytic behaviour and surface reactivity. Nanoscale biocomposites are more effective against microorganisms as compared to their micro or macro scale counterparts. The investigation for antimicrobial activity have been carried out as growth inhibitors (Cioffi et al. 2005), antimicrobial agents (Hong and Rhim 2008), antimicrobial carriers (Bi et al. 2011) or antimicrobial packaging films (Rhim et al. 2006; Wang et al. 2006). The antimicrobial bionanocomposite films to protect various food products like meat, fish, poultry, bread, cheese, fruits and vegetables have been studied (Moreira et al. 2011; de Oliveira et al. 2007; Kerry et al. 2006) (Table 2).

Table 2 Applications of Soy based nanocomposites in food packaging application

Sl. no.	Soy protein based bionanocomposites	Nanofiller in biocomposite	Food packaging application
1.	Soy/Boron Nitride	Boron Nitride	1. Formation SPI controlled film 2. Oxygen barrier food packaging 3. Antimicrobial food packaging
2.	Soy/Cloisite®30B	Cloisite®30B	1. Formation of biodegradable composites 2. Raspberries 3. Boil in bag foods 4. Processed meat & cheese
3.	Soy/SiC	Silicon Carbide	1. Extruction coating application in association with paper board for juice and dairy products 2. Formation of thermoformed containers

7 Conclusion and Future Prospective

Soy protein based bionanocomposites are the innovative invention for the packaging application, in particular food packaging and antimicrobial food packaging application. Soy based biocomposites have unique unmatchable properties and most importantly these are economically suitable for all groups of society. Hence universally accepted in food packaging sectors. In future, attention has to be given for the synthesis of smart bionanocomposite materials for food packaging sector having antioxidant releasing film, colour containing film, light regulating film having advanced oxygen barrier property and anti microbial property.

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Green Biocomposites: A Prospective Utilization in Automobile Industry

Deepak Verma and Sanjay Sharma

Abstract Natural fiber reinforced polymer composites becomes the most promising and identified research area. As these composites not only offer the good mechanical strength but also are light in weight and cost effective. The reasons of popularity of this area reside in many important parameters such as recyclability, biodegradability and environment friendly. Now scientists have developed biopolymer derived from corn, soy etc. which is used to reinforce the natural fibers and developed a fully biodegradable composite material. The application of the natural fiber composites not only found in the building and constructions sectors but also in the automotive and aircrafts structures sectors. In this chapter we are discussing about the Green Biocomposites and their utilization in the automobile fields. The chapter also highlighted a general class of the various available natural fibers and their application in the automotive sectors. This chapter also provides an insight of the safety measures such as crashworthiness of the vehicles. Also a review of the current research in the field of automotive industry is presented and some conclusions for the future vehicle design using composites are suggested.

Keywords Natural fibres · Polymer matrix · Mechanical properties · Automotive applications · Manufacturing techniques

1 Introduction: A History of Natural Fibers in Automobile Sector

Natural fibers are easily and abundantly available in the environment. The use of natural fibers in matrix material for composite development is not a new area of research as in ancient days (in Egypt) people were using wheat straws as reinforcement in clay for increasing the strength of the material and built their houses

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and dwelling walls. Natural fibers are composed of a cellulose, hemicellulose, lignin, pectin etc. Lignin generally acts as a binder or can be treated as a matrix material. In year 1900 the natural fibers were recognized as a good application in the automotive sectors. Ultimately scientists of Ford motor company observed that soybean can be used for the extraction of the soy oil which again could be used for the production of a good-quality paint enamel and molded into a fiber based plastic. This gives around ten times more shock resistance as compared to steel. But the disadvantage of this material is that it takes too much time for curing and also it is very difficult to mold. The actual use or applications of the natural fibre were found in the later 1940s. That was the time of the World War II. During this world war there was a huge shortage of the aluminum arises. So the scientists were discovered the application of these natural fibers for the development of the various aircrafts parts such as seat belts, back rest, bearings and fuselages etc. The example of this fuselage was the Gordon–Aerolite, a unidirectional composites made by using Phenolic Resin as a matrix material reinforced with the unbleached flax yarns (Hughes 2002).

In the later years between 1950 and 1990, first car known as Trabant car was made in East Germany. They utilized the natural fibers for the development of this car. The matrix material used in this car was polyester resin and cotton fiber (natural fiber) was used as reinforcement in this matrix material.

Daimler Benz also introduced the use of natural fibers in the automotive sector in the later 1991. The subsidiary of Daimler Chrysler Mercedes-Benz headed a project namely “Beleem-Project” in South Africa’s Sao Paulo and utilized natural fibers such as coconut fibers in their commercial vehicles for a period of 9 years. Again in the late 1996 Daimler-Chrysler used Jute as natural fibers and used in making the door panels of their Mercedes E class vehicles. Also in year 2000, Daimler Chrysler started their plant and utilizes natural fibers for the production of vehicles in East London, South Africa and transfers their technology from German Plants to South Africa for the entire processing.

In European countries, from year 2005 to 2010, the use of natural fibers has increased from 70,000 to 100,000 tons in the automobile industries (Suddell and Evans 2005a, b).

In 2014 Van Eko Company utilized the natural fibers and makes an eco-friendly scooter Be.e. The various types of natural fibres such as Flax, Hemp, and even synthesized cellulose fibers are used for the development of the automotive components for scooter.

The shape of the exteriors of the scooters is hull shaped type, assuming be the stronger and also functions as the frame of the scooter.

This scooter was fitted with a 4 kW and 100 Nm motor placed in the rear wheel. The 1.9 kWh battery provides a range of 60 km at a top speed of 55 kph (van eko www.vaneko.com).

The natural fibers or cellulosic fibers can be classified into five common subgroups such as bast fibers, seed fibers, leaf fibers, fruit fibers and wood fibers. The same can be shown in Fig. 1 with some common examples of these fibers.

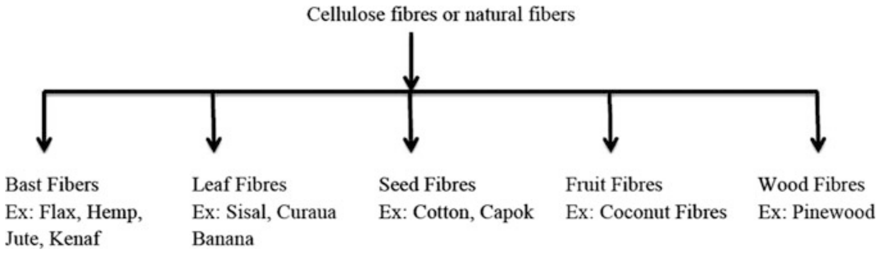

Fig. 1 Examples of natural fibres. Reproduced with permission from Elseveir Ltd. (Faruk et al. 2012)

(a) ***Flax Fibres***:

Flax fibers also known as Linum usitatissimum, generally comes under the category of bast fibres. This is termed as the oldest crop in the world and grows in temperate regions. The flax is most frequently used in the textile markets. At present the wide application of these fibers can be found in the areas of composite materials.

(b) ***Hemp Fibres***:

Hemp is the next significant fiber which comes under the category of bast fibers and cannabis family. This plant grows annually in temperate regions. At present Hemp is generally considered as an important subject of European Union Subsidy only for the non-food agriculture in Europe.

(c) ***Jute Fibres***:

Jute can be extracted from the plants of genus Corchorus, includes around 100 species. The jute fiber is considers to be one of the less expensive natural fiber available at present with the maximized production volume. The good growing conditions of the jute fiber can be seen in Bangladesh, India and China.

(d) ***Kenaf Fibres***:

Kenaf generally goes to the family of genus Hibiscus. Kenaf is generally observed as a potential raw material for its applications in composite materials products.

(e) ***Sisal Fibre***:

Sisal belongs to the family of agave (Agave sisalana) and commercially grew in Brazil and East Africa. But on the other side, between 1998–2000 and 2010 the demand for sisal fibers and its products decreased by an expected annual rate of 2.3%.

(f) ***Banana Fibres***:

The abaca/banana fiber, which can be extracted from the banana plant, is strong and resistant to seawater. Abaca, the strongest of the commercially available cellulose fibers, is locally available in the Philippines and in Ecuador. Banana fibers have good applications in marine.

Table 1 Chemical composition of some common natural fibers (Faruk et al. 2012)

Fibre	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Waxes (wt%)
Bagasse	55.2	16.8	25.3	–
Bamboo	26–43	30	21–31	–
Flax	71	18.6–20.6	2.2	1.5
Kenaf	72	20.3	9	–
Jute	61–71	14–20	12–13	0.5
Hemp	68	15	10	0.8
Ramie	68.6–76.2	13–16	0.6–0.7	0.3
Abaca	56–63	20–25	7–9	3
Sisal	65	12	9.9	2
Coir	32–43	0.15–0.25	40–45	–
Oil palm	65	–	29	–
Pineapple	81	–	12.7	–
Curaua	73.6	9.9	7.5	–
Wheat straw	38–45	15–31	12–20	–
Rice husk	35–45	19–25	20	14–17
Rice straw	41–57	33	8–19	8–38

(g) ***Cotton Fibre***:

Cotton is nearly pure cellulose, having properties such as softness and breathability which ultimately tuned it the world's most accepted natural fibre. The length and diameters of the fibres are varied from 10 to 65 mm, and 11 to 22 μ respectively. The other properties of the cotton fibres is the good moisture absorption which ultimately utilized in the production of cotton clothes (recommended to wear in hot weather), having high tensile strength and easily washable.

(h) ***Coconut Coir Fibre***:

Coir fibers are positioned between the husk and the outer shell of the coconut. Plentiful quantities of coconut husk suggested that the availability of labor and other inputs can adjust rapidly to market conditions and prices. It is calculated that around 10% of all husks are used for fiber extraction, fulfilling the increased demand for fiber and products made by coir fibers.

Table 1 represents the mechanical properties of the some common and important natural fibres (Faruk et al. 2012).

So based on the previous studies of natural fiber utilizations it is found that because of the easy availability, low cost and less weight, natural fibres are the good alternative to synthetic or man-made fibres. In this chapter the utilization of natural fibers in the automotive sectors has been elaborated. The various manufacturing techniques of composite development are also discussed in the present chapter. The mechanical properties of the developed automotive components have been included in the present chapter.

2 Basic Needs of the Materials Used in Automotive

The materials selection in the automotive industries is very important task as those materials have to satisfied some standard before approbation. Those standards are generally related to the environmental and safety issues and some of them are the need of the customers. However following are the different factors which can be considered for the basic requirement for the selection of the materials in automotive industries:

2.1 Less Weight

In present days increasing environmental issues such as greenhouse emissions and related air pollutions, it is very difficult for the automotive industries to achieve high fuel efficiencies with conventional or heavy weight automotive parts. Many research and development departments of the automotive industries, parts or component manufacturers, suppliers and assemblers are remarkably working together to make lightweight materials components. The objective behind the manufacturing of light weight material/component is to achieve high fuel efficiency in the transportation sector. Most of the companies or industries are focusing on the utilization of the lightweight materials and to get more market insight by manufacturing parts and different vehicle structures manufactured from lightweight materials. The only disadvantage of using lightweight materials is their high cost; this can be overcome by the development of the new manufacturing technologies and processes. In transportation sector, the reduction in fuel consumption and greenhouse gases can only be achieved by the reduction in weight of the materials. It has been noticed that the fuel economy (about 7%) can only be achieved by the reduction/elimination of weight (about 10%) from the vehicle's total weight. Now a days various research have been carried out by the automotive industries for the replacement of steel by aluminium, magnesium, composites and foams (Lotus Engg Company Report).

2.2 Cost

Cost is one of the most significant factor in automobile industries. The cost of a new material is comparable to the currently utilized material in a product. It is one of the most significant variables that decide the selection of new material for the vehicle parts or components. Cost basically involves three main components, these are: Existing cost of raw materials, manufacturing cost, and the design and testing cost of the product. It has been observed that the cost of Aluminum and magnesium alloys is greater than that of the existing materials such as steel and cast irons that they might substitute. As the improved performance or functionality of the material ultimately justified the selection of light metals by avoiding their higher.

2.3 Crashworthiness

Crashworthiness of the structure in the vehicle can be defined as the capacity to absorb impact energy resulting the safety of the passengers. The two significant safety factors that can be consider in the automotive industries are Penetration Resistance and the crashworthiness. Scientifically the crashworthiness can be further defined as the absorption of impact energy by different modes and mechanisms that give moderate deterioration during absorption. On the other hand the penetration resistance. On the other hand the penetration resistance dealt with total absorption without projectile or fragment penetration (Jacob et al. 2002). It has been observed that the present law for design of automobiles required that if an impact arises at speed up to 15.5 m/s with immovable object then the passenger in the compartment undergo a resulting force that ultimately produces a total deceleration more than 20 g (Jacob et al. 2002; Ghassemieh 2011).

Now days the automobile industries are focusing more and more towards the reduction of the weights of the automobiles which ultimately increases the fuel efficiency of the vehicles. This is only achieved by replacing the metal parts by polymer composites. It is also noticed that the behavior of failure in compression of the metal part is just opposite to the composites failure. From study it has been found that mostly composites are characterized by a brittle and not by ductile under the action of load. If we are talking about the failure mechanisms of the metal structures and composites it is found that they both are quite different with each other. As metal structures generally fails under crush or impact by buckling having substantial plastic deformation. On the other hand the composites failure takes a sequence of fracture mechanisms like fibre fracture, de-bonding of fibre–matrix, delamination and interplay separation. This is also observed that the failure mechanisms are mostly dependent on the structure, lamina orientation, crush speed and high energy absorbing mechanisms (Ghassemieh 2011).

3 Crashworthiness: A Safety Perspective

The main objective of the crashworthiness is to have an optimized or defect free vehicle structure which ultimately can absorb impact energy generated by controlled vehicle deformation and provides sufficient space so that the remaining crash or impact energy can be govern by restrain systems to lessen the loads transfer to the vehicle passengers. In actual form the collisions of vehicles are distinct dynamic occurrence where the vehicle may collide with the other vehicle of similar or dissimilar shape and mass and stiffness. There may be the case that vehicle may collide with the stationary objects like tree, pole etc. the safety experts describes and categorized the vehicle collisions as frontal, rear, side crashes etc. the reasons of vehicle crashes is due to the extensive range of speeds, impact with stationary objects such as when a vehicle hits a tree, or for few seconds as in rollover events.

3.1 Requirement of Crashworthiness

The following requirements for a range of occupant sizes, ages, and crash speeds for both genders:

- Should be deformable but stiff, front structure should have crumple zones that can absorb the kinetic energy resulting from frontal collisions and develop plastic deformations and block intrusions into the passenger's compartment specifically in the case of collisions with narrow objects such as trees etc.
- Should have deformable rear structure so that the robustness of the rear occupants compartment can be maintained and also the protection of the fuel tank.
- There should be perfectly designed side structures so that the intrusions from the side impact can be minimized which ultimately block the doors from opening caused by the crash loads.
- There should be well built roof structure for rollover protection.
- There should be some arrangements which can accommodate different chassis designs for various power train locations and drive configurations (Khalil 2014).

4 Reinforcements Used for Making Automobile Components

4.1 Glass Fibres and Glass Mats

Glass fibres are made by feeding molten glass bushings of platinum alloy. Generally the diameter of the filament is varied from 5 to 25 μ. The filaments are coated with a silane chemical "coupling agent". This is because coupling agent gives a strong bond between the glass and the polymer matrix and increased the reinforcing effect. There are various types of fibres are available as per the requirement such as E-glass fibres and R-glass for high mechanical performance, D-glass where high dielectric strength is required and AR-glass which is alkali and corrosion resistant. For the thermoplastics, the glass fibres can be distinguished as short fibres of less than 1 mm length and long fibres of 1–5 mm length for injection molding applications. Similarly for the compression molding, long fibres should be of 5–25 mm length and glass mat, 10 mm to infinite. On the other hand thermosets are reinforced with chopped strands, glass mat. Also for car applications (automotive), sheet moulding compound (SMC) or bulk moulding compound (BMC) are used. All of these products are known as composites.

4.2 Natural Fibres

Natural fibres are frequently used by a number of car producers such as Ford and Mercedes-Benz. These automakers have particularly flax, sisal or hemp as a replacement for glass fibre. Natural fibres ultimately lower the weights of the automobiles as the density is lower than conventional metals. Further, the most important factor to be considered is the environmental and ecological point of view. The famous automaker such as Ford Cologne lab has performed substantial experiments with flax-PP (Polypropylene) and found that this is approximately equivalent to GF-PP. To avoid discoloration the injection moulding temperature should be kept low. Audi Avant A4 utilizes flax-PP for the development of the hatch door cover. It has been observed that at low temperatures the product is not brittle at all. The same product has upgraded noise reduction and also 30% lower in weight than the GF-PP equivalent. On the other hand Johnston Controls supplies door trim panels to Mercedes Benz made by "Fibropur" natural fibre mat-PE composite. In this the fibres are a blend of 50% sisal and 50% flax. Similarly, SAI Automotive AG, Europe's leading system supplier of cockpits and doors, has made "Lignoprop", a blend or mixture of wood fibre and PP.

4.3 Aramid Fibres

These fibres are made from aromatic polyamides with a high amount of 1.4 chemical bonds right between the aromatic rings, provided additional linear molecules. The main manufacturers of fibres are DuPont with Kevlar and Akzo Nobel with Twaron. These expensive fibres have a very high strength and heat resistance and are generally used in bullet proof vests, ropes, performance tyres, e.g. trucks and reinforcement in car drive and timing belts. A good application of aramid fibres reinforced thermosets are found in aero plane construction. As aramid fibres are so expensive and no significant use is foreseen in car applications.

4.4 Carbon Fibres

The two main processes used for the manufacturing of these fibres are carbonization under exclusion of air and from pitch. It has been found that the carbon fibre have high strength fibre just like aramid fibre and are necessarily used as a plastic reinforcement in sport applications and in aerospace industry. The wide applications of these carbon fibres (CF) epoxy resins composites can be found in aeroplanes wing flaps and tail parts also the body parts of Formula 1 racing cars are made by CF-thermosets by using hand lay up techniques. The main manufacturers of these composites are Akzo Nobel in USA, Mitsubishi and Toho Rayon in Japan and Carbon in Germany.

4.5 Particulate Reinforcements

The reinforcement generally means to improve or enhance the properties such as mechanical properties of the material or plastics. The main mechanical properties that can be improved by the reinforcements are tensile strength, impact strength, stiffness, compression and many more. But these properties can only be improved if we reinforce the fibrous material into the matrix material. However the particulate reinforcement like talc, surface treated calcium carbonate (which improves the bond strength) presents a marked reinforcing results with polymer matrix (if it is a matrix material) which again improves the mechanical properties (Mann et al. 1999a, b).

5 Types of Polymer Matrix Used for Composite Development

5.1 Thermoplastic Matrix

Thermoplastic comes under the category of polymers and can be softened or melted by the application of heat. It can be processed either in the softened state or in the liquid state. As compared to the thermosets, another classification or category of polymers cannot be melted by the application of heat. However the thermoplastic polymers can be repeatedly processed by the application of heat and can be recycled for making new products. But it should be noted that repeated processing may cause degradation or failure in some of their properties. The various fabrication techniques used for the development of the thermoplastic parts are such as injection molding, blow molding, and thermoforming are detailed further in the next headings of this chapter. The main advantage of using thermoplastics is its recyclability. But additionally it has several other advantages over thermosets also. These are good ductility, good impact resistance etc. Thermoplastics can also be joined by using various types of welding processes such as resistance welding, vibration welding and ultrasonic welding. Also in regard to the processing time for thermoplastic parts is notably lesser than that for thermoset parts. The reason for this is that thermoset parts involves a cross linking chemical reaction in the mold, which, depending on the various parameters such as mold temperature and part thickness, may take several minutes to several hours for final processing. On the other hand processing of thermoplastics composites does not require any chemical reaction in the mold.

5.2 Thermosets Matrix

The main function of thermoplastic matrix is to transfer load from one fiber to the next. It affects the compressive strength and shear strengths of the composite material and contributes to the fracture resistance and energy absorption properties of the composite. Moreover, it shields the fibers from environment and controls the following properties of a polymer based composite.

- Chemical resistance
- Maximum temperature
- Moisture absorption
- Tolerance to fluids

The selection of matrix material also plays an important role and controls the processing aspects of polymer–matrix composite. The important processing attributes applicable for thermoset matrix resins are:

- Should have low initial viscosity which results good resin flow through the fibre bundles and provide good impregnation. This also removes the air and solvents from the bundles before the completion of the curing reaction.
- Should have fast curing for high productivity.
- Should have good fiber surface wettability, which can be enhanced by using fiber surface treatment.
- Low curing shrinkage.

It has been noticed that thermoset polymers generally used in the automotive industries are either polyester or vinyl ester resins. The epoxy resins certainly have better mechanical properties as compared to polyesters and vinyl esters, and are frequently used thermoset matrix in aerospace composites. Although, epoxy resins are more expensive and also the curing time for epoxies is too high (several hours). Because of this reason, epoxies are not generally considered as the main matrix material for automotive composites. The properties of polyester, vinyl ester and epoxy resins are given in Table 2.

Table 2 Properties of different resins

Polymer	Density (g/cm^3)	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at failure (%)	Coeff. of thermal expansion ($10^{-6}/^\circ C$)	Shrinkage (%)
Polyesters	1.1–1.43	2.1–3.45	34.5–103.5	1–5	–	5–12
Vinyl Esters	1.12–1.32	3–3.5	73–81	3.5–5.5	–	5.4–10.3
Epoxies	1.2–1.3	2.75–4.10	55–130	–	55–80	1–5

Because of low cost and simplicity in processing due to low viscosity and rapid cure time, polyesters are generally used for many automotive applications. On the other hand vinyl esters are just like polyesters in regard to their processing attribute, but more costly than polyesters. Their mechanical properties are also superior to the mechanical properties of polyesters. Both polyesters and vinyl esters showed greater mold shrinkage than epoxies and both also have superb moisture resistance as compared to epoxies (Mallick 2010).

6 Manufacturing Technologies Used for Composite Fabrication (Automotive Components)

6.1 Thermoplastic Processing Techniques

6.1.1 Injection Moulding

Injection Moulding Process is related to pressure die casting technique, and used where the precision and accuracy of the parts is prerequisite. This process is basically used to make the parts or components by using thermoplastics polymer but after certain modification, the same process can be used to make the components or parts made by thermosets polymer. In this technique thermoplastic granules are first melted and then injected into steel or aluminum dies. After melting resin achieved highly viscous state and at that time a high moulding pressure is required for injection. The main benefits of injection moulding technique is short cycle times, complex shaped components can be easily made by this technique, superior dimensional tolerances and finishing etc. At present this technique is fully computerized and robotically controlled. On the other hand if we talk about the disadvantages of the process then we found that this process highly expensive, required longer lead times for making moulds, used complex machineries. The Computer-aided engineering can be used for the reduction in the lead times.

6.1.2 Extrusion

Extrusion is the process in which the molten material (polymer) is forced through a die for the production of the sheets, films, hoses, sheaths etc. This technique comes under the category of continuous production and has good economic benefits. Now extrusion becomes fully computer controlled with various functions and parameters such as drying temperatures, pressure and temperature, delivery rate. This process involves or used different types of extruders such as single screw extruder and twin screw extruders which are used to compressed and removes the air entrapped between the polymers.

6.1.3 Blow Moulding

Blow moulding technique used a shaped mould and involves the blowing of a thermoplastic into tube shape. This process is generally used to make hollow items such as, tanks, containers etc. This process gives maximum flexibility in the shapes that can be produced. This process involves a low mould cost. But on the other side it has been observed that the finishing of the articles or items made by this process is poor. To remove this disadvantage, the design team is working on this. This process can be utilized to make multi-layer items. The main application in which this process is suitable is the manufacturing of the fuel tanks.

6.1.4 Thermoforming

This process requires heating material in the form of sheet then takes it to a mould and forming it by the application of the vaccum from inside the mould. This process incorporates very low tool costs, swift set-up and economic short runs. This process is also suitable for the production of layered laminates of different materials. The main demerits of the system include longer cycle times, lower dimensional accuracies. However the advancement in the system in process control provides good dimensional accuracy and stability or regularity in finishing. Thermoforming process is economic and can be used for runs of 200–10,000 units. It has been observed that the machine costs involved in this process is just the half of comparable injection moulding process.

6.1.5 Foam Moulding

Foam moulding also known as steam chest moulding is generally used to manufacture bumper cores, sun visors, door energy absorbing foam and head-rest cores by utilizing expanded polypropylene pellets. In this process, Polypropylene pallets are first blown into the mould. After this a steam is injected into the system which makes a rigid PP structures. The mould is only opened after the required cooling actions. The aluminum moulds are generally used in this technique as they are relatively cheap than others.

6.2 Thermoset Processing Techniques

6.2.1 Contact Moulding

Contact molding generally consists of the two main processes such as hand lay-up and spray-up process. These can be defined as follows:

6.2.2 Hand Lay-up

In this process firstly a mould release agent is generally applied on the walls of the mould after that a coating of gel is applied on this and allow it to cure. After this staggered layers of resin and chopped strand mat (CSM) are applied. On the other hand, woven mats can also be applied alternatively with layers of CSM. After processing for several hours, the same piece should be detached from the mould. In this process no pressure is used and the moulding only has one smooth surface. As this process is very slow and rigorous, large and complexed shape materials can be made with smaller limitation on size. The application of this process is to mould short-run car bodies, especially monocoque designs.

6.2.3 Spray-up

This is another contact moulding process, which provides maximum production rates as compared to the hand lay up process. In this process, catalysed and accelerated resin and chopped glass rovings are sprayed simultaneously, with a fixed amount of peroxide catalyst, onto the gel-coated mould surface. This process can be repeated till a layer of the required thickness has been achieved. It has been noticed that both processes, mainly hand lay-up, are slow which is a demerit in long runs. Also as these processes are open mould process, so there may be a chance of the emission of styrene fumes. Nevertheless this can be overcome by using satisfactory ventilation system or low smoke resin systems. Contact moulding processes are sometimes experiences in small run models (e.g., racing cars) and in prototype work.

6.2.4 Compression Molding

Compression moulding generally requires high pressure moulding of sheet moulding compound (SMC). In this process, SMC is provided as a rolled sheet of material, in which glass fibres with upper and lower release film are separated from the each layers of resin. The resin may be Polyethylene etc. The amount of filler content can be limited to 60%. In this system, the material is filled into two steel die surfaces. The hot mould should be closed and requisite pressure is applied so that the SMC can flow into the mould and cure and sufficient strength can be achieved after opening the mould. To achieve uniformity in die matching, a good technical development is needed. It has been observed that the SMC mouldings surfaces are even on both faces and present almost no glassy structure (Mann et al. 1999a, b).

6.2.5 Resin Transfer Molding (RTM)

RTM is generally used for the manufacturing of automotive and aircraft components. In this process, the fibre reinforcement, either long or woven fibres are firstly cut out by using a knife or scissors. The reinforcements are generally known as the preforms are reinforced into the thermoplastic binder and then placed it inside the mould cavity in the closed mould process. After that the resin is being transferred into the mould cavity by means of pressure or vacuum. The resins that are particularly used in this process include polyester, epoxy, vinyl ester, and phenolic (Verma 2015).

6.2.6 Filament Winding

Filament winding is an automated composite fabrication process which involves winding of resin-impregnated fibre or tape around a mandrel to achieve the desired shape. In this process the continuous reinforcement of fibres which passes through a batch of resin to a feeding head and winds around a mandrel of suitable design. The curing of the mandrel is achieved by heating it in an oven or by infrared radiation. Process parameters which are generally considered in this process includes exact filament tow, longitudinal placement, and mandrel winding speed (Mann et al. 1999a, b).

7 Mechanical Properties of Natural Fiber Composites as Automotive Components: A Past Research

It has been observed from the last few years that so many researches were carried out in the field of the use of natural fibers in composites as load bearing components (Du et al. 2012; Akil et al. 2011; Summerscales et al. 2010; Joshi et al. 2004). The credit of the utilization of natural fibers in composites goes to their high strength, cost effectiveness, availability and recyclability.

Natural fibres represents a prospective as a substitution of inorganic fibres like glass fibres, aramid fibres etc. in automotive components like dashboards, door panels, seat cushions and cabin linings (Jacob and Thomas 2008; Koronis et al. 2013; Ashori 2008). Mercedes-Benz utilizes epoxy matrix system with the reinforcement of jute fibers in the door panels in their E-class vehicles (Suddell and Evans 2005a, b).

Wambua et al. (2003), investigated the mechanical properties of different type of natural fibers such as, sisal, hemp, coir, kenaf and jute reinforced polypropylene composites. It has been observed that the tensile properties such as tensile strength and modulus values increased by increasing fibre volume fraction. They also compared the mechanical properties of the natural fibre composites with glass mat polypropylene composites. After comparison it is found that certain properties of the natural fibre composites were superior to those of glass reinforced composites. Based on this it is advised that natural fibre composites have ability to replace glass in those applications where very high load bearing capabilities are not the prerequisite.

The utilization of natural fibres or bio-fibres in automotive components is supposed to improve by 54% per year (EU 2002 Annual Report). Some types of strong, lightweight and cheap natural fibres are come together and replace glass fibre reinforced polymers specifically in interior applications. In general the application part of the natural fibre reinforced polymers is found in door panels, seat backs, headliners, package trays, dashboards etc. There are so many research review papers published by researchers which describe the reinforcement of the natural fibres in polymer matrix and recognized as green composites (Koronis et al. 2013; La Mantia and Morreale 2011; Zini and Scandola 2011). These review papers described the mechanical properties of various natural fibers and their composites. They also discussed that how natural fibers are superior than synthetic fibers from the environmental point of view.

Koronis et al. (2013) discussed the possible utilization of bio fibres/natural fibres composites for automotive applications. They have demonstrated that natural fibre reinforced composites have good mechanical properties as compared to synthetic fibre reinforced composites.

Davoodi et al. (2012) reviewed the literature on bumper design and delivered the optimal bumper beam design process. The main focus of the design process is based on the important parameters needed in the design of bumper beam and their most satisfactory values. The outcome of this research can help designers and researchers who are working in the field of bumper beam design and analysis. The design process includes a hierarchy which consists of the conceptual design phase. In this phase various properties of materials and their processing was discussed. These are further considered in the later stage to confirm the performance of the final product. The various factors that should be considered in the material selection of the bumper design are safety regulations, cost effectiveness, performance improvement and reliability. Figure 2 shows the bumper beam design process.

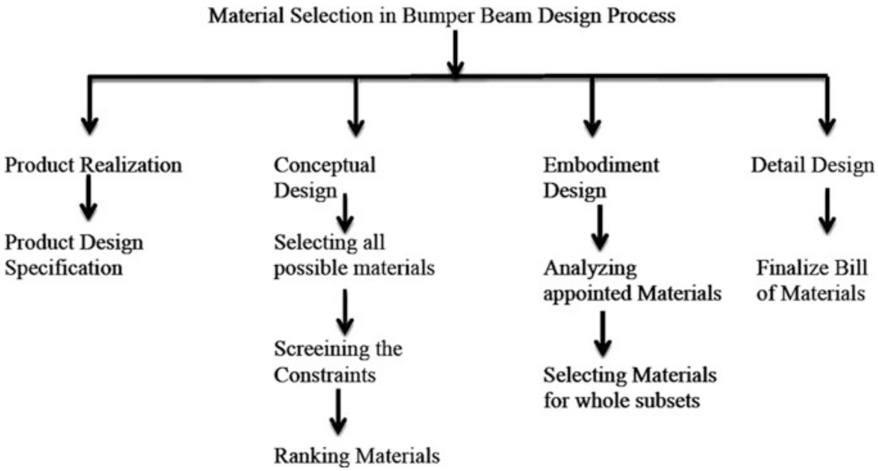

Fig. 2 Bumper beam design process. Reproduced with permission from Elseveir Ltd. (Davoodi et al. 2012)

Ahmad et al. (2014) reported that BMW Company used natural fiber composite since the early 1990s in various models such as 3, 5, and 7 series models. They utilized up to 24 kg of renewable materials in their models. On the other hand BMW utilizes 4 000 tons of bio fibers in their BMW M3 series in 2001. They mainly concentrated on the flax fibres i.e. they utilizes 80% flax fibres in combination with 20% sisal for the improvement in impact resistance. The main application of natural fibre reinforced composites was found in interior door linings and paneling. The applications of Wood fibers were found in seat backrest. The inner board of the door panel of BMW M7 series was made by press molding technique by reinforcing natural fibers in Polypropylene matrix. The application of this composite was found in inner board of the door panel of a BMW M3 series. On the other side Bast fibres were also used in the door panels of the BMW M5 series.

Marzbanrad et al. (2009) used three materials such as aluminum, glass mat thermoplastic (GMT) and sheet molding compound for the development of front bumper beam. The impact modeling was carried out for the determination of the deflection, impact strength and stress distribution. The comparison was made based on the mentioned characteristics for the selection of the best materials, their shape and thickness. They concluded that modified SMC bumper beam minimizes the deflections in bumper beam and stress distribution and maximizes the elastic strain energy.

Notable differences in impact velocities were observed among magnesium, steel and aluminum bumpers and showed by Figs. 3, 4 and 5. From study it has been observed that in case of aluminum bumper the difference between impactor velocity and vehicle velocity will be maximum as compared to magnesium bumper. This means that the maximum kinetic energy will be transferred from the impactor to the vehicle.

Hosseinzadeh et al. (2005) suggested that composite structures are generally reduce the weights of the passenger cars and making vehicles more fuel efficient. They observed that the Bumper beams are the main structures of the passenger vehicles from the safety point of view which ultimately protect them from the

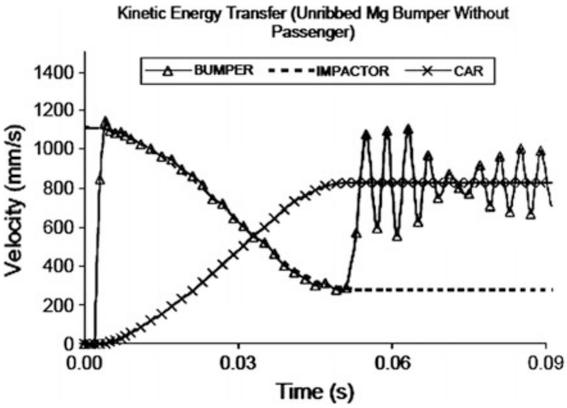

Fig. 3 Kinetic energy transfer in magnesium bumper (Marzbanrad et al. 2009)

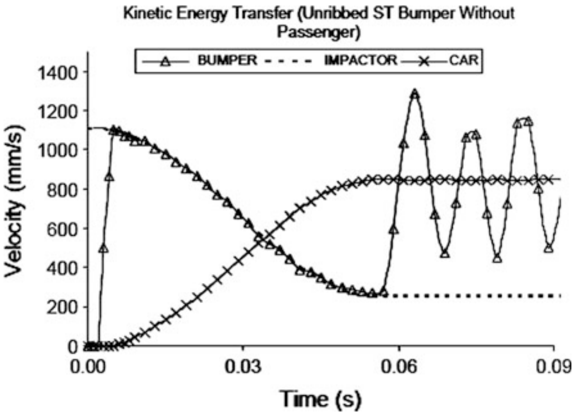

Fig. 4 Kinetic energy transfer in steel bumper (Marzbanrad et al. 2009)

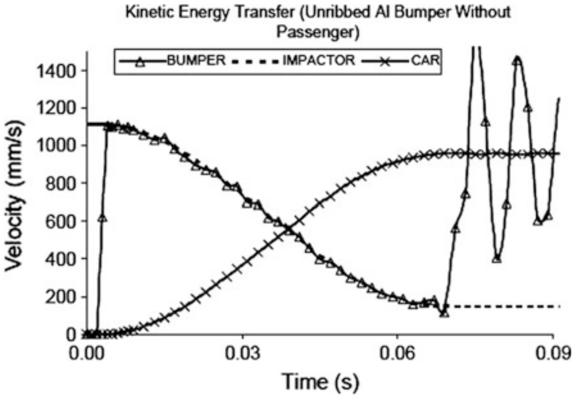

Fig. 5 Kinetic energy transfer in aluminum bumper (Marzbanrad et al. 2009)

collisions i.e. front and rear collisions. They have made a front bumper by utilizing glass mat thermoplastic matrix material and then model them by using the various software available by using LS DYNA ANSYS 5.7 according to the E.C.E. United Nations agreement.

The GMT bumper was fabricated by using short fiber glass fibers. The size of the fibers was maintained as 12–25 mm long. These fibers were then mixed/reinforced with the thermoplastic resin. The GMT bumper used in this research is a structure made from short fiberglass fibers, 12–25 mm long randomly mixed with thermoplastic resin. The thickness of the fabricated Glass Mat Thermoplastic sheets is 1-mm with different fiber mats such as continuous, randomly laid, unidirectional and mixtures of these arrangements with particular attributes (Glass Mat Reinforced Thermoplastics Processing Guidelines). About three to four arbitrary laid chopped fibre sheets are positioned in a die and heat formed by a press. After this the molten resin ultimately flows in the cavities of the dies and take its shapes. The main purpose for the use of thermoplastic resin is because of their facileness in melting and recycling properties. On the other hand loose tolerance in manufacturing bound their uses in places where good accuracy is the prerequisite. To stop the deflection of the lateral surfaces (which ultimately make the structure rigid), the ribs or strengthening plates of thickness 5 mm were placed in the vertical direction. These ribs are formed in the concave cavities of the dies and makes die design complicated. Figures 6, 7 and 8 showed the observation of the kinetic energy and linear conservation. The observation in this case generally termed as the impact velocities between "with passengers" and "without passengers" conditions. It is generally observed that the impactor weight is equal to the car weight without passengers, therefore its velocity becomes zero as car reaches the initial velocity of 4 km/h. on the other hand if we considers the car with passengers, the impactor is unable to transfer the momentum completely to the structure weighing more (see weights in Table 3).

Ashori (2008) suggested that the Wood–plastic composite (WPC) is a very favorable and feasible green material to attain endurance without any toxic chemicals. The wood plastic composites was termed as a composite which is composed of by utilizing natural or plant fibres as reinforcement in the polymer

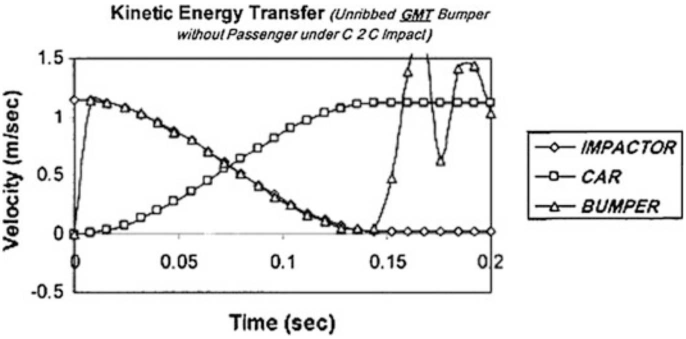

Fig. 6 Kinetic energy conservation in GMT bumper (Hosseinzadeh et al. 2005)

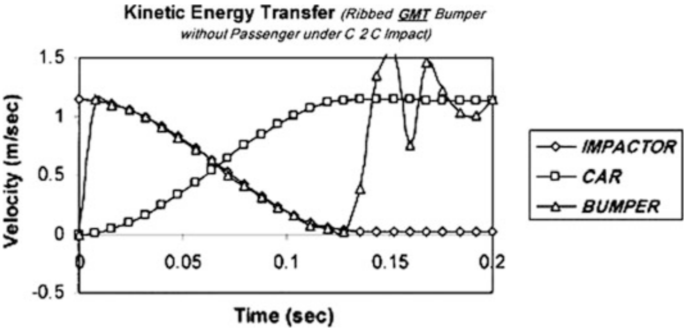

Fig. 7 Kinetic Energy Transfer (Ribbed GMT Bumper without passenger under C2C impact)

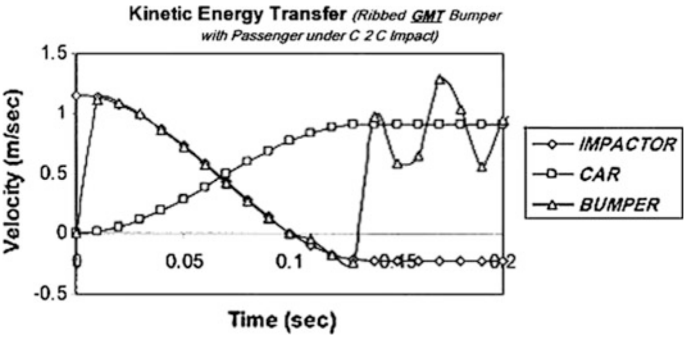

Fig. 8 Kinetic Energy Transfer (Ribbed GMT Bumper with Passenger under C2C impact)

Table 3 Material properties of the model (Hosseinzadeh et al. 2005)

Material	E (GPa)	υ	Sy (MPa)	ρ (kg/m^3)
Steel	210	0.3	700	7850
Aluminum	70	0.33	480	2710
GMT	12	0.41	230	1280
SMC	20	0.33	309	1830
PEP	1.2	0.4	27	900

matrix materials such as thermosets or thermoplastics. The advantage of utilizing natural or plant fibres to reinforce plastics is that as these are having high strength, high stiffness, less cost, low density and biodegradable in nature, and renewable annually. As in present scenario automobile manufacturers are focusing on recyclability and biodegradability of the parts, so we can find good scope of green composites in the field of automobile sectors.

There are so many automobile manufacturers are available in the market utilizes natural or plant fibres for making automotive components such as: Audi, Opel, Daimler-Chrysler, Fiat, Ford, Mercedes Benz, Renault, Volvo, BMW etc. (Bismarck et al. 2006). The specified amounts of plant fibers used for different applications in the automotive industry are as follows (Ellison and McNaught 2000):

- Front door linens: 1.2–1.8 kg.
- Rear door linens: 0.8–1.5 kg.
- Boot linens: 1.5–2.5 kg.
- Parcel shelves: up to 2.0 kg.
- Seat backs: 1.6–2.0 kg.
- Sunroof sliders: up to 0.4 kg.
- Headliners: average 2.5 kg.

8 Natural Fibre Composite Applications in Automobile Sector

Natural fibers can be derived from agricultural plants and are frequently used for making ropes, hand bags, etc. Natural fibres can be classified into three groups: (i) bast fibers, e.g. flax, hemp, jute and kenaf, (ii) leaf fibers, e.g. sisal, pineapple and banana, and (iii) seed or fruit fibers, e.g. cotton and coir.

8.1 *Interiors of Automotive*

The German automotive industries such as BMW, AUDI and Daimler Chrysler are the first industries which utilizes the applications of natural fibres in the automotive parts or components. Now, almost all automobile industries or manufacturers integrate natural fiber composites in their automotive components. At present the German industries are the superior in utilizing natural fibres in their automobile sectors. Table 4 shows the applications of the natural fibre composites used by the major automobile tycoons of Germany such as DaimlerChrysler, Mercedes, Volkswagen Audi Group, BMW, Ford, and Opel (Suddell and Evans 2005a, b). DaimlerChrysler, a major manufacturer of automobile sector, targeted to use

Table 4 Automotive manufacturers, car models, and components utilizing natural fibers (Suddell and Evans 2005a, b)

Automotive manufacturer	Model and applications
Audi	A2, A3, A4, A4 Avant, A6, A8, Roadster, Coupe: seat backs, side and back door panel, boot lining, hat rack, spare tyre lining
BMW	3, 5 and 7 series and others: door panels, headliner panel, boot lining, seat backs
DaimlerChrysler	A, C, E and S-series: door panels, windshield/dashboard, business table, pillar cover panel
Fiat	Punto, Brava, Marea, Alfa Romeo 146, 156
Ford	Mondeo CD 162, focus: door panels, B-pillar, boot liner
Peugeot	New model 406
Renault	Clio
Rover	Rover 2000 and Others: Insulation, rear storage shelf/panel
Saab	Door panels
SEAT	Door panels, seat backs
Vauxhall	Astra, Vectra, Zafira: headliner panel, door panels, pillar cover panel, instrument panel
Volkswagen	Golf A4, Passat, Bora: door panel, seat back, boot lid finish panel, boot liner
Volvo	C70 V70

Table 5 Well-established interior automotive components utilizing natural fibers (Suddell and Evans 2005a, b)

Automotive component	Typical weight of fibres (kg)
Front door liners	1.2–1.8
Rear door liners	0.8–1.5
Boot liners	1.5–2.5
Parcel shelves	<2

maximum amount of natural fibres in their vehicles or cars. Johnson Controls Inc., manufactured the interior components like dashboards and door panels by utilizing natural fibres in polypropylene matrix exclusively for the DaimlerChrysler (Controls 2000). Currently the utilization of the natural fibres in the automobile industries such as BMW are limited to about 8–13 kg per vehicle however the limitation of use of natural fibres in Ford company is from 5 to 13 kg per vehicle (Taylor 2002).

Table 5 showed the applications of natural fibres (by weight) for making automotive components. The main difference between the American market and the European market lies in the use of wood and Kenaf which effectively grows in United States. In year 2000, Audi launched a light weight car manufactured by all-aluminum body and their door trim panels were manufactured by polyurethane reinforced with flax or sisal fibre mat. These panels not only showed extremely low mass per unit volume but also have very high-dimensional stability.

8.2 *Exteriors of Automotive*

The German company namely DaimlerChrysler has expand its research and development speculation in flax-reinforced polyester composite for exterior or semi exterior applications (Automotive Industries 2000). A truck with flax-based exterior skirting panels is now in production. Tests performed by the DaimlerChrysler Research Centre, Germany showed that these composite components resist impact without breaking into fragments, which is a main crash worthiness test of vehicles. It has also been noticed that the developed composites are weather resistant. In Germany, by considering the environment point of view car producers are targeting to manufacture each and every part of their vehicles either recyclable or biodegradable. The research scientists at DaimlerChrysler made the exterior components of the vehicles that must be able to resist extreme such as exposure to wetness and chipping. The first use of natural fibres for making standard exterior components is flax-reinforced engine/transmission cover of the Mercedes-Benz Travego travel coach. The benefit of using natural fibres includes a 10% weight reduction of the engine/transmission cover and a reduction in cost of around 5%. At present the inclusive use of natural fibers such as flax, hemp, and kenaf are growing at the fastest rate. On the other hand the use of jute and sisal is actually decreasing. Flax, hemp, and kenaf are used frequently due to their outstanding combination of economic and functional properties.

9 Advantages of Natural Fiber Composites in Automobile Sector

The natural fibres showed considerable advantages as compared to conventionally used glass fibers in the automotive sector. The significant feature here is that these advantages are achieved without a particular change in material functional performance like degradation of their mechanical or acoustic properties. The most important advantages include:

- Cost effective: The cost of natural fibers are between 25 and 50% lesser than glass fiber composites.
- Weight reduction: It has been noticed that the weight of injection-molded ABS car door panels is 9 kg however the same panels manufactured by natural fibers weigh only 5 kg with same mechanical properties.
- Light weight (less than half the density of glass fibers): This is also an important environmental benefit as ~85% of energy usage is when a vehicle is being driven. Plant fibers have a maximum density of 1.5 g/cc (that of cellulose), which results in high specific strength and stiffness and hence low component weight.
- Safer: Safer crash behavior.
- Good acoustic properties.
- Good thermal insulation.
- Identical strength values to glass fiber composites.
- Displayed outstanding formability.
- Natural fibers are superior to glass fibers from a health point of view.
- Abundantly available worldwide.

The main reason for the utilizations of natural fiber composites is the cost and weight. Although, natural fibers also showed considerable environmental benefits as compared to glass fibers, which includes:

- Ecological sustainability.
- Less energy requirements for production.
- End of life disposal. Can be composted at the end of their life.
- Carbon dioxide neutrality. As natural fibers are derived from plants and plants ultimately have carbon dioxide neutrality properties, i.e., carbon dioxide do not recur into the atmosphere when they are combusted.

Technically natural fibers do not have good mechanical properties as compared to synthetic fibres. Natural fibres showed variations in strength properties. This depends upon the regions where they have grown, which is not noticed with synthetic fibers. However, natural fibres showed only half the density of synthetic fibres.

10 Disadvantages of Natural Fiber Composites in Automobile Sector

The prospective of natural fibre as a reinforcement is substantially declined by its hydrophilic nature which is an unavoidable disadvantage and the lack of adhesion ability between natural fibers and the matrix materials being employed (Van de Weyenberg and Verpoest 2002). In this regard, notable efforts are currently being administered towards enhancing the mechanical properties of natural fiber-reinforced composites through optimization of the adhesion strengths between the natural fibers and the polymer matrix (Thomas 2002). As we can see there are various types and qualities of the natural fibres available in the world. These varieties or qualities are mainly depends upon the growing conditions of the environment. Also another drawback of these fibres are their processing techniques which ultimately affects the technical application part of these fibres into matrix (breakage of the fibre or crack development in the fibre after retting or processing). The natural fibers also showed reduced impact strength, which ultimately a result of a fiber defects present into the material during the growing or fibre processing stages.

11 Conclusion/Summary

Globally many researchers are following the useful applications of the natural fibres in the composites applications on a very large scale. As an outcome, most of the parts/components for the automobile industries are now manufactured by using natural fiber reinforced composite materials. The main matrix materials utilized for the development of these composites are Polypropylene and Polyester matrix. The important natural fibres utilized by automotive industries are flax, hemp, and jute fibres. At present the inspiration of using these fibres has been marketing and cost instead of technical needs. Accordingly, the end products are restricted to lesser strength interiors automotive parts. The main disadvantages of these materials are hydrophilic (due to the use of natural fibres) and lower impact strengths. Although, many efforts are being carried out to enhance the mechanical properties of these materials in such a manner that they can be utilized in exterior components which generally require high impact strength and become hydrophobic in nature. Ultimately the truth is, the use of natural fibres experiencing high level revolution and also have a potential to replace synthetic materials.

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Polylactic Acid Green Nanocomposites for Automotive Applications

Reza Arjmandi, Azman Hassan and Zainoha Zakaria

Abstract In the past decade, a growing interest in the use of green nanocomposites in industrial applications has been observed because of many advantages such as biodegradability, renewability and their relatively low cost to substitute the conventional petroleum-based polymers. The nanocomposites based on polylactic acid (PLA) have the potential to be used in automotive applications due to good mechanical properties and processability. This chapter highlights the recent developments on PLA nanocomposites as potential materials for automotive applications. One of the common methods to improve the performances of PLA is the combination of PLA with various nanofillers including layered silicates and carbon derivatives such as graphene and carbon nanotubes. Mechanical and thermal properties are the focus of this chapter as the properties are important for automotive applications. Further research in this area is also being proposed.

Keywords Polylactic acid · Green nanocomposites · Automotive applications · Montmorillonite · Carbon nanotubes · Graphene nanoplatelets · Mechanical properties

1 Introduction

Composite materials are formed by combining two or more materials to improve performance of their original components. When one or more of the materials derived from biological origins they are defined as green composites (Fowler et al. 2006; Arjmandi et al. 2015a, b, c, d). The increasing demand for eco-friendly

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materials, soaring prices of petroleum based plastics, increasing depletion rate and pressing environmental regulations have all triggered a growing interest towards the field of green composites (Netravali and Chabba 2003; Khalil et al. 2012). The composites deriving from renewable resources bring very promising potential to provide benefits to natural environment due to reducing petroleum resources. The shift to more sustainable constructions in automotive industry is an initiative towards a more viable environment and cost efficiency.

Renewable composite materials have been extensively used in interior and exterior automotive applications such as door panels, dashboards, seat cushions, and cabin linings (Herrmann et al. 1998; Koronis et al. 2013). Many studies have been conducted on natural based materials from forestry feedstock and agricultural crop by-products but the use of these materials has not been widespread. Future market of green nanocomposites depends on their production cost which need to be competitive with present thermoplastics used in automotive applications. The use of nanocomposite materials is expected to reduce the auto-body weight of vehicles by approximately 40–55 and 25–30% compared to current similar sized aluminum and optimized steel auto-body, respectively (Davies 2012; Koronis et al. 2013). Mass reduction of automotive application is an important issue especially for the future electrical vehicles to maximize their battery’s weight and capacity while at the same time reducing the total weight.

Recently, polylactic acid (PLA) has attracted the attention of polymer scientists and leading position on the market of biobased polymers as a most promising potential biopolymer to substitute the conventional petroleum-based polymers. The high interest for PLA is mainly due to its interesting physical and mechanical properties, recycling possibility and biodegradability, low carbon footprint and broad possibilities of processing using different methods (Drumright et al. 2000; Vink et al. 2003; Nampoothiri et al. 2010; Auras et al. 2011). Figure 1 shows the life cycle of PLA. Nowadays, PLA is receiving considerable attention for some specific utilizations such as sustainable packaging materials or production of fibers. Recent trends and forecasts also reveal that PLA is more appealing for durable applications such as automotive, electrical and electronic products and mechanical components, which require high performance materials and low environmental impact (Lim et al. 2008; Notta-Cuvier et al. 2014; Notta-Cuvier et al. 2015).

In automotive industry, the use of polymers significantly increased over the last few decades due to their numerous advantages such as being lightweight, good thermo-mechanical properties, durability and superior corrosion resistance, easy processing and relatively low cost. Nowadays, due to increasing environmental consciousness, the use of PLA in automotive industry is undoubtedly appealing. Figures 2 and 3 shows the use of PLA in Röchling Automotive’s air filter box and interior trim parts, respectively (Maruschke 2016). However, some performance of PLA such as thermal and hydrolysis resistance, ductility, impact strength and crystallization rate have to be improved for PLA to compete with conventionally used polymers in automotive applications (Raquez et al. 2013). For this purpose, PLA can be combined with different dispersed phases such as micro- and nano-fillers, plasticizers, impact modifiers or other polymers and additives

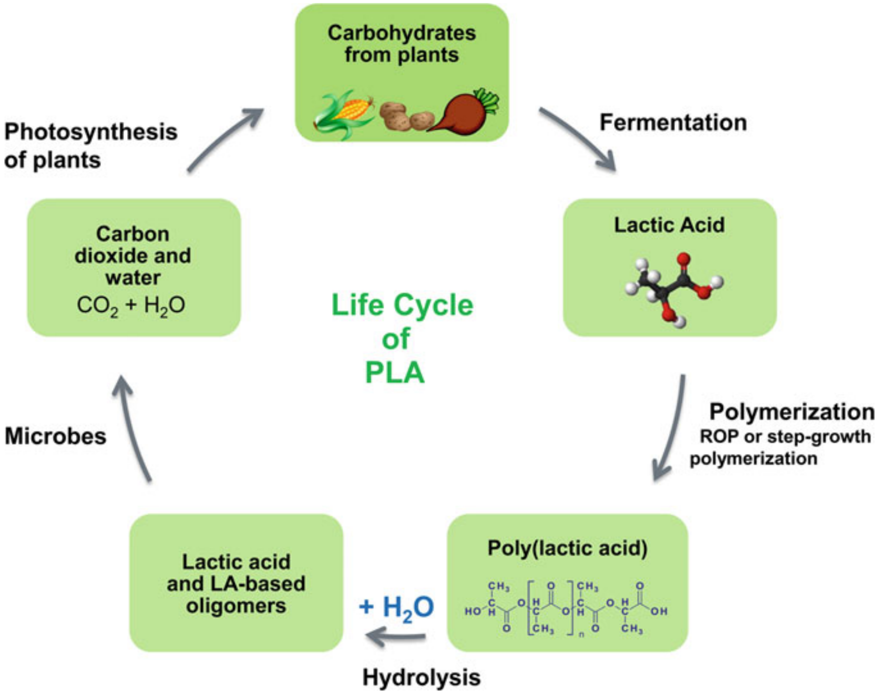

Fig. 1 Life cycle of PLA

Fig. 2 PLA used for Röchling Automotive's air filter box (Maruschke 2016)

Fig. 3 PLA used for an interior trim supplied by Röchling Automotive (Maruschke 2016)

(Dubois and Murariu 2008; Anderson et al. 2008; Murariu et al. 2008; Notta-Cuvier et al. 2014).

Several literatures have shown that PLA has improved its properties in terms of thermal stability, stiffness, rigidity and crystallization enhancement for highly loaded parts in automotive applications by combining PLA with various nanofillers such as layered silicates, carbon nanotubes (CNT) and graphene nanoplatelets (GNP) (Sinha Ray et al. 2002; Goffin et al. 2007; Murariu et al. 2010; Bourbigot et al. 2011; Murariu et al. 2011). This chapter focus on green nanocomposites manufactured from PLA for automotive applications. The mechanical, thermal, morphological and electrical performances of PLA nanocomposites were investigated in order to determine its suitability for automotive applications.

2 Polylactic Acid Green Nanocomposites: Single Filler

2.1 Polylactic Acid/Montmorillonite Nanocomposites

Recently, preparation of PLA nanocomposites with organically modified layered silicate as nanofillers have been extensively investigated because they often exhibit considerable improvement in mechanical, thermal, optical and physical properties at low filler content (Hong and Kim 2013). PLA/layered silicate nanocomposites have been shown to exhibit increased tensile strength and Young's modulus compared to neat PLA (Sinha Ray and Okamoto 2003). Montmorillonite (MMT) is the most commonly used layered silicate in this respect. Nam et al. (2003) studied the morphology and detailed crystallization behavior of neat PLA and PLA/MMT nanocomposites. They found that the overall crystallization rate of neat PLA was enhanced after the incorporation of MMT into PLA. Lee and co-workers (2003) also reported that the crystallization temperature (T_c) of PLA/MMT nanocomposites decreased by incorporation of MMT nanofiller. The researchers have reported that the MMT could act as effective nucleating sites for crystallization of PLA due its large surface area (Nam et al. 2003; Lee et al. 2003).

Chang et al. (2003a) reported on nanocomposites made from PLA with three types of MMT (C16–MMT, dodecyltrimethyl ammonium bromide-MMT (DTA-MMT) and Cloisite 25A) using solution intercalation method. The reinforcement effect of the MMT content on the mechanical and morphological properties of PLA nanocomposites were investigated. The results showed that these properties are depend on the type and amount of MMT in the PLA matrix. From morphological studies, they found uniform dispersion of MMT in the PLA matrix, although some clusters or agglomerated particles were detected. Tensile properties of the PLA nanocomposites film initially increased and then decreased with increasing of the MMT fillers compared to neat PLA. In another study, Di et al. (2005) successfully obtained fully exfoliation MMT in PLA matrix due to the good interfacial interaction between the MMT and PLA matrix. The strong interaction between MMT and PLA matrix due to their high surface area, resulted in reduce molecular mobility of PLA. Petersson and Oksman (2006) also reported a significant improvement in tensile modulus and yield strength of PLA/MMT nanocomposites by incorporation of 5 wt% MMT due to good interaction between MMT and PLA matrix. They concluded that good interaction between nanofillers and PLA matrix in nanocomposites allowed good stress transfer from matrix to the nanofillers which resulted in significant improvement in mechanical properties. In our recent publications, the effect of MMT on tensile and morphological properties of PLA nanocomposites were also investigated (Arjmandi et al. 2014; Arjmandi et al. 2015a, b, c; Arjmandi et al. 2016). Based on the tensile strength, the optimum MMT content was achieved at 5 parts per hundred resin (phr) which is approximately 30 MPa. In addition, good dispersion of MMT nanoparticles was achieved at optimum MMT content. However, the agglomerations were observed at high concentration of MMT (>5 phr), which resulted in decreased tensile strength. These studies show that only a small amount of nanofillers is needed to bring about similar improvement to the properties of PLA compared to using micro-fillers.

Mechanical, thermal and morphological properties of PLA/MMT nanocomposites fabricated by two different methods (melt and solution intercalations) reported by Shyang and Kuen (2008). The results showed that the mechanical properties of PLA/MMT nanocomposites produced by solution interaction is relatively higher compared to melt interaction method, which indicated better dispersion of MMT in PLA matrix using solution interaction. In addition, the results confirmed intercalated of PLA in between the intergallery of MMT. Furthermore, the incorporation of MMT into PLA matrix did not influence the glass transition (T_g) and melting temperature (T_m) of PLA nanocomposites as shown by differential scanning calorimetry (DSC). However, Nam et al. (2003) and Lee et al. (2003)

reported that the addition of MMT into PLA matrix decreased the T_c of PLA. In another study by McLauchlin and Thomas (2009), cocamidopropylbetaine (CAB) modified MMT (CAB-MMT) reinforced PLA nanocomposites using solution casting was produced. They found that the CAB-MMT have similar thermal stability to a commercial MMT that has been reported to be compatible with PLA. Thermogravimetric (TGA) analysis showed that the thermal stability of the PLA/CAB-MMT nanocomposites are depended on the CAB-MMT content, which the highest thermal stability obtained at 4 wt% of CAB-MMT content. In addition, Huang et al. (2010) reported an intercalated structure of PLA/MMT nanocomposites with improved thermal stability.

He et al. (2011) successfully prepared PLA/MMT nanocomposites by masterbatching and in-situ polymerization process. Melt index test indicated that the nanocomposites had better processability compared to neat PLA. The maximum tensile strength was achieved at 3 wt% MMT content. XRD and transmission electron microscopy (TEM) analyses confirmed an exfoliated structure of PLA/MMT nanocomposites. DSC analysis showed that the intercalated clay acted as nucleating agent, and the exfoliated layers played a template role for crystallization of PLA, which both of them accelerated the crystallization rate of PLA. It was found that by increasing the MMT content, the crystallinity of PLA in PLA/MMT nanocomposites significantly increased from 7.34 to 16.66%.

Balakrishnan and co-workers (2012) investigated the effect of MMT on the properties of PLA/Biostrong (an ethylene copolymer from DuPont) nanocomposites. XRD analysis showed an increase in the *d*-spacing of MMT, which indicated that the PLA polymer chains were intercalated in between the intergallery of MMT. This improvement in *d*-spacing was attributed to the possible hydrogen bonding interaction. TGA result showed that the incorporation of Biostrong and MMT had resulted in a significant improvement in the initial thermal stability of PLA in nanocomposites. DSC analysis showed an increase in crystallinity percentage (X_c) and a decrease in $T_{c,}$ which indicated that the presence of Biostrong and MMT platelets significantly promotes the degree of PLA crystallization. The addition of MMT had lowered the biodegradability of PLA/Biostrong nanocomposites. They believed that the presence of dispersed MMT layers decreased the microorganism diffusion through the PLA matrix.

Li et al. (2013) produced PLA/OMMT nanocomposites films through solution intercalation using dichloromethane as solvent. Good nanofiller dispersion was achieved for nanocomposites with OMMT content less than 3 wt%. Although OMMT did not improved the degree of crystallinity of the PLA/OMMT nanocomposites significantly, it gave the PLA the potential to crystallize more, as confirmed by DSC analysis. The XRD patterns indicated that OMMT was well intercalated. TEM analysis showed that a majority of OMMT was uniformly dispersed in the PLA matrix at low filler loading, whereas aggregates of OMMT existed at high loadings. The tensile strength and Young's modulus of the PLA/OMMT nanocomposites were first increased by incorporation of OMMT (less than 3 wt%) and then decreased at high concentration of OMMT (>3 wt%).

In a study by Lai et al. (2014), the OMMT was incorporated into PLA matrix using melt-blending process in order to produced PLA/MMT nanocomposites. Fully exfoliated OMMT was achieved when only 1 phr OMMT was added to the PLA matrix. Interestingly, only this particular nanocomposite had a lower modulus and exhibited significant stress-whitening and necking behavior with a large extension and elongation at break compared to neat PLA. Based on morphology analysis, the highly exfoliated platelets produced a relatively large interfacial area between the clay platelet and PLA matrix, which resulted in a comprehensively plasticized interfacial region. The highly plasticized interfacial region and the well dispersed clay platelets with high aspect ratio, particular for thin samples, enhanced the multiple shear-banding which induced the plastic deformation and substantial shear yielding behavior. However, increasing the OMMT content decreased the extent of exfoliation greatly. In another study by Olewnik and Richert (2014), PLA/MMT nanocomposites were fabricated by an extrusion technique using a twin-screw extruder. To improve the MMT dispersion in the PLA matrix, polycaprolactone (PCL) was introduced as compatibilizer. It was confirmed that the introduction of PCL into PLA/MMT nanocomposites systems did not change the structure of the obtained nanocomposites. The incorporation of the PCL into PLA/MMT resulted in an increase in the ΔH_c and ΔH_m, and a decrease in T_g of PLA/MMT nanocomposites.

Sabatini et al. (2015) produced PLA/MMT nanocomposites using in-situ ring opening polymerization. Surface treatment of MMT was performed using 3-Glycidoxypropyltrimethoxysilane. It was found that even very low amounts of MMT content (0.1 wt%) greatly affect nanocomposites properties. 0.1 wt% of MMT content was enough to get improvements previously observed with higher contents of MMT (5 wt% or more). They found that untreated MMT reduced the *Mn* of the polymers, while treated MMT increased the molecular weights compared to neat PLA and also dispersion of the nanoparticles in the polymeric matrix significantly improved by treatment of MMT. In addition, MMT nanoparticles slightly increased crystallinity of the polymers, especially promoting melt crystallization compared to neat PLA. Furthermore, PLA nanocomposites showed better thermal stability at the presence of treated MMT compared to neat PLA, while the thermal stability of nanocomposites decreased with the addition of untreated MMT into PLA matrix.

2.2 *Polylactic Acid/Carbon Nanotubes Nanocomposites*

CNT is a nanoreinforcement for PLA matrix which attracted great interest of academicians and industrialists (Breuer and Sundararaj 2004; Coleman et al. 2006). CNT is an excellent nanomaterial in term of tensile strength (up to 500 GPa) and stiffness and also possess excellent electrical and magnetic properties (Treacy et al. 1996; Xie et al. 2005). Moreover, the tubular features of CNT can withstand large strain under compression thus making it suitable to be used as nanoreinforcement in polymer matrices (Endo et al. 2007). Many researchers attempted to incorporate CNT in PLA matrix to unlock the full potential of CNT for engineering applications. Due to CNT's unique structure and properties, the development of PLA/CNT nanocomposites is favored.

Wu (2009) investigated the effect of aspect ratio on the properties of CNT reinforced PLA nanocomposites. The PLA/CNT nanocomposites with high aspect ratio CNT indicated higher modulus compared to low aspect ratio, which showed that the dispersion of CNT is highly depends on its aspect ratio. Mechanical and thermal properties and also electrical conductivity of PLA/CNT nanocomposites were reported by Moon et al. (2005). The results showed that the tensile strength and elongation at break of PLA/CNT nanocomposites reduced by incorporation of CNT, whereas the Young's modulus slightly increased. In addition, the thermal stability of PLA/CNT increased while and the electrical surface resistivity decreased. Song et al. (2007) successfully produced PLA/CNT nanocomposites through in-situ polycondensation. It was reported that the addition of CNT improved solubility and biocompatibility of PLA/CNT nanocomposites. In another study, PLA/CNT nanocomposite was successfully produced by Barrau et al. (2011) using melt mixing and solution methods and their crystallization behavior were investigated. The results showed that the presence of CNTs significantly increased the crystallization kinetics of the PLA matrix.

Extremely high strength, large surface area and high aspect ratio of multiwalled carbon nanotubes (MWCNT) showed its potential to improve the properties of the PLA. Villmow and coworkers (2008) investigated the temperature and screw profiles, rotation speed and also variation of MWCNT content. According to the results, the highest impact determined for the rotation speed of 100 to 500 rpm which led significantly better dispersion of MWCNT in PLA matrix. In addition, the MWCNT content and its level of dispersion in PLA matrix effected the degree of crystallinity. In a study by Kuan et al. (2008a), MWCNT reinforced low-crystalline PLA (LC-PLA) and high-crystalline PLA (HC-PLA) by melt mixing technique. The results revealed that the electrical properties of PLA/MWCNT nanocomposites is highly dependent on degree of crystallinity. In addition, the incorporation of MWCNT improved the electrical conductivity of PLA nanocomposites, where the high electrical conductivity was obtained at low MWCNT content. Furthermore, an improvement in MWCNT dispersion in PLA matrix is observed due to formation of hydrogen bonding between modified MWCNT (MA-g-MWCNT) and PLA matrix. It was reported that the addition of 0.5 phr MA-g-MWCNT into LC-PLA decreased the surface resistance of the PLA nanocomposite due to the improved dispersion of MWCNT in PLA matrix. Furthermore, the degree of PLA crystallinity affected the electrical properties of PLA/MWCNT nanocomposites (Kuan et al. 2008a, b; Avella et al. 2009).

Wu et al. (2008) produced PLA/MWCNT nanocomposites with various functionalized MWCNTs using melt blending method. They reported that the surface functionalization significantly influenced the level of MWCNT dispersion in the PLA matrix; as the carboxylic functionalized MWCNT revealed relatively better dispersion than hydroxyl and purified MWCNTs due to the good affinity between carboxylic group and PLA. PLA/MWCNT showed no significant improvement in thermal stability at the initial stage of degradation, whereas with increase of decomposition level, the presence of carboxylic and purified MWCNTs retards the thermal depolymerization of PLA due to their barrier and thermal conductive effects, respectively. In addition, Wu et al. (2010) reported that the incorporation of CNT nanotubes effected the melt crystallization and the cold crystallization of PLA. The biodegradation rate of PLA significantly reduced because of inhibiting effects of CNT.

Kuan and co-workers (2008b) successfully prepared PLA/MWCNT nanocomposites using melt mixing process. The results showed that the tensile strength of PLA/MWCNT nanocomposites increased by incorporation of 1 phr MWCNT (approximately 13%). In addition, they found that the degradation temperature of PLA increased by increasing MWCNT content. Furthermore, the heat deflection temperature of PLA increased significantly by incorporation of 1 phr MWCNT (from 62 to 106 °C) after 7 h of cross-linking reaction. Interestingly, incorporation of higher MWCNT (>1 phr) and longer cross-linking reaction time (>7 h) showed no significant improvement in tensile strength of PLA/MWCNT nanocomposites. They also noted that further addition of MWCNT (>1 phr) reduced the degree of water cross-linking. Kim et al. (2009) reported the thermal and mechanical properties of MWCNT reinforced poly(L-lactic acid) (PLLA) nanocomposites. The results revealed that the incorporation of MWCNT into PLLA significantly improved the mechanical properties and thermal stability of PLLA/MWCNT nanocomposites compared to neat PLLA. In another study, PLA/MWCNT nanocomposites prepared by melt extrusion showed an improvement in properties of PLA such as mechanical, thermal and crystallization kinetic due to the good interfacial interaction between nanofillers and PLA matrix (Ramontja et al. 2009). Flame retardancy of PLA/MWCNT nanocomposites also improved by incorporation of MWCNT as reported by Bourbigot et al. (2011).

2.3 Polylactic Acid/Graphene Nanoplatelets Nanocomposites

GNP is a single and thin layer of neat carbon and a tightly packed layer of carbon atoms which are bonded together in a hexagonal honeycomb lattice, where the carbon-carbon length in GNP is approximately 0.142 nm (Heyrovska 2008; Norazlina and Kamal 2015). The dispersibility of neat GNP in water is rather poor due to its hydrophobic nature, which required surfactant to prevent aggregation and obtain uniform suspension in biological fluids (Goenka et al. 2014). Graphene oxide (GO) is capable in forming hydrogen bonds due to its polar basal plane and negative charges associated with carboxylate groups at the edge site (Hsieh and Chen 2011). The hydrophobicity of reduced graphene oxide (rGO) is less than GO due to its basal vacancy defects which occurred during oxygen removal (Cote et al.

2008; Yang et al. 2010; Hasan et al. 2010; Hsieh and Chen 2011). The CNTs have a tendency to form bundles which need some chemical modification to achieved good dispersion, whereas the formation of bundles is not a problem for the GNP and GO, although fully exfoliation may not occur (Roy et al. 2012; Young et al. 2012). The mechanism of interaction in graphene based nanocomposites is depends on hydrophobicity, molecular weight and the number of reactive groups (Zhang et al. 2010).

In a study by Yang et al. (2012), PLLA/rGO nanocomposites produced using in-situ polymerization. Although the in-situ polymerization is an effective method to obtained uniform dispersion with good interfacial interactions, the synthesis of high molecular weight in PLLA needs severe conditions (Garlotta 2001; Achmad et al. 2009; Li et al. 2014). In addition, the structure, morphology, thermal, mechanical and electrical properties of PLA/GNP nanocomposites were compared with PLA/micron-sized natural graphite (PLA/NG) nanocomposites reported by Kim and Jeong (2010). They found the GNPs with 15 nm thickness were uniformly dispersed in the PLA, while the NGs were aggregated. Moreover, the thermal stability and Young's modulus of PLA/GNP nanocomposites significantly increased up to 3 wt% GNP, whereas the PLA/NG nanocomposites were unchanged regardless of NG content. Furthermore, the electrical percolation threshold of PLA/GNP nanocomposites were found to be lower compared to (at 3–5 wt% GNP) PLA/NG nanocomposites (at 10–15 wt% NG). In another study, Cao et al. (2010) produced the lyophilized graphene nanosheets (GNS) reinforced PLA nanocomposites. Morphology analysis confirmed the homogenous dispersion of GNS in PLA matrix without sever aggregation which suggested good interaction between GNS and PLA matrix. In addition, thermal stability of PLA/GNS nanocomposites increased by approximately 10 °C with incorporation of 0.2 wt% GNS at 5% weight loss due to the tortuous path effect of GNS, which delayed the permeation of oxygen and the escape of volatile degradation products; and also char permeation. Furthermore, incorporation of 0.2 wt% of GNS into PLA increased the tensile strength and Young's modulus of nanocomposites by approximately 26 and 18%, respectively. The increase in mechanical properties was attributed to efficient load transfer from PLA to GNS.

Several researchers reported that GO have superior mechanical and thermal properties and expected to become essential materials in automotive applications (Zhu et al. 2010; Compton and Nguyen 2010; Ang et al. 2010; Ryoo et al. 2010). GO is also expected to provide ease of dispersion in PLA matrix due to their oxygenated surface functionalities, which caused stable dispersibility by electrostatic repulsion and possible chemical interactions in PLLA/GO nanocomposites (Sun et al. 2008; Paredes et al. 2008). Wang and Qiu (2011) fabricated PLLA/GO nanocomposites with different GO content (0.5, 1 and 2 wt%). They found that the non-isothermal melt crystallization peak temperatures of PLLA/GO nanocomposites were slightly higher than neat PLLA. Incorporation of 1 wt% GO into PLLA increased the crystallization peak temperature of PLLA from approximately 95.1 to 100.4 °C. In addition, isothermal melt crystallization temperatures were also increased by the addition of GO into PLLA matrix. Furthermore, the T_g of neat

PLLA (61 °C) and its nanocomposites showed that the incorporation of GO into PLLA does not affect the T_g of PLLA/GO nanocomposites compared to neat PLLA.

3 Polylactic Acid Green Nanocomposites: Hybrid Fillers

Recently hybrid green nanocomposites have received considerable attention because of their capability of providing a more cost-effective utilization of expensive nanofillers using partially replacing them with less expensive one. In addition, the properties of hybrid nanocomposites depend on the individual nanofiller, where a balance properties can be obtained through hybridization of nanofillers (Hasan et al. 2016). Various researchers reported the use of hybrid nanofillers in PLA matrix to produced PLA hybrid nanocomposites (Chang et al. 2003b; Meng et al. 2010; Santangelo et al. 2011; Gorrasi et al. 2013). In a study by Gorrasi et al. (2013), PLA/clay/CNT hybrid nanocomposites prepared and the effect of nanofillers content and UV radiation time on the elastic moduli of the hybrid nanocomposites were investigated. The elastic modulus of the PLA hybrid nanocomposites was higher than neat PLA due to the reinforcing effect of the nanofillers. However, the elastic modulus of neat PLA decreased with increasing radiation time due to UV which induced chain cleavage. In addition, thermal degradation temperature of hybrid nanocomposites decreased with increase in radiation time; where the higher the radiation time, the faster the decomposition rate, which was due to the formation of low molecular weight species during photo-ageing. Furthermore, the electrical conductivity of the PLA hybrid nanocomposites showed an increasing trend with irradiation time due to the formation of percolation pathway by the CNT, whereas the electrical conductivity of neat PLA was found constant at different irradiation time.

Chang and co-workers (2003b) prepared PLA/MMT/mica hybrid nanocomposites using solution casting technique. They reported that the tensile strength of the PLA hybrid nanocomposites significantly increased by the addition of hybrid nanofillers and reached a maximum value at 4 wt% clay. However, the tensile strength decreased by further addition of clay due to the aggregation of clay particles. The tensile modulus of hybrid nanocomposites increased gradually up to 4 wt% and then decreased by further addition of fillers. In addition, the elongation at break of the neat PLA increased with the incorporation of fillers. Moreover, they found a decreased in thermal stability of PLA hybrid nanocomposites with increasing clay content. In another study, Meng et al. (2010) produced PLA/MMT/wood nanocomposites using melt blending. The tensile modulus of PLA hybrid nanocomposites increased from approximately 3.8 to 7.1 GPa compared to neat PLA. However, the tensile strength experienced a decrease of about 20 MPa with the incorporation of 5 wt% MMT. In addition, thermal decomposition temperature of PLA hybrid nanocomposites increased by approximately 10 °C compared to PLA/wood composites. The melting temperature and T_g of PLA hybrid nanocomposites was found to be unchanged compared to neat PLA. Santangelo et al. (2011)

produced PLA/CNT/smectite clay hybrid nanocomposites using melt mixing followed by compression molding. They reported that the incorporation of hybrid CNT/clay improved the electrical properties of the neat PLA.

4 Conclusion and Future Prospects

This chapter aims to highlight previous studies on PLA green nanocomposites and provides relevant data for automotive applications. PLA nanocomposites showed comparable mechanical properties with synthetic nanocomposites and have potential to be used in interior and exterior automotive applications such as door panels, door handles, instrument panels dashboards, seat cushions, cabin linings, fuel systems, engine covers, timing belt covers and bumpers. Although many attempts have been done by scientists to improve the properties of PLA, there are still some challenging issues to be addressed. The current major limitation of PLA nanocomposites for use in automotive industries is their high cost. This requires an extensive research to find a far reaching solution in this aspect that would make PLA to be more competitive to other synthetic polymers. One possible solution is to use by-products of other industries as the starting material in the production of PLA. Another possible solution is to blend PLA with a cheaper polymer as a minor component. Another challenge for the use of PLA in automotive industries is their brittleness and limited thermal stability. This could be overcome by the use of suitable additives and modifiers. Interaction between various additives such as reinforcements and impact modifiers is another interesting research area which is widely reported. Finally, life cycle assessment of the use PLA nanocomposites should also be carried out to confirm the advantage of using such materials in automotive industries.

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Bamboo Fiber-Polymer Composites: Overview of Fabrications, Mechanical Characterizations and Applications

Kenan Song, Xiaofeng Ren and Longhe Zhang

Abstract The utilization of bamboo fibers in polymer-based composites has expanded in the past few years due to the demand for biodegradable, sustainable and recyclable materials. This article reviews the processing of extracted bamboo fibers and their composites, ultimate mechanical properties/thermal stabilities and corresponding characterizations, as well as the applications. Currently, the challenges regarding bamboo fibers-filled polymer composites involve extraction of high quality bamboo fibers, uniform fiber dispersion/distribution in polymer matrix and/or formation of interphase between matrix-filler phases. Relationships among processing techniques, properties and structural orders are significant to guide the design of future composite.

Keywords Bamboo fibers · Composites · Characterization · Mechanical · Interphase · Application

List of symbols

Materials

BF	Bamboo fiber
BFCP	Bamboo fibers reinforced polymers
CF	Carbon fiber
CFRP	Carbon fiber reinforced polymers
CNT	Carbon nanotubes
GF	Glass fiber
GFRP	Glass fiber reinforced polymers
GP	Graphene platelets
GPRP	Graphene platelets reinforced polymers

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HNT	Halloysite nanotubes
MA	Maleic anhydride
MWNT	Multi-wall carbon nanotubes
MTM	Montmorillonite
nCs	Nano-carbons
PA	Polyamide
PANI	Polyaniline
PDDA	Poly(diallyldimethylammonium chloride)
PE	Polyethylene
PET	Polyethylene terephthalate
PI	Polyimide
PP	Polypropylene
PS	Polystyrene
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PU	Polyurethane
UHMWPE	Ultra-high molecular weight polyethylene

Processing

AT	Annealing with temperature
ATT	Annealing with both temperature and tension
LBL	Layer-by-Layer

Characterizations

AFM	Atomic force microscopy
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTA	Differential thermogravimetric analysis
FTIR	Fourier transformed infrared spectroscopy
QCM	Quartz crystal microbalance
ROM	Rule of Mixture
SAXS	Small-angle X-ray scattering
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
WAXD	Wide-angle X-ray diffraction

Units

$g\cdot cm^{-3}$	Gram per unit centimeter cube
vol.%	Volume percentage
wt.%	Weight percentage

μm	Micrometers
nm	Nanometers
MPa	Megapasca
GPa	Gigapasca
J	Joules

Symbols

f_c	Herman's orientation factor
φ	Misalignment angle
$\tan \delta$	Dampening parameter
T_c	Crystallization temperature
T_d	Degradation temperature
T_m	Melting temperature
χ_c	Crystallinity degree
H_c	Enthalpy of crystallization
H_m	Enthalpy of melting
E	Tensile/elastic modulus
E'	Storage modulus
E''	Loss modulus
E_f	Tensile/Young's modulus of filled particles
E_m	Tensile/Young's modulus of matrix
σ_f	Tensile/failure stress of filled particles
σ_m	Tensile/failure stress of matrix
σ	Tensile/failure stress (general notation)
σ_y	Yield stress
σ_i	Impact stress
σ_b	Bending stress
ε_t	Tensile/failure strain (general notation)
ε_y	Yield strain (general notation)
V_f	Volume fraction of filled particles
V_m	Volume fraction of matrix

1 Introduction

The requirement for sustainability due to depletion of petroleum resources has stimulated the search for renewable, reusable, and recyclable materials. Currently used synthetic fibers, including high-performance aramid fibers (The National Academies Press 1992; Sikkema et al. 2003; Song et al. 2015a, b, c, d; Song et al. 2012), carbon fibers (Song et al. 2013a, b; Zhang et al. 2013a, b; Meng et al. 2014; Song et al. 2015a, b, c, d; Zhang et al. 2015) and glass fibers (Nishii et al. 1992), have been mixed with both renewable and non-renewable polymers to produce composites. The usages of these composites are still dominating the reinforcement industry (Song et al. 2013a, b); however, the natural fibers as reinforcements have gained much impetus to substitute these synthetic fibers in various applications (Belcher et al. 2001; Beckwith 2008; Faruk et al. 2012; Ren and Li 2013, Aug, 1; Ren et al. 2013). Among these natural fibers, bamboo, banana, coir, cotton, flax, hemp, henequen, jute, kenaf, ramie, and sisal have attracted the most attentions (Faruk et al. 2012; Ku et al. 2011; Koronis et al. 2013). The usages of these fibers greatly depend on the geological locations. For example, bamboo and cotton are abundant in Asia, South America, and Africa; India and Sri Lanka produce 90% of the coir produced every year; and sisal is mainly cultivated in southern Mexico (Beckwith 2008). Banana, flax, hemp, henequen, jute, kenaf, ramie, and sisal, are produced in alternative regions and comparatively, they provide fibers for structural and functional materials, and simultaneously serve as important food resources. The usage of these materials may not only jeopardize sufficient supplies of oil, milk, protein, and vegetable, but can also occupy the existent forests and further damage the environmental soil protection (Faruk et al. 2012). Bamboo, on the other hand, is one of the most natural-abundant crops and has a long application history in living facility and life tools. Practically, apart from bamboo strip based composites (i.e., household storages, furniture, floors, fences, panel, decoration products) it is also optional to extract bamboo fiber (BF) from bamboo trunk in controllable way for structural composites.

Currently BFs are considered as important plant fibers that have great potential in polymer composite industry. Its mechanical robustness, thermal stability, and facile extraction of BFs as well as easy chemical modification have made it versatile in composite industry. The economic value, lightweight, high specific strength, and nonhazardous nature of BFs are among the most attractive and well-known properties of this material. Mechanical characterizations have proven them to possess great potential applications in automobile, aerospace and household usage (Qiu et al. 2012; Li et al. 2012). This contribution will review the processing, characterizations and properties as well as applications of BFs filled polymers, to achieve the goal of better usage of bamboo materials.

2 Fabrication of Bamboo Composites

Polymer-matrix composites, such as carbon or glass fiber reinforced plastics (CFRP or GFRP) have been widely used in industry due to their high strength and stiffness (Song et al. 2013a, b; Chand 2000; Hussain et al. 2006). Nonetheless, when thermoset plastics are involved, it is very difficult to recycle these materials. The thermoplastics, on the other hand, are also unpractical to recycle due to high cost and low quality issues in the current applications. The recycling of polymer/filler composites is mainly related to two ways: dump and calcination. Some dumped fiber reinforced plastics cannot decompose naturally, while others burnt in the furnace may damage the furnace (e.g., glass fiber will cause reduce in net heat and the solid residue in the incinerator will lead to disposal problems). Therefore the usage of reinforcement fibers and choice of fabrication methods should be cautious. Bamboo is abundant in natural resources, especially in Asian and South Africa, because of its fast growing (as fast as a few months) and little protection cost. Bamboo is also called "natural glass fiber" for its high specific strength and stiffness (Okubo et al. 2004). To take advantage of these benefits, it is necessary to review the fabrication procedure, compare their pros and cons, and choose the optimal method.

2.1 Extraction of Bamboo Fibers

BFs are difficult to extract due to the brittleness. This brittleness is caused by the surface-covered lignin. Therefore knowledge of BF composition and structure as well as development of appropriate procedure to extract BFs is of great significance. The chemical composition of BFs is mainly cellulose (74%), hemicellulose (13%) and lignin (10%). Based on the components, 90 wt% is high-glycans. The other 10 wt% includes protein, fat, pectin, tannins, pigments and ash (Low et al. 2006). The presence of lignin provides stiffness and yellow color to BFs. In some applications these limitations in flexibility are not desirable and various chemical treatments have been found to be effective in removing lignin. Non-cellulose components contribute to the strength, flexibility and moisture absorption. Physically, the BFs align uniquely along growth direction, with 2°–10° disorientation angles (Jain et al. 1992).

Both physical and chemical methods have been generally used for BF extraction. Based on several studies listed in Table 1, bamboo extraction generally involves mechanical separation (i.e., cutting, blending, milling, sieving, steam explosion, combing, scrapping, etc.), and/or chemical extraction (i.e., alkali extraction and acid neutralization, fermentation with enzyme, oil soaking, etc.). In both methods, original BFs are necessary to be peeled off the bamboo trunk/strips. The fibers were often peeled off along bamboo length direction. According to Rao and Rao (2007), BFs from combing and scrapping, namely physical separation, break less than those from decorticating and degumming, namely chemical procedure. Later on, the steam explosion technique was found to be a more effective method to extract BFs as compared to other mechanical methods (Okubo et al. 2004). Nonetheless in most mechanically peeled bamboo components the obtained fibers show discrepancies in fiber shape, length and diameter dependent on the processing technique. Other mechanical methods using mechanical devices of miller, blender, and machine have simple processes and high efficiencies (Okubo 2004; Rao and Rao 2007; Thwe and Liao 2003; Bo 2004; Ogawa et al. 2008). Nonetheless due to the roughness and brittleness, BFs produced are scattering in thickness, length, and flexibility, thus have achieved very limited practical applications such as fiberboard.

Table 1 Extraction methods of bamboo fibers

Techniques	Year	Details
Physical or mechanical method		
Extruding, cutting and blending (Thwe and Liao 2003)	2003	Bamboo rods were obtained by passing wider strips through an extruder. Short BFs were obtained by cutting these rods into chips, which were then grinded in blender for half an hour
Steam explosion (Okubo 2004)	2004	Bamboo was heated at around 170 °C under 0.8 MPa for 100 min for 8 times, washed and dried
Cracking (Bo 2004)	2005	High-pressure cooking vessel soften bamboo slices, form micro-cracks and delamination by spliting the bamboo through machine, propagate cracks and expand delamination along the fiber direction which lead to bamboo detaching. Then in another external load synergies, the macro-crack of bamboo continues to expand, achieve its interfacial debonding stratified, to obtain crude fiber bamboo
Combing and scrapping (Rao and Rao 2007)	2007	The cylindrical portion of culm is peeled in the longitudinal direction to make strips. The strips are bundled and are kept in water for three days in order to soften them. Gentle beating, scrapping using sharp knife and combing were repeated until individual fibers were separated
Machining center (MC) (Ogawa et al. 2008)	2008	MC program was designed based on cutting theory. Fiber shape, length and diameter can be controlled by the spiral toll path, axial depth of the cut and the vascular bamboo-bundle size
Chemical method		
Decorticating and chemical degumming (Rao and Rao 2007)	2007	The manually decorticated bamboo fibrous strips are dried off in the sun. These strips of fiber contain tissues and gums. After decorticating, the dry fiber is extracted by means of a chemical process of decomposition called degumming, in which the gummy materials and the pectin are removed
Semi pilot scale extraction technique (Chattopadhyay et al. 2011)	2011	Bamboo culms were digested in NaOH/NaS_2/ digestion solution, washed with HCl solution and cold water, and finally dried/blended/grinded into short BFs
Retting (Mounika et al. 2012)	2012	This process involves the action of bacteria and moisture on dried bamboo strips to dissolve and rot away cellular tissues and gummy substances that surround the fiber bundles and strips

On the contrary, chemical method showed comparatively higher efficiency. However, during the chemical of degumming it also leaves out some lignin within the fibers, which weakens the mechanical reinforcement. Although the extraction of

BFs may suffer from deteriorated integrity in the degumming treatments, in most cases the alkali treatment is effective in fiber surface modifications and further improves mechanical stiffness/strength, and subsequent interfacial interactions between polymer and BFs (Das and Chakraborty 2008a, b). Therefore, exploration of softening BF methods, lignin removal technology and special machine development has to be conducted for fine fiber productions.

2.2 Solution Processing Film

In solution processing technique, the BFs are generally dispersed in solvent and then mixed with polymer solution by mechanical mixing, magnetic agitation or high-energy sonication. Subsequently the polymer composites can be obtained by vaporizing the solvent at elevated temperature. This method is considered as an effective measure to prepare composites with a homogeneous BF distribution and often used to fabricate composite films. Epoxy and polyurethane are the thermoset polymers that are usually employed in BFs filled composites by solution mixing. Other polymers such as PS, PVA, PMMA, PVC, and so on can also be prepared in the same method.

2.3 Melt Processing Film

During melt processing, polymers were melted at elevated temperature and mix with extracted BFs. BFs are dispersed within the polymer matrix by rheological shear stress generated from blending the BFs with polymer melt. However, it is known that the BFs can easily be damaged to shorter fibers or defected in some sense. After uniform mixing of the fibers and the polymer matrix, the resultant fiber-polymer matrix mix was shaped from extruder (Phuong et al. 2010), injector (Samal et al. 2009), mold, compounder or roller (Ismail et al. 2002). Pressure sometimes is applied for regular shape and for getting rid of voids.

2.4 In-situ Polymerization Film

Surface modification of cellulose fibers by in situ graft copolymerization has been intensively investigated (Roy et al. 2009; Thakur 2015). The copolymerization can be achieved by various types of polymerization techniques while free radical polymerization, including conventional free radical polymerization (Odian) and reversible deactivation radical polymerization (RDRP) (Matyjaszweski and Xia 2001; Zhang et al. 2014, 2015; Sciannamea et al. 2008), are the most popular methods due to their versatility and simplicity compared to other polymerization techniques. By grafting polymer chains onto the cellulose surface, the adhesion between modified cellulose and polymer matrix could be dramatically increased. Therefore, in situ polymerization is considered as a very efficient method to significantly improve the BFs dispersion and the interaction between BFs and polymer matrix. Generally BFs should be chemically modified to generate suitable functional groups that allow further graft-from or graft-to polymerization. Various monomers, including methyl methacrylate (Yu et al. 2014), poly(ethylene glycol) methyl ether methacrylate (Bao et al. 2011), or methacrylamide (Kushwaha and Kumar 2010a, b, c), have been employed for in situ graft copolymerization to fabricate BFs/polymer composites. Generally the mechanical properties of the resulting composites were improved due to the stronger interfacial adhesion between the BFs filler and polymer matrix.

2.5 *Laminate*

Hand lay-up is usually used to fabricate BF included composites (Chen et al. 2004). In this procedure, BF were extracted carefully and cut into fibers with various lengths. First, the inner surfaces of the mold are sprayed with a thin layer of release agent. Next, the BFs are placed into the mold uniformly at designed concentrations (Chen et al. 2004). Several classic researches regarding laminate layering-up have been summarized in Table 2. Hot pressing with pressure application, melt compounding as well as in situ polymerization methods have been selectively used for various polymers.

In order to bring out the anisotropic nature of BFs, it is important to align BFs in a polymer matrix during processing of BFs/polymer composites. Achieving suitable BFs-polymer matrix interfacial bonding that provides effective stress transfer is another critical challenge for fabrication of BFs based polymer composites especially for BFs/polymer structural composites. In the following sections these issues influencing the mechanical reinforcement efficiencies will be discussed.

Table 2 Processing of polymer/bamboo composites

Literature	Materials	Processing
2004 (Okubo et al. 2004)	PP/bamboo ~41–51 vol. % film	Hot-pressed at 190 °C under 2 MPa for 30 min
2004 (Takagi and Ichihara 2004)	Starch based resin/short BFs	Hot pressing at 130 °C under 20 MPa for 5 min
2008 (Han et al. 2008)	HDPE/MAPE/bamboo	Melt compounding
2011 (Verma and Chariar 2012)	Epoxy/dry bamboo culms lamina	In situ epoxy curing with bamboo culms dispersion

MAPE, maleated polyethylene

3 Mechanical Characterization of BF/Polymer Composites

For polymer/bamboo composites, mechanical enhancement could be achieved through three aspects: (i) well dispersed fillers, (ii) effective interfacial interactions between matrix and fillers and, (iii) preferential alignment of polymer chains/fillers in line with mechanical loading direction. To understand these factors, their influence on final composites' mechanical properties and the optimal test method, a review on static tensile properties, dynamic mechanical behavior as well as tribology is provided here.

3.1 Mechanical Properties of Extracted BFs

Static tensile test is a straightforward way to study the reinforcement effects (Song 2014). To understand the mechanical reinforcement efficiency, basic properties of BF were listed in Table 3, as compared to other natural fibers and commercial fibers. Among the most popular natural fibers, flax, hemp, jute, kenaf, ramie, and sisal fibers were extensively researched and employed in different applications. But nowadays, abaca, bagasse, coir, oil palm, pineapple leaf, and rice husk fibers are gaining interest and importance in both research and applications due to their specific properties and availability. Among all of them, bamboo shows distinguished mechanical properties, with even higher specific modulus and strength than glass fiber. Materials with high specific stiffness and specific strength are likely to have special merit in applications in which weight will be a critical factor. Because the values of Young's modulus and tensile strength used for the charts calculations were found to be different in every study, the generally used values were marked in ranges. In parallel to that occurrence, the variation of values in the physical properties of the fibers is attributable to different harvesting seasons, ages and/or regions of the planet.

One disadvantage of BF is its poor adhesion to most polymers because of the relatively high moisture absorption. Therefore surface modification or interphase formations become necessary to improve stress transfer from filled BFs to polymer matrix. It is found that alkali treatment influences bamboo mechanical properties (Das and Chakraborty 2008a, b). The important modification achieved with alkaline treatment is the disruption of the hydrogen bonding in the network structure, thereby increasing the surface roughness and interfacial area. An optimal NaOH/water solution of 20% improves BF in tensile strength from 25 to 200 MPa, flexural strength 100–400 MPa, and corresponding toughness from 0.1 to 0.35 MPa, despite a drastic drop in failure strain from 18 to 5%. Improvements in tensile modulus from 1.5 to 7.5 GPa, and flexural modulus from 3.5 to 5.5 GPa also reach maximum when BF was dipped in 20% concentration alkali. Higher alkali concentration will cause a NaOH penetration, material swelling and bamboo

Table 3 Mechanical properties of BFs as compared to other natural fibers and commercial fibers

Fibers	Literature	Physical properties		Mechanical properties				
		Density (g/cm^3)	Diameter (μm)	Tensile Modulus (GPa)	Tensile strength (GPa)	Average specific modulus (GPa/(kg·m^{-3}))	Average specific strength (GPa/(kg·m^{-3}))	Average tensile strai (%)
BFs								
Bamboo	2004 [a](Okubo et al. 2004), 2007 [b](Rao and Rao 2007) 2008 (Das and Chakraborty 2008a, b), 2011 (Osorio et al. 2011)	0.60–1.50	88–250	Up to 43	Up to 0.8	44.90–67	0.55–1.00	1.3
Natural fibers								
Abaca	2002 (Shibata et al. 2002), 2007 (Munawar et al. 2007), 2009 (Bledzki et al. 2009), 2009 (Rahman et al. 2009)	1.50	10–30	12	0.40	8.00	0.26	0.03–0.10
Bagasse	2006 (Cao et al. 2006), 2007 (Zheng et al. 2007)	1.25		17	0.07–0.29	13.60	0.23	0.3
Banana	1982 (Hatakeyama et al. 1982), 2002 (Joseph et al. 2002), 2006 (Sapuan et al. 2006), 2007 (Rao and Rao 2007)			17–85	0.60–0.80	2.50–22	0.44	3.36
Coconut	1963 (Betrabet et al. 1963), 2007 (Rao and Rao 2007)			2.50	0.50	2.17	0.43	20.00
Cotton	2008 (Kim et al. 2008a, b)	1.50–1.60	20	5–13	0.29–0.60	5–13		7–8
Coir	1982 (Hatakeyama et al. 1982), 2003 (Wambua et al. 2003)	1.20		4–6	0.18	3.3–5	0.15	30

(continued)

Table 3 (continued)

Fibers	Literature	Physical properties		Mechanical properties				
		Density (g/cm^3)	Diameter (µm)	Tensile Modulus (GPa)	Tensile strength (GPa)	Average specific modulus (GPa/ ($kg{\cdot}m^{-3}$))	Average specific strength (GPa/ ($kg{\cdot}m^{-3}$))	Average tensile strai (%)
Curaua	2004 (Gomes et al. 2004)	1.38	66	11.8	0.5–1.15	8.56	0.36–0.83	3.7–4.3
Date (A)	2007 (Rao and Rao 2007)			1.91	0.46	1.99	0.48	24
Flax	1997 (Hornsby et al. 1997), 2000 (Garkhail et al. 2000)	0.60–1.10	50–100	20–70	0.35–1.04	50–70	0.33–1.73	2.7–3.2
Hemp	2003 (Wambua et al. 2003)	1.10–1.48	120	35–70	0.39–0.90	47.29–63.6	0.26–0.82	1.6
Henequen	1991 (Cordemex 1991), 1999 (Canche-Escamilla et al. 1999), 2004 (Herrera-Franco and Valadez-Gonzalez 2004)		180	10–16	0.43–0.57	10–16		3.7–5.9
Jute	1982 (Hatakeyama et al. 1982), 2000 (Hill and Abdul Khalil 2000)	1.30	260	13–26.5	0.40–0.80	7.69–23.1	0.31–0.62	1.5–1.8
Kenaf	2003 (Wambua et al. 2003)	1.31	106	26.50	0.43–0.52	19.85–38.17	0.38	1.5–1.8
Oil palm	1997 (Sreekala et al. 1997), 2004 (Jacob et al. 2004)	0.80–1.60	2.6–4	3.20	0.25	40	0.31	0.8–1.6
Palm	2007 (Rao and Rao 2007)			2.70	0.38–0.77	2.67	0.37	13.71
Pineapple	1997 (Devi et al. 1997), 1999 (Luo and Netravali 1999)	0.80–1.60		1.44	0.40–0.63	25–29	0.80	2.4–14.5

(continued)

Table 3 (continued)

Fibers	Literature	Physical properties		Mechanical properties				
		Density (g/cm^3)	Diameter (μm)	Tensile Modulus (GPa)	Tensile strength (GPa)	Average specific modulus (GPa/ ($kg \cdot m^{-3}$))	Average specific strength (GPa/ ($kg \cdot m^{-3}$))	Average tensile strai (%)
Ramie	2003 (Wambua et al. 2003)	1.50	34	9.40–22	0.40–0.94	24–32	0.21	3.6–3.8
Sisal	2003 (Wambua et al. 2003), 2007 (Rao and Rao 2007)	1.50	50–80	8–10.40	0.57	8–10	0.39	2.0–5.45
Vakka	2007 (Rao and Rao 2007)			15.85	0.55	19.56	0.68	3.46
Commercial fibers								
Glass fiber	1992 (Nishii et al. 1992)	2.50	9–15	70	1.20–1.50	28	0.6	1.9–3.2
Carbon fiber	1997 (Tang and Kardos 1997), 2013 (Song et al. 2013a, b)	1.40	5–9	230–240	4.00	130–171.4	2.86	1.4–1.8

[a] Tested bundle samples containing 100 fibers

[b] BFs extracted using physical method and chemical method

hemi-cellulose depletion. These factors will contribute to softening and frangibility (Das and Chakraborty 2008a, b). Instead, studies according to Gassan and Beldzki (1999) and van de Weyenberg (2005), 3% of NaOH is enough to remove surface waxy materials and impurities on the surface of the fiber. As a result, this increases the fibers' wetting ability, the aspect ratio, and the effective area that comes into contact with the matrix, which will further improve the mechanical interlocking at interface. The removal of the cementing constituents of hemicelluloses, a less dense and less rigid interfibrillar region, allows the fibrils to re-arrange along the fiber major axis during tensile deformation and hence improving some properties of the fiber bundles, which in turn influence the properties of the final composites. Alkali treatment effects studied by several authors (Rong et al. 2001; Das et al. 2006; Mukherjee and Satyanarayana 1984) have been shown to make the mechanical properties of composites become higher than that of untreated versions.

3.2 Reinforcement and Interfacial Interaction Efficiency from Static Tests

Static tests are straightforward to examine the interaction between polymer and BFs. The alkali treated BFs have included into polymers to examine their reinforcement efficiency (Kushwaha and Kumar 2009a, b, 2010a, b, c). This would allow for a larger degree of chemical modification on BFs. To improve the stress transfer between BFs and polymer, an interphase adhesion was improved by forming covalent bonds between the –OH group of the fiber and the –COOH group of the maleic anhydride (Kushwaha and Kumar 2010a, b, c). An optimal 5% NaOH solution treatment on BFs exhibited best compatibility with epoxy. Tensile and flexural strength were extensively studied and the enhanced results were attributed to the less water uptake by the composites. In addition, the alkali treatments make the composites more durable. In another recently published work (Kushwaha and Kumar 2010a, b, c), several different chemicals (i.e., maleic anhydride, permanganate, benzoyl chloride, benzyl chloride, pre-impregnation treatment) were used to modify the BF to estimate various mechanical, physical and morphological properties of bamboo reinforced polyester composites (Kushwaha and Kumar 2010a, b, c). It was concluded that different modifications of BF show variations in mechanical, physical and morphological properties of bamboo reinforced polyester composites.

Tensile and flexural tests have been effective in estimating the interfacial interactions between polymer and BFs. Depending on the polymer and material treatments, properties may vary from one to another. For example, tensile tests showed an increase in tensile strength and a decrease in modulus for maleic anhydride-treated bamboo epoxy composites (Kushwaha and Kumar 2010a, b, c). The improvement in tensile strength signifies the interaction efficiency increases; while the deteriorated modulus may be due to the swelling and partial removal of lignin and hemicellulose in BFs. As well known, lignin contributes to the stiffness and modulus. These phenomena have also been observed in SEM images. On the contrary, opposite trend was observed in another study that the tensile modulus increases while fracture strength decreases in BF/rubber composites (Ismail et al. 2002). In this study, bonding agents were used to improve interfacial interactions; SEM and curing time measurements also showed consistent trend.

Flexural strength is a combination of the tensile and compressive strength, which directly varies with the inter-laminar shear strength. In flexural testing various mechanisms such as tension, compression, shearing, buckling, etc. take place simultaneously. The loading in flexure causes normal stresses in the direction of fibers and shear stresses in the plane perpendicular to the load. Composites when loaded in flexure can fail the tension either longitudinally or transversely, or shear in the matrix, interface or fiber. In three-point flexural test, failure occurs due to bending and shear failure. The lower strength of the inter-laminar resin should account for the fact that flexural strengths of the laminates are lower than tensile strengths. Therefore an increase in only tensile modulus and flexural modulus in composites were found to be related to a better chemical bonding between the maleic anhydride modified bamboo and polyester (Kushwaha and Kumar 2010a, b, c), while an improvement in both tensile strength and modulus of the acrylonitrile-treated fiber-reinforced thermosetting resins correlated to the enhanced chemical bonding and minimized defects in BFs (Kumar and Kushwaha 2009).

The study of interfacial bonding also improves the understanding about moisture absorption in final composites (Qiu et al. 2011, 2012). The aim of these studies is to visualize the hydrophobic character of bamboo based reinforced composites in order to support the current demand of utilization of bamboo in outdoor applications. The moisture regaining greatly weakens the interfacial stress transfer from BF to polymers therefore becomes an important illustrator in evaluating composites' mechanical stabilities (Kumar and Kushwaha 2009). For example, silane treatment resulted in reduction of water adsorption and has been studied regarding their effects on moisture reduction degree (Kushwaha and Kumar 2009a, b, 2010a, b, c). Among the many silanes used in this study, amino functional silane showed best results with epoxy resins, and triethoxy derivative gave better results than trimethoxy amino slicanes; however, the best water absorption results were achieved by both alkali and amino-propyltriethoxy silane treated bamboo epoxy composites. Later on in a similar study (Kushwaha and Kumar 2010a, b, c), no alkali treatments were conducted to compare the results. It was observed that amino-propyltriethoxy silane exhibited better results than amino-propylthiemthoxy, for same reason due to enhanced adhesion between BFs and polymer matrix.

The interfacial interactions were not only studied in thermoset polymers but also in thermoplastic composites. PP as matrix is an example. Instead of modifying BFs, some researchers found that modified polymer matrix could be used for reinforcement in composites. The maleic anhydride grafted PP (MA-g-PP as shown in Table 4) was included as compatibilizer in order to improve adhesion between BF and polymer matrix (Chattopadhyay et al. 2011). The direct effects of different maleic anhydride concentrations and modification of BF on various physical and mechanical properties of PP composites suggested that both concentration and

Table 4 Mechanical properties of BF/polymer composites

References	Sample (polymer/% CNT)	Mechanical properties			
		Elastic modulus (GPa)	Strength (GPa)	Strain (%)	Toughness
Thermoset composites					
2003 (Saxena and Gowri 2003)	Polyester/68% Bamboo composite	8.2 ± 1.8	101.8 ± 2.8		
	Polyester/69% Bamboo composite with surface treatment	9.8 ± 2.4	112.2 ± 2.2		
	Epoxy/60% Bamboo composite	7.8 ± 3.8	112.8 ± 1.4		
	Epoxy/60% Bamboo composite with surface treatment	8.2 ± 2.1	144.8 ± 0.7		
2002 (Ismail et al. 2002)	Rubber	1.3	0.020	750	
	Rubber/50 vol.% BF	4.5	0.004	190	
2010 (Wong et al. 2010)	BF	5.96 ± 0.43	0.518 ± 0.051	10.4 ± 0.2	
	Resin	2.0–4.5	0.040–0.090	2	0.5
	Resin/40 vol.% BF	3.8	0.062		1.7
2010 (Kumar and Kushwaha 2009)	Polyester/bamboo	4.2	0.074		
	Polyester/1 h acrylonitrile treated bamboo	8.4	0.097		
	Polyester/5 h acrylonitrile treated bamboo	5.8	0.087		
	Epoxy/bamboo	6.736	0.086		
	Epoxy/1 h acrylonitrile treated bamboo	9.9	0.125		
	Epoxy/5 h acrylonitrile treated bamboo	9.0	0.102		
2011(Prasad and Rao 2011)	Polyester	0.63	0.0315		
	Polyester/40 vol.% Jowar	2.75	0.124		
	Polyester/40 vol.% Sisal	1.90	0.0655		
	Polyester/40 vol.% bamboo	2.48	0.126		

(continued)

Table 4 (continued)

References	Sample (polymer/% CNT)	Mechanical properties			
		Elastic modulus (GPa)	Strength (GPa)	Strain (%)	Toughness
Thermoplastic composites					
1997 (Okubo et al. 2004)	PP	5	0.032		
	PP/0.5% MA-g-PP/50 vol.% BF	6	0.036		
2002 (Thwe and Liao 2002)	PP				
	PP/30 vol.% BF	2.5	0.015		
	PP/10% MA-g-PP/30 vol.% BF	2.6	0.0165		
	PP/10 vol.% GF/20 vol.% BF	2.7	0.016		
	PP/10% MA-g-PP/10 vol.% GF/20 vol.% BF	2.8	0.0175		
	PP/20 vol.% GF/10 vol.% BF	2.9	0.017		
	PP/10% MA-g-PP/20 vol.% GF/10 vol.% BF	3.0	0.0185		
2003 (Thwe and Liao 2003)	PP/10% MA-g-PP/20 vol.% BF	2	0.0205		
	PP/10% MA-g-PP/15 vol.% BF/5 vol.% GF	2.6	0.023		
2004 (Takagi and Ichihara 2004)	Starch		0.010		
	Starch/10% BF		0.020		
	Starch/20% BF		0.026		
	Starch/30% BF		0.036		
	Starch/40% BF		0.040		
	Starch/50% BF		0.042		
[a]2004 (Okubo et al. 2004)	PP	0.018	0.23		
	PP + ∼50 wt% BF1	0.004 ± 0.00	0.030 ± 0.00	1.21	
	PP + ∼50 wt% BF2	0.005 ± 0.00	0.035 ± 0.002	1.18	

(continued)

Table 4 (continued)

References	Sample (polymer/% CNT)	Mechanical properties			
		Elastic modulus (GPa)	Strength (GPa)	Strain (%)	Toughness
[b]2008 (Samal et al. 2009)	PP	0.586	0.032		
	PP/10%BF	0.710	0.036		
	PP/20%BF	0.813	0.038		
	PP/30%BF	1.240	1.240		
	PP/1%MA-g-PP/30%BF	1.423	0.047		
	PP/3%MA-g-PP/30%BF	1.550	0.0485		
	PP/1%MA-g-PP/15%BF/15%GF	1.491	0.0545		
	PP/3%MA-g-PP/15%BF/15%GF	1.520	0.0583		
[c]2008 (Kim et al. 2008a, b)	PVC/5%P[(SMA)-b-(SAN)]/55 wt% bamboo flour	9	0.036		
	PVC/10%P[(SMA)-b-(SAN)]/55 wt% bamboo flour	11	0.037		
	PVC/15%P[(SMA)-b-(SAN)]/55 wt% bamboo flour	13	0.044		
	PVC/20%P[(SMA)-b-(SAN)]/55 wt% bamboo flour	15	0.047		
[d]2008 (Han et al. 2008)	PE	0.83 ± 0.06	0.021 ± 0.001		
	PE + 30 wt% BF +3.5 wt% MA-g-PE	2.45 ± 0.29	0.029 ± 0.001		
2010 (Mohanty and Nayak 2010)	HDPE	0.153	0.0214		
	HDPE/10% BF	0.330	0.0189		
	HDPE/20% BF	0.758	0.0220		
	HDPE/30% BF	2.674	0.0255		
	MA-g-HDPE/30% BF	2.878	0.0285		

(continued)

Table 4 (continued)

References	Sample (polymer/% CNT)	Mechanical properties			
		Elastic modulus (GPa)	Strength (GPa)	Strain (%)	Toughness
2010 (Wong et al. 2010)	Polyester	2.0–4.5	0.04–0.09	2	0.4–0.6
	BF	5.96 ± 0.43	0.52 ± 0.005	10.4 ± 0.2	
	Polyester + BF	1.1–3.8			1.1–1.7
2011(Chattopadhyay et al. 2011)	PP	0.56 ± 0.004	0.0245 ± 0		
	PP/30 vol.% BF	1.357 ± 0.009	0.0258 ± 0		
	PP/MA-g-PP/30 vol.% BF	1.370 ± 0.006	0.0374 ± 0		
	PP/40 vol.% BF	1.776 ± 0.008	0.0263 ± 0		
	PP/MA-g-PP/40 vol.% BF	1.527 ± 0.008	0.0428 ± 0		
	PP/50 vol.% BF	1.721 ± 0.010	0.0290 ± 0		
	PP/MA-g-PP/50 vol.% BF	1.633 ± 0.011	0.0503 ± 0		
	PP/60 vol.% BF	1.643 ± 0.012	0.0255 ± 0		
	PP/MA-g-PP/60 vol.% BF	1.586 ± 0.008	0.0465 ± 0		

[a] BF2 has more single BF separations than BF1

[b] GF, glass fiber

[c] P[(SMA)-b-(SAN)], Poly(styrene-co-maleic anhydride)-block-poly(styrene-co-acrylonitrile)

[d] MAPE, maleated polyethylene. MA-g-PP, maleic anhydride grafted PP

modification play significant roles in tailoring the properties. The mechanical properties are listed in Table 4. In addition, in this study SEM morphology studies, TGA thermal behavior and FTIR spectra analyses revealed better bonding pattern, respectively. In another study, the effects of the chemical treatment of BF surface (alkaline and acetylation) on fiber structure and composite mechanical, thermal, rheological properties have been investigated (Phuong et al. 2010). Mechanical properties in treated BF incorporated composites as compared to those without treatment showed increases, related to increased adhesion at interphase.

Similarly, in hybrid composites where both BFs and other fibers were included, compatibilizer showed exactly increasing trend in mechanical properties as compared to those without compatibilizer. In one study, use of MA-g-PP in PP matrix results in moderate improvement in tensile modulus and strength of BFRP, while substantial improvement in flexural modulus and flexural strength of BFRP and BGRP were seen (Thwe and Liao 2002, 2003). The researchers believed that MA-g-PP could be utilized in enhancing the better interaction of hydroxyl groups on BFs. The SEM images were used to examine the morphology variations. Voids were observed to decrease greatly due to the impregnation of polymer matrix into BFs. For this reason, tensile strength due to less defects density and modulus due to the more perfect structure were improved to a great content. The same mechanism was applied in HDPE composites. The composites treated with maleic anhydride grafted polyethylene (MA-g-PE) exhibited improved mechanical properties, which confirmed efficient fiber/matrix adhesion. Dynamic mechanical analysis showed that the storage modulus increased in the untreated and especially in treated composites as compared with original high-density polyethylene (HDPE), indicating an increase in the rigidity of the matrix polymer with reinforcement. Optimum stress transfer at the interface region by forming chemical bonds between the fibers and the matrix has been widely accepted as a primary mechanism of the stiffening reasons.

3.3 Composite Mechanics

An understanding of the intrinsic mechanical properties of BFs will help the estimation of composites' mechanical behavior. A simple calculation method is modified Rule-of-Mixture (ROM) by taking filler length and orientation factor into consideration,

$$E_c = E_m V_m + \eta_o \eta_l E_f V_f \tag{1}$$

where E and V stand for the modulus and volume fraction for composites (i.e., E_c and V_c) and fibers (i.e., E_f and V_f). Here orientation factor, η_l and length efficiency factor, η_o were defined based on Krenchel's method (Cox 1952) and shear lag theory (McCrum et al. 1997),

$$\eta_o = \frac{\int_0^{\frac{1}{2}\pi} I(\varphi)\cos^4\varphi d\varphi}{\int_0^{\frac{1}{2}\pi} I(\varphi) d\varphi} \quad (2)$$

It is often assumed that the distribution of rods, *I(φ)* as a function of φ, can be described by a Gaussian or Lorentzian distribution. η_o is 0 for perpendicular distribution to loading axis, 1 for unidirectional along loading direction and 0.325 for randomly distributed particles. *I(φ)* have been measured in polarized microscope, Raman (Young et al. 2010; Blighe et al. 2011), and X-ray diffraction (Song et al. 2015a, b, c, d; Chen et al. 2004; Pichot et al. 2006) as well as scattering (Zhou et al. 2004) techniques.

Researches have studied effects of BF loading variations and also orientation effects on mechanical properties of bamboo reinforced polyester composites. The relationship is also plotted in Fig. 1, assuming a polymer modulus of 5 GPa, BF modulus of 40 GPa and volume fraction/orientation factor of a range between 0 and 1. It can be observed that the optimal design of advanced composites is to improve both parameters of orientation and volume fractions. The effects of loading effects on mechanical properties have been widely studied. The optimal parameters were reported to be 60 vol.% (Das and Chakraborty 2009), 50 vol.% (Okubo et al. 2004), 40 vol.% (Wong et al. 2010; Prasad and Rao 2011) or even lower down to 30 vol.% (Han et al. 2008) and 20 vol.% (Thwe and Liao 2002). The optimal concentration

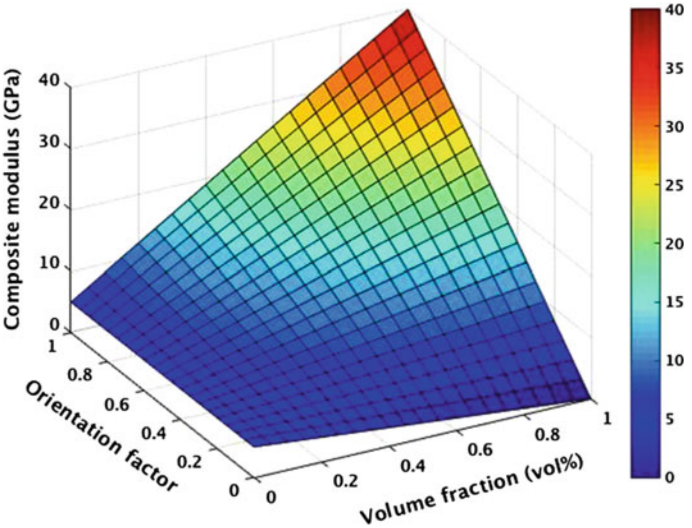


Fig. 1 Composite modulus as a function of parameters of both orientation factor and volume fraction

greatly depends on processing techniques, which determines both dispersion of BF and interaction between BF and polymer matrix.

Uniform dispersion of BFs in polymers is also a fundamental challenge. In fact, no matter what preparation method is adopted, the main purpose is to uniformly disperse BFs within a polymer matrix and obtain composites with as high as intrinsic properties. In general, several factors that influence the dispersion of BFs in a polymer matrix have to be considered in the preparation process of BF/polymer composites. The tightly bundled structure of BFs during growth process and the attraction between single BFs by van der Waals force and hydrogen bonding during processing make BFs themselves hard to be separated. So it is even more difficult for BFs to be separated from one another within the polymer matrix in mixing stage. These factors prevent BFs from being well dispersed within polymers. The obtained BF/polymer composites are poor in their mechanical performance and the intrinsic properties of the composites cannot be achieved. As shown in Sect. 3.1 and Table 1, presently, there are two main kinds of bamboo extractions to improve their dispersion within a polymer matrix: mechanical separation and chemical treatment. However, laborious work is required in mechanical separation, in addition to the scattering size in obtained bamboo fibrils. Chemical treatment may be more facile and practical processing technique considering the time needed and homogeneity in final composites. For example, the maleic anhydride grafted polycaprolactone was used to obtain even distribution of BFs in polymers. The mechanical properties were found to be much enhanced in composites as compared to control samples (Su and Wu 2010). Nevertheless, BFs treated by different surfactants may decrease the contact between BFs, and thereby reduce the stress transfer efficiency properties of BF/polymer composites (Kushwaha and Kumar 2010a, b, c). Silane treatments were studied about their effects on composites' mechanical properties. Take one study for another example; two sets of samples including silane treatment only and siliane treated simultaneously mercerized bamboo. Tensile and flexural properties were examined. It was observed that the silane treated bamboo showed comparable properties to untreated bamboo while the silane treatment after mercerization improved only the flexural modulus, and at the same time decreased the tensile modulus, tensile strength and flexural strength (Kushwaha and Kumar 2010a, b, c).

The interaction between these two phases can be determined by FTIR (Das and Chakraborty 2009), and revealed that the main cause of interaction is due to hydrogen bonding. The fractured surfaces with varied degree of topography were visualized by SEM studies. Bonding interaction between bamboo and polymers was observed with least pullout of fibers. The shear-strength as fiber was pulled out from polymers is a standard for evaluating the interaction between these two phases. Research has shown that the shear strength ranges between polymers (i.e., epoxy, PMMA) and carbon nanotubes of tens to 632 MPa (Chen et al. 2015), and boron nitride of 125–728 MPa. However, interactions between most natural fibers and polymers have not been appreciated and require more attentions.

Preferential orientation is another factor greatly influencing not only mechanical but also electrical properties in final composites (Kumar et al. 2011). The resulted composites possess two fiber orientations, parallel and perpendicular to electrical field. Based on dielectric dissipation factor (tanδ), 0° oriented bamboo/epoxy composites were higher than that of 90° oriented composites. The BF orientations were also examined in flexural tests (Osorio et al. 2011). BFs were first obtained using pure mechanical extraction instead of chemical procedure or high temperature processing. After that alkali treatment was conducted to remove organic and other impurities from the fibers thus enhance the interfacial bonding. BFs were arranged as parallel as possible to make unidirectional samples. The flexural and Young's modulus and strength along longitudinal direction were measured to be much higher than transverse direction. In addition, the strength and modulus were calculated theoretically, which were close to single fiber properties and indicated efficient interfacial interactions.

For length efficiency factor,

$$\eta_l = 1 - \left[\frac{\tan h(na)}{na}\right] \tag{3}$$

$$n = \sqrt{\left[\frac{2G_m}{E_f \ln(2R/d)}\right]} \tag{4}$$

$$a = \frac{l}{d} \tag{5}$$

where G_m is the shear modulus of polymer matrix, $2R$ is the distance from the fiber to its nearest neighbor fiber, l and d mean the length and diameter of the particle.

Researchers studied the effect of fiber length on the mechanical properties of polymer composites by using starch resin and short BFs (Takagi and Ichihara 2004). BFs with 200 μm in diameter and 4–25 mm in length were obtained by steam explosion and then hot pressed with into sheets with starch. At fixed fiber concentration and assumed even dispersion, length efficiency is only dependent on aspect ratio as shown in Eq. 2. Tensile strength and flexural strength in 48 vol.% loaded composites were found to increase constantly from around 10 MPa in matrix up to 50 MPa. However, when fiber aspect ratio drops to 20 (i.e., length of 4 mm and diameter of 200 um), there was no reinforcement effect as composites showed comparable properties with bamboo powder filled composites. Figure 2 also shows clearly how the length efficiency factor changes with parameter *na*. Based on this curve from Eq. 3, shear modulus of 100 MPa, tensile modulus of 40 GPa, and concentration of 48 vol.% generate a value of 0.05 for *n*. A multiplication of aspect ratio of 20 provides a length efficiency of 100%. This is also consistent with the experimental observation that lower length of BF will not reinforce the composites (Takagi and Ichihara 2004). Similarly, this length effect of larger reinforcement from longer fibers in various polymers including polyester (Wong et al. 2010) has been observed.

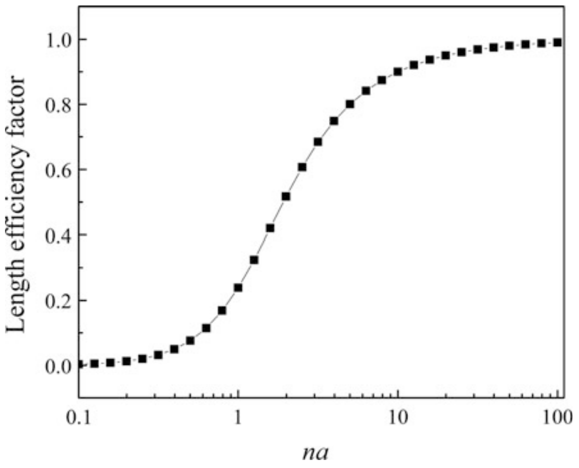


Fig. 2 Length efficiency factor (η_l) as a function of parameter *na*

3.4 Dynamic Mechanical Analysis on Interfacial Bonding Efficiency

DMA provides information regarding rheological/viscoelastic properties of polymeric materials as a function of temperature or frequency. The storage, (E'), and the loss (E'') dynamic moduli as well as dampening parameter (tan δ) are monitored during the temperature sweep test. In contrast to traditional thermal analysis techniques for polymers (e.g., differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and differential thermal analysis (TMA)), DMA provides more sensitive characterization of transitions associated with chain movements, molecular relaxations, and their relationship to the interactions between the matrix and filled fibers. The dynamic parameters were ominously influenced by the increase in fiber length, aspect ratio, and orientation as well as loading but not in a geometric progression. Thus DMA is important toward understanding the characteristics for the confined polymer regions as well as other microstructural parameters such as morphology and nature of constituents in polymer composites. The general dynamic mechanical properties of several polymer and polymer based composite materials (i.e., PVA (Park et al. 2001; Nishio and Manley 1988; 2015a, b, c, d), epoxy (Zeng et al. 2014), PMMA (Saha et al. 1996), carbon fiber (Saha et al. 1996), PP (Wielage et al. 2003)) have been previously investigated in details, and reinforced effects of filled particles have been examined. The DMA analyses greatly depend on the composites compositions (i.e., fiber content, concentration, compatibilizer, plasticizer, additive, orientation) and the test mode (i.e., tension, compression, temperature sweep, frequency sweep).

To understand the dynamic mechanisms, physical meanings of measured parameters should be understood. The storage modulus relates to Young's' modulus. This data is associated with stiffness or a material and determines how stiff or flexible the material is. It also reflects the materials' capability to store energy applied on it for future mechanical response. Loss modulus relates to the viscous response to mechanical loadings and reflects the material's capability to dissipate energy. In some studies, researchers believe that the loss modulus is sensitive to internal segment motions, transitions, relaxations, morphology variations or phase generations. Here in this section, damping parameter, the ratio between storage modulus and loss modulus will be focused to relate to the microstructure in polymer/bamboo composites. Usually the higher the damping parameter in specific materials with unit phase, the more content of non-elastic components; however in multi-phase composites, this data may be dealt with cautions for its complicated suggestions of phases.

Matrix-fiber interface (interfacial region) condition strongly affects the mechanical properties of composites and quite often its dampening level too. Interfacial bonding in fiber-reinforced composites can be considered to be weak, ideal or strong. Ideal interface plays the role of transferring loads and do not contribute to dampening. Kubat et al. (1990) proposed a parameter A (relative dampening at interface to that of matrix) and interfacial dampening (tan δ) to describe poor adhesion in composites, and Ziegel and Romanov (1973) derived a parameter B to depict strong adhesion that do not contribute to dampening in composites, as shown in Eqs. 6 and 7. The property derived composition and interphase models will be presented in this section.

$$A = \frac{1}{1 - V_f} \frac{\tan \delta_c}{\tan \delta_m} - 1 \tag{6}$$

$$B = \left(\frac{\tan \delta_m}{\tan \delta_c} - 1 \right) / 1.5 V_f \tag{7}$$

where tan δ_m *and* tan δ_c stand for dampening parameters in control and composites and V_f means the fiber concentration.

3.4.1 Three-Phase Model

PVA macromolecules have been found to possess a template growth on nano-filler surface (Minus et al. 2006, 2009, 2010, 2011, 2012, 2013; Song and Minus 2014). This newly formed interphase is playing a role of stress-transfer between polymer matrix and nano-fillers and can be assessed quantitatively by DMA. BFs-containing PVA have been prepared in many research groups (Rao and Rao 2007; Chattopadhyay et al. 2011; Yao and Li 2003; Rajulu et al. 1998, 2004; Cao and Wu 2008; Deshpande et al. 2000; Jain and Kumar 1994; Rao et al. 2010, 2011; Tran et al. 2013) but the interphase formation characterizations have not been found in any DMA analyses. This fractional constrained region of PVA can be computed in the following manner (Song et al. 2015a, b, c, d). According to the linear viscoelastic behavior, the relationship between the energy loss fractions *W* and dampening parameter tan δ can be given in Eq. 8. It is well known that loss of energy during dynamic tests on pure polymer fibers (i.e. control) mainly arises due to the presence of less constrained and amorphous/low-ordered regions (Menard 2008). This phenomenon can be analyzed by examining the tan δ peak associated with the glass transition region for the polymer material. This peak amplitude diminishes and/or shifts as ordering in the polymer material increases. By assuming a proportional relationship between W and the fractions of amorphous/low-ordered regions (V_a) (Eq. 9) the more constrained/ordered regions (V_c) can be calculated using Eq. 10. The baseline portions pertaining to the amorphous and constrained regions are determined using the DMA tan δ data from the control fibers. Therefore, Eqs. 9 and 10 use the loss fraction from the control fiber ($W_{control}$), where $V_{a\_control}$ is the volume fraction of the unconstrained (lower ordered regions), $V_{c\_control}$ is the volume fraction of the more constrained regions (crystalline regions), and α is the proportionality constant.

$$W = \frac{\pi E''}{\pi E'' + E'} = \frac{\pi \tan \delta}{\pi \tan \delta + 1} \tag{8}$$

$$V_{a\_control} = \alpha W_{control} \tag{9}$$

$$V_{c\_control} = (1 - \alpha) W_{control} \tag{10}$$

It is recognized that for the nano-composite fibers the ordered portion consists of both crystalline ($V_{c\_composite}$) as well as interphase (V_{m2}) regions. Therefore a modification of the constrained regions in composites is included in Eq. 11, where $W_{control}$ and $W_{composite}$ represent the energy loss fraction of the control and composite fiber samples, respectively. These loss fractions are measured from the glass transition peak amplitude. Equation 12 is derived from Eqs. 10 and 11 to determine the ratio $V_{m2}/V_{c\_control}$. This provides an indication for the presence of interphase regions in the composite samples, which go beyond the general semi-crystalline polymer matrix structures present in the control fibers.

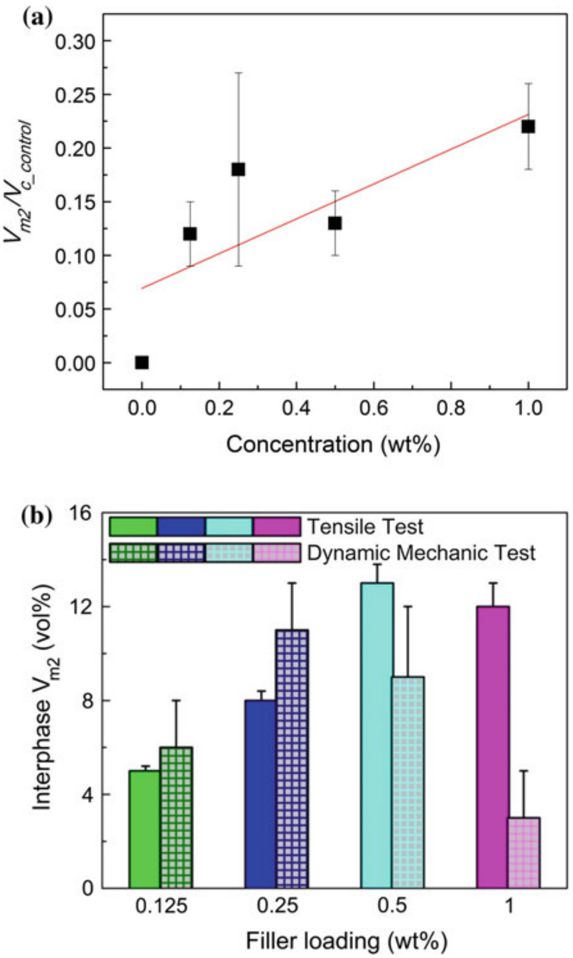
$$V_{c\_composite} = V_{c\_control} - V_{m2} = (1 - \alpha) W_{composite} \tag{11}$$

$$\frac{V_{m2}}{V_{c\_control}} = 1 - \frac{W_{composite}}{W_{control}} \tag{12}$$

Figure 3 shows a plot for $V_{m2}/V_{c\_control}$ as a function of filler concentration, where all composite fibers show an increasing presence of interphase regions as compared to the control fibers. Comparison between the Rule-of-Mixture analysis and these DMA measurements (Fig. 3b) indicate that the composite fibers exhibit regions of self-reinforcement (interphase), which enhances stress-transfer mechanisms in the materials (Song et al. 2015a, b, c, d).

The three-phase model described above has actually been studied theoretically before (Chaturvedi and Tzeng 1991), the interphase is referred as distinct third phase between the fiber and bulk matrix with its own viscoselastic properties.

Fig. 3 **a** Plot shows $V_{m2}/V_{c\_control}$ versus the filler loading (wt%). **b** Plot of interphase volume fraction (V_{m2}) predictions for all composites using DMA analysis as compared with measurements from static tensile tests. Interphase growth is shown to increase with filler concentration. (Permission of reprint in this book was grated from John Wiley and Sons)



Parametric study indicate that the fiber aspect ratio, the elastic modulus and dampening properties of the interphase materials appear to be dominant parameters which significantly influence the dynamic stiffness and viscoelastic dampening properties of the three phase composite system. The main drawback of the model is that the input data for the interphase, i.e., geometric and material properties of interphase have been interpolated and no experimental values are available (Chaturvedi and Tzeng 1991).

3.4.2 Two-Phase Model

The interfacial interaction between the filler and the polymer matrix in a two-phase model can also be studied by correlating dampening parameter and interaction efficiency. The theoretical estimation has been observed experimentally.

$$\frac{\tan\delta_{control}}{\tan\delta_{composite}} = 1 + 1.5V_f B \tag{13}$$

$$B = \left(1 + \frac{\Delta R}{R_o}\right)^3 \tag{14}$$

where the term $\frac{\Delta R}{R_o}$ is the relative increase in particle diameter for spheres, V_f represents the volume fraction of the fillers, B is the intercalation parameter describing the interfacial adhesion between the fillers and the polymer matrix quantitatively. A larger value of B means a better interaction between the two phases.

This phenomenon has also been taken advantage by creating hydroxylation functional groups on fibers (i..e, halloysite tubes, carbon nanotubes, boron nitride tubes, glass fibers, carbon fibers, as well as natural fibers) to further reinforce the epoxy nanocomposites (Zeng et al. 2014). The calculated interaction parameters for composites without and with hydroxylation were listed in Table 5. The low and negative value in epoxy/p-HNTs indicates a weakly physical interaction between the two phases. However, there is a higher B value in epoxy/h-HNTs, which is ascribed to the hydroxylation group density on the external surface of h-HNTs and led to better stiffening and toughening effects. Similarly, BF, powder, and strip reinforced composites are also applicable from this mechanism (Shih 2007). Dampening parameters and interaction parameters were recalculated and listed in Table 5. It can be shown that the bamboo powder showed the highest interaction efficiency with epoxy matrix (Shih 2007). This is sensible due to the easier dispersion and also interactive area caused by the even bamboo powder distributions. Inversely, BFs were observed to be more difficult to disperse. Appropriate coupling agent (i.e., Z6040) was found to increase the BF/epoxy compatibility and therefore increased its storage modulus, loss modulus and also thermal stabilities.

Mercerization effects on BF composites were also examined using DMA (Das and Chakraborty 2008a, b). The bamboo stripes were treated using varied NaOH concentrated solutions from 10 to 20 vol.% before composite preparations. The storage modulus, and dampening parameter were found to increase with increased alkali concentration in treatments. It was explained that with higher concentration of alkali treatments, more and more non-cellulosic material has been removed, and as a result the polymer matrix can penetrate more in the crevices. As a result of this the amount of matrix by volume has become adequate to dissipate the vibrational energy of molecules properly and therefore the dampening parameter value increases. This is also consistent with the differential scanning calorimetry tests,

Table 5 Dampening parameter of epoxy and HNT reinforced composites

Samples	Concentration (wt %)	Dampening parameter (*tan* δ)	*B*
Pure epoxy (Zeng et al. 2014)	0	0.82	N/A
Epoxy/p-HNTs	4.8	0.84	−0.65
Epoxy/h-HNTs	4.8	0.76	1.78
Epoxy (Shih 2007)	0	0.200	N/A
Epoxy/Bamboo powder	10	0.071	12.11
Epoxy/BF	10	0.120	4.44
Epoxy/coupling agent treated BF1	10	0.125	4.00
Epoxy/coupling agent treated BF2	10	0.114	5.03
Phenolic resin (Das and Chakraborty 2008a, b)	0	0.4755	N/A
Phenolic resin/bamboo strips	25	0.159	7.96
Phenolic resin/10% alkali-treated bamboo strips	25	0.1634	7.64
Phenolic resin/15% alkali-treated bamboo strips	25	0.1638	7.61
Phenolic resin/20% alkali-treated bamboo strips	25	0.1808	6.52
HDPE (Mohanty and Nayak 2010)	0	0.6	N/A
HDPE/20% BF	20	0.4	2.5
MA-g-HDPE/20% BF	20	0.2	10
PP	0	0.17	N/A
PP/30% BF	30	0.15	0.44
PP/2% MA-g-PP/30%GF	30	0.11	1.82
PP/15% BF/15%GF	30	0.14	0.71
PP/2% MA-g-PP/15% BF/15%GF	30	0.08	3.75

Note p-HNTs were prepared using H_2O_2 to remove organic impurities while h-HNTs were further treated using NaOH to form hydroxylation functional groups on HNT surfaces. The pure and composite films were prepared using cast mold method (Zeng et al. 2014). Similarly BFs were treated using coupling agents Z6020 (BF1) and Z6040 (BF2) (Shih 2007)

which showed the highest transition temperature in 20% alkali treated bamboo composites.

Maleic anhydride treatment was examined in a similar way to alkali treatment using DMA. The composites treated with maleic anhydride grafted polyethylene (MA-g-PE) exhibited improved mechanical properties, which confirmed efficient fiber/matrix adhesion (Mohanty and Nayak 2010). In dampening parameter peaks, MA-g-PE-based composites produced a higher magnitude of a peak, which is indicative of the fact that the treated fibers have strongly adhered to the matrix and thereby hindered the mobility of the polymer chain in the crystallites (Table 5).

Hybrid composites of polymers reinforced with bamboo (BFRP) and glass fibers (BGRP) were examined using DMA. This tactic of hybridization allows tailoring the composite mechanics for desirable properties. Maleic anhydride grafted polypropylene (MAPP) has been used as a coupling agent to improve the interfacial interaction between the fibers (i.e., both glass fiber and BF) and matrix (Samal et al. 2009). The tan δ spectra presented a strong influence from fiber content and especially from coupling agent, that is, a great depression of this dampening parameter was observed. This suggests a more robust interfacial interaction. With inclusion of coupling agents at various concentrations, the mobility of the macromolecular chains located in the fiber surface interface reduces with the increase in the fiber–matrix interaction that results in a shift in the glass transition temperature T_g towards higher temperature range and a simultaneous decrease in tan δ. Kuruvilla et al. (Joseph et al. 1993) has also reported that incorporation of short sisal fiber into low-density polyethylene (LDPE), results in an increase in storage and loss modulus, whereas the mechanical loss factor (tan δ) decreases.

Two-phase model and three phase model have also been studied theoretically in micromechanics models (Vantomme 1995). For various longitudinal, transverse, and shear loss factors in composite materials (Epoxy/glass fiber composites), the percentage contribution of dampening from fiber, matrix and interphase are predicted. The three-phase model suggested that in unidirectional laminate, poor adhesion between matrix and fiber would lead to low elastic stiffness and high dampening. The method mentioned above derived the interphase in interphase highly occupied composites; however for a normal quality interphase, more sensitive and accurate dampening measurement methods are needed to identify the contribution from interphase to the overall dampening parameter.

3.4.3 Interfacial Interaction Improvement

Low cost, availability with ease, low density, high specific mechanical properties, less wear or corrosion in processing techniques, and environmentally friendly characteristics of the bamboo reinforcement in polymers have been the primary benefits for their commercialization. Despite these advantages, use of BFs, same as other natural fibers, have been limited mainly due to the poor adhesion with polymer matrix as compared to their synthetic counterparts. Various BF surface treatments have been reported and also summarized in Table 6. The interfacial interaction improvements due to these surface treatments have been achieved in both physical and chemical means.

3.5 Tribology Properties

Besides mechanical properties, tribological performance of fiber reinforced polymer composites is critical to many industrial applications, since composites could be constantly exposed to tribological loadings, e.g. abrasive environments. However, there are considerably fewer studies on tribological properties compared to

Table 6 Interfacial interaction improvement methods for better composites' properties

Year	Techniques	Details
2000 (Deshpande et al. 2000)	Alkali/mercerization treatment	NaOH solutions of various concentrations were examined for optimal properties
2002 (Thwe and Liao 2002)	MA-grafting	The effects of Maleated PP/PE/LDPE/HDPE/polyester on tensile and flexural properties of BF reinforced composites were studied. Polar Maleic anhydride grafted polymers can improve fiber dispersion and interfacial interactin trhough hydrogen bonding between hydroxyl groups of natural fibers and carbonyl groups on the maleic anhydride segment of MA-grated polymers
2003 (Saxena and Gowri 2003)	Polymer bridging effects	The effect of surface treatment on the properties of bamboo/epoxy, and bamboo/polyester composites were studied. An improvement in the properties was observed when the surfaces of BFs were modified with polyester amide polyol, which acts as a bridge between the fibers and polymer matrix
2004 (Kumar and Siddaramaiah 2004), 2009 (Kim et al. 2008a, b), 2011 (Kumar and Siddaramaiah 2005)	Polymer coating	BFs were coated with polymers for more efficient polymer-interphase interactions
2004 (Okubo et al. 2004)	Cellulose enhancer	Use poly-lactic acid and BFs extracted by steam explosion method with micro-fibrillated cellulose from wood pulp as an enhancer
2007 (Shih 2007), 2008 (Han et al. 2008), 2009 (Kushwaha and Kumar 2009a, b), 2010 (Kushwaha and Kumar 2010a, b, c)	Coupling agent/Silane treatments	The effects of various coupling agents on filler dispersion and interfacial interaction were studied
2009 (Kumar and Kushwaha 2009)	Monomer grafting	Acrilonitrile treatments at various durations were examined for property modifications in polyester composites
2010 (kushwaha and Kumar 2010a, b, c)	Both silane and alkali treatments	Silane treatment on mercerized BFs was found to improve the mechanical properties the most as compared to only silane or alkali treatments

mechanical properties (Shalwan and Yousif 2013). The wear and friction performance of BF reinforced epoxy composites were also studied (Nirmal et al. 2012). The introduction of BFs influences the anti-shear properties. The friction performance in composites was enhanced around 44% as compared to pure epoxy. Morphology studies confirmed that the orientation of BFs affects the anti-shear behavior, that is, antiparallel to shear direction causes the most resistant properties compared to random and parallel orientation.

4 Thermal Characterizations

A large number of thermal characterizations of natural plant fiber, including BF, based composites have been reported. The most frequently thermal characterization methods include DSC, TGA, and DMA. The increase of thermal transition temperatures has been observed in epoxy (Shih 2007), PP (Chattopadhyay et al. 2011; Samal et al. 2009), polyester (Mounika et al. 2012) and so on. The better thermal stability is mostly due to an increased interfacial interaction between the reinforcing filler and bulk polymers. At the same time, the good dispersion of BFs will help the dissipation of thermal heat and improve thermal transition temperatures. Mercerization treatments can actually decrease the fibers' affinity to water absorption. As soft metal ions replace original hydroxyl functional groups and subsequent neutralization generates the new cellulosic bonds between parent cellulose molecules, the regaining of water moisture greatly decreased. These changes can easily be detected from DSC and DMA. For example, PP is known for its α- and β-crystalline forms. It was observed that the addition of BF to PP or maleated PP causes an increase in the overall crystallization rate. In addition, a considerable amount of β-crystals were present as long as BFs were introduced while in PP matrices, there were only α-forms (Mi et al. 1997). These evidences can be provided from both DSC and WAXD. The nucleation effect for generating β-crystal from BF is also a significant indicator for improved interfacial adhesion. The crystallization peak temperatures detected from DSC or DMA were found to be proportional to BF content, assuming same heating/cooling rates.

Thermal degradation temperatures, unlike glass transition or crystallization temperatures, which can be detected using either DSC or DMA, are derived from TGA. The degradation behavior of many natural fibers was summarized by Yao and coworkers (Yao et al. 2008). Similar to other natural fibers, BFs exhibit an onset degradation temperature at about 214 °C and a major degradation at around 310 °C. These decomposition characteristics should be carefully considered in the design and manufacturing of BFs reinforced polymer composites. Compared to pure PLA or PBS matrix, BFs-filled PLA or PBS composites show relatively lower onset degradation temperature, which might be attributed to the reduced molecular weight of the polymer matrix after intensive processing. To improve the thermal stability, diisocyanates crosslinkers were added to build up the molecular weight of the matrix. Thermal degradation temperature of the resulting composite was increased. Lee and Wang (2006) Fiber content in composites is one of the most important factors that affect thermal property directly. Another important factor is the silane and similar surface treatments. It was observed in one comparative biodegradation study that partial degradation is a good reason that has direct impact on thermal stability of bamboo composites.

5 Application of BF/Polymer Composites as Structural Materials

The applications of bamboo-based materials have been found traditionally in housing, furniture, packaging, transport cargo and so on. Their advantages include low cost, low maintenance, nontoxic, high abrasion resistance, high impact resistance, and dimensional flexibility. Currently on market, most bamboo composites are mostly PE, PU and PP filled BFs or sheets. The application has been extended from fencing, railings, and outdoor furniture to automobile and sport goods (i.e., car doors and surfboards). This section will review these potential usages in the future.

5.1 Automobile Applications

Automobile industry has shifted to more sustainable constructions, including usage of green composites, mainly due to high efficiency and government regulations. Based on the European guidelines, 95% of the vehicle weight has to be recycled by 2015 (Energy and Polytechneio 2003). In the United States, such requirements have not been regulated. Nonetheless up to now the most recyclable parts are still metallic. Auto-body could be reduced in weight by up to around 70% if currently used steel auto-body is all replaced by composites (Yang et al. 2012); and this is specifically important for the appearing electrical vehicles so as to increase the maximum mile range. One way to reduce the cost and simultaneously balance sustainability is to use degradable materials, including polymer based BF composites. Currently most polymer-based composites contain talc, calcium carbonate, mica, and glass and carbon fibers. Most of the parts are used as trim parts in dashboards, door panels, parcel shelves, seat cushions, backrests and cabin linings.

BFs, like other natural plant fibers, have certain drawbacks before preparing successful automobile parts. For example the tendency to form aggregates during processing, low thermal stability, low resistance to moisture and seasonal quality inconsistencies. Besides, the high moisture adsorption of plant fibers leads to swelling and presence of voids at the interface or porous regions, which will greatly deteriorate mechanical properties and reduces dimensional stabilities. Another advantage is the poor compatibility between fibers and polymers. The polymers used in automobile are thermoset, including mainly epoxy and phenolic, and thermoplastic, mainly PE, PVC and PP. Most of these polymers are hydrophilic while cellulose in bamboo is hydrophilic. For better affinity between these two, chemical treatments by chemicals as coupling agent or compatibilizer are necessary (Ren et al. 2012a, b). Thirdly, the lower thermal stability of BFs also limits the possible processing techniques, such as color change, odor variation, gas generation and mechanical property decreases. Strategies such as coating of high-temperature stable polymer or monomer may be valid modifying this property.

5.2 Sports Goods

Application of bamboo composites in sports industry has been well known (Subic et al. 2010). These reinforced composites have been used to produce surfing boards, baseballs, polo balls, etc. The advantages of using Bamboo fibers in sports apparel include their softness, moisture permeability and thermal property. These products are lightweight with particular design and waterproof surfaces. The multi-layered boards are with epoxy matrix with specialty over glass boards. This specialty allows for stiffness and long mechanical durations.

5.3 Construction and Building Materials

Application of natural fibers, such as coconut, sisal, jute, ramie bast, eucalyptus pulp, malva, banana, hemp, kenaf bast, flax, pineapple leaf, sansevieria leaf, abaca leaf, bamboo, date, palm, sugarcane fiber and cotton as indicated in Table 4, are being commonly reinforced in the polymer system to complement the certain specific properties in the final product. Among these different natural fibers, hibiscus sabdariffa, henequen, pines, esparto, sabai grass and banana fibers are still some of the unexplored high potential fibers having similar chemical constituents (cellulose, hemicellulose and lignin), mechanical properties and thermal resistance to other more explored natural fibers such as jute, sisal, hemp, bamboo, oil palm. Construction and building materials are the most interesting application area, which relates to enhancing the functional properties of concrete, steel, wood, and glass, as the primary construction materials. The government policy requires the usage of recyclable and reusable materials for sustainable development.

Due to their light weight, high strength, and abundant sources, bamboo fibers composites have been identified as great eco-products for construction industry. Bamboo-based biocomposites are used as structural components or interior design components in buildings. Bamboo is still being investigated as concrete reinforcement for future housing construction due to the low moisture resistance of bamboo mateirals. The topic has been discussed by Aziz and coworkers (Aziz et al. 1981).

6 Potential Concerns of BF and BF-Based Composites

In addition to the advantages of using BFs in polymer-based composites, the disadvantages include their mechanical and thermal performances, their adhesion with polymer matrix and their processing optimizations. First of all in different growing regions or even different season, BFs are not capable to provide consistent physical properties. These properties can vary from both physically and time-dependent based on interchangeable sunshine levels, water supplies, wind levels, thermal history, and soil conditions. Additionally, these variations can also be observed even in the same forest in between the crops. All of these factors result in significant variations in properties in contrast to their synthetic fiber counterparts (such as synthetic carbon fiber, aramid high performance fibers or E-glass fibers as well as natural clay particles). One possible approach to address this issue is to develop new crops or new mixture of hybrid fibers by evenly distributing these varied bamboo seeds or baby crops. Blending fibers provides a barrier against variability in any single fiber crop. And more essentially is to develop processing techniques so that fine and even fibers are obtained before mixing in polymers.

Another major negative issue of BFs is their poor interaction with most of the polymer matrices. The uneven dispersion may lead to uneven distribution of fibers within the matrix and what is worse, the inefficient stress transfer between the polymer and fibers. Most polymers are hydrophobic and natural fibers are hydrophilic, resulting in poor adhesion and ineffective stress transfer at the interface (Ren et al. 2013). BFs are sensitive to moisture, which leads to reduction of mechanical properties and delamination. Moreover, their susceptibility to microbial corrosion, rotting, and long-term storage may also limit the shipment and composite processing. The commonly suggested solution to this problem is to use chemical coupling or adhesion, aimed to improve the interface compatibility by increasing bonding energy between polymer and fillers.

The third drawback of using BFs is their limited thermal stability. The highest processing temperature is around 300 °C, above which the fibers significantly decompose and deteriorate the mechanical properties of the composites. This greatly limites the variety of resins they can be blended with. To avoid the defects or damages caused by processing techniques, the range of thermal treatment temperature and processing time has to be carefully chosen based on the fiber stability.

Last but not the least, the choices of matrix may also require careful considerations from biodegradability. For example, traditional thermosets render the overall products not easily recyclable in addition to their high melt viscosity and less processing ease. On the opposite side, the novel bio-based thermosets, such as plant-oil based resins, can be decomposed in most cases. Therefore it would be preferable to opt for bio-thermoplastics, which do not need polymerization process and may also combine both benefits of recyclability and prospect disposal.

7 Conclusion

The study of bamboo fibers in various applications has opened up new routines for sustainable, recyclable and self-degradable green composites. Various polymer matrices have been taken advantage for fabricating optimal composites with high mechanical performance. To design such composites thorough investigation of fundamental, mechanical, and physical properties of bamboo fibers are necessary. This review has reviewed the extraction of bamboo fibers, fabrication of polymer composites, mechanical characterization and thermal properties, as well as brief information regarding applications. Although basic scientific questions about bamboo fibers and polymer matrices have been answered, the full content of composites' properties has not been fully achieved and a great deal of research efforts are still required to develop the next generation of BFs-based composites.. It is worth believing that the challenges confronted now will lead toward high performance, biodegradable and renewable eco-friendly materials.

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Biocomposite Materials and Its Applications in Acoustical Comfort and Noise Control

Md Rezaur Rahman, Sinin Hamdan, Elammaran Jayamani, Muhammad Khusairy Bin Bakri and Md Saiful Islam

Abstract In this chapter, an overview of various composite materials for sound absorption applications were reported and discussed in details. This includes composites made of polymer matrix reinforced with synthetic fibers and with natural fibers. This chapter also deals with composites made of recycled materials, bio-based matrix and bio-based fiber materials, hybrid biodegradable materials and surface treatment fiber composites for sound absorption applications. New developments dealing with composite materials made of lignocellulosic fiber and the pros and cons of synthetic fibers and natural fibers were also studied. This chapter also examines the critical issues regarding on composite materials and the scientific challenges faces by researchers and industries that require further research and development of composite materials made from polymer composites for their increased acceptance in the modern world for sound absorption purpose.

Keywords Materials science · Polymer · Plastics · Natural fiber · Synthetic fiber · Sound absorption

1 Introduction

It is noticeable that time elapses before the noise becomes inaudible when a source of sound in a living room is turned off. Less sound absorbing materials in a room, causes the sound to take longer time to fade away. The reverberation time, usually

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defined as the time required for sound to decay in seconds, as it decreases in level less by 60 dB of its original intensity. The sound absorption in the room depends on the frequency of the sounds being considered, it is the same concept as reverberation time (Warnock 1980). For a given noise source, the noise levels it produces within a room and the behavior of the sound it emits are largely determined by the sound absorbing properties of the materials in the room. The sound absorption coefficient of a material is the fraction or percentage of incident sound energy that is absorbed by the material. It is known that the sound absorption coefficient is usually depends on the sound frequency and the values, which are provided in certain literature at the standard frequencies of 125, 250, 500, 1000, 2000 and 4000 Hz. Meanwhile, the noise reduction coefficient (NRC) is the average of the values from 250 to 2000 Hz, inclusive, rounded to the nearest 0.05. The sound absorption coefficient is also used to characterize and rank sound absorbing materials, especially which involve in reduction of noise.

Recently, sound absorption coefficients are also expressed as percentages. A lot of researches and studies have been carried out in this field to find new ways or findings. Thus, many new ways or findings were uncovered, which leads to the potential use of new materials for sound absorption applications. Sound absorbing material is used in a variety of locations, either by making it close to the sources of sound or noise, various in the pathway, or close to the receivers (Ver and Beranek 2006). A wide range of sound absorbing materials that exists which provides varieties of sound absorption properties dependent upon the frequency, thickness, composition, method of mounting, and surface finish. However, most of the materials that have a high value of sound absorption coefficient are usually porous.

A porous absorbing material is a solid material that contains channels, cavities, or interstices that enable sound waves to enter through them. The function of absorptive materials is to transform or impinging the acoustic energy into heat energy. Generally, sound absorptive materials are used to counteract the undesirable effects of sound reflection due to the rigid and hard interior surfaces, which usually help to reduce the reverberant noise levels (Jayaraman 2005). Other than that, sound absorbing materials can also be used either by combination with barriers or inside enclosures to improve its effectiveness (Arenas and Crocker 2010). This chapter addresses the overview of various composite materials used for sound absorption purposes and also addresses various recent researches have already done on composite materials for sound absorption. The following sections present the details of various researches done in the field of polymer matrix composite materials for sound absorption applications.

2 Sound Absorbing Materials

Sound absorbing materials are materials that reduce the acoustic energy of a sound wave as the wave passes through it by the phenomenon of absorption. Sound absorbing materials are commonly used to soften the acoustic environment of a closed volume by reducing the amplitude of the reflected waves. Absorptive materials are generally resistive in nature, either porous, fibrous, or reactive resonators in rather special cases (Bell 1994). Most sound absorbing materials absorbed the sound energy that strikes or projected on it or just reflect a very little amount of sound energy. Therefore, sound absorbing materials have been found to be very useful for noise control. By applying the basic theory on the fiber sound absorption, the kinetic energy of the sound is converted to heat energy when the sound strikes the fibers. Hence, the sound disappears after striking the material due to its conversion into heat. The main reasons for the acoustic energy losses when sound passes through the sound absorbing materials are due to the momentum losses, frictional losses, and temperature fluctuations.

It is known that there are several parameters that may influence the sound losses, especially in sound energy of fibrous materials. It is either caused by the size, number, and type of pores, which are the important factors that affect the sound absorption. To allow sound dissipation by friction, the sound wave has to enter the porous material. This shows that there should be enough pore structures on the surface of the material for the sound to pass through and get dampened (Krcma 1971). To define the normal incidence sound absorption, three parameters (plus the sample thickness) such as tortuosity, airflow resistivity, and porosity are sufficient to be used (Wassilieff 1996). One method to increase the flow resistivity is by creating a flow resistant either by scrim or film layer. Scrim means a fibrous cover layer with finite flow resistivity and film means a plastic cover layer with an infinite flow resistivity (Zent and Long 2007).

To further improve the acoustic characteristic, a perforated plate design can be used in the construction of the panels. The perforated panel porosity and porous material density will significantly change the absorption and coefficient acoustic impedance of the acoustic absorber (Davern 1977; Ver and Beranek 2006). The expression indicated that the influence factor may include the thickness, pitch and radius of the hole, and porosity of the perforated plates and the air contained in the holes. According to Delany and Bazley (1970), for porous material, the characteristic impedance and complex wave propagation constant can be expressed in terms of the wave number, air density, flow resistivity, and sound frequency. Characteristic of sound absorption for porous material is not just a function of type of material, but covered the airflow resistivity and how well material construction can be executed to achieve desirable properties for sound absorbers (Lee and Chen 2001). Thus this showed that all materials have some of its own sound absorbing properties. The incident sound energy which is not absorbed are most probably be reflected, transmitted or dissipated.

Sound absorbing material properties can be described as a sound absorption coefficient in a particular frequency range. The absorption coefficients of the many types of sound absorbing materials available are influenced by a number of factors. In general the greater is the porosity of a given volume of material, the greater its sound absorbing capability. Particularly, the performance of sound absorbing materials is evaluated by the sound absorption coefficient (Horoshenkov and Swift 2010; Bell 1994). The absorption coefficient is a useful concept when using geometrical acoustic theory, especially to evaluate the decay and growth of sound energy in a room. However, when sound is considered as a wave motion, it is necessary to use the concept of acoustic impedance.

Sound absorption coefficient or alpha (α) is defined as the measurement upon incidence of the acoustical energy absorbed by the material and is commonly expressed as a decimal varying between 0 and 1. If 50% of the incident sound energy projected is absorbed, the material sound absorption coefficient is said to be 0.50. A material that absorbs all incident sound waves will have a sound absorption coefficient of 1. Sound absorbing materials are generally used to counteract the sound reflection of undesirable effects created due to the hard and rigid interior surfaces which also help to reduce the reverberant noise levels (Beranek 1960). They are used as interior lining for apartments, automobiles, aircrafts, and ducts, enclosures for insulations and noise equipment's for appliances (Knapen et al. 2003). Sound absorbing materials may also be used to control the artistic performance response of the transient and steady sound sources, thereby affecting the intelligibility of unreinforced speech, the character of the aural environment, and the quality of unreinforced musical sound (Fahy 2001).

2.1 Synthetic Fibers

Glass or mineral fiber materials are the most practical sound absorbing products used in the building construction industry. Sound absorption characteristic values of rock wool were measured and found to be similar to those available commercial sound absorption materials for acoustic treatment, which includes of glass or mineral fiber material (Takahashi and Tomiku 2005). A composite structure with a combination of perforated panel, porous material, polyurethane (PU) foam, rubber particle, and glass wool were also found to demonstrate significant sound attenuation (Wang and Torng 2001). Generally, an industrial application of sound insulation includes the use of materials such as glass wool, foam, mineral fibers and its composites. Although these materials possess good thermal heat and acoustical insulating properties, it may cause environmental pollution and poses a threat and danger to human health.

A very high sound absorption property exhibits by a porous laminated composite material manufactured by premix, lamination, preheating, and molding technique in the frequency range from 500 to 2000 Hz (Hong et al. 2007). Two-stage compression molding of polyolefin-based packaging wastes along with plastic coated aluminum foils, expanded polystyrene and coir pith yields sound absorption properties are comparable to those glass wool (Yang et al. 2003). The combination of non-woven fabric and para-aramid paper was studied and a sound absorption performance at over 2000 Hz was found to be better than that of glass wool (Murugan et al. 2006). Sintered aluminum fiber of 10 mm thickness and 0.6 relative densities demonstrates a high sound absorption coefficient of 0.70 for the frequency range of 800–2000 Hz. Similarly, metal foam yields good sound absorption rate at

2000–4000 Hz (Kosuge et al. 2005). However, when reviewing the issue of safety and health, these fibers can interference human health mainly lungs and eyes when exposed to human. These issues exploration of an opportunity to find alternative materials made from organic fibers to be developed as noise absorption materials.

Using organic fibers as basic material for absorber materials has several benefits. It is renewable, abundance, non-abrasive, cheaper, and safer and less potential health risks concern during handling and processing. Several researchers (Bozkurt et al. 2007) have succeeded in developing particle composite boards using agricultural wastes. Rice straw-wood particle composite boards have properties that tend to absorb noise, preserve the temperature of indoor living spaces and to be able to completely or partially substitute for wood particleboard and insulation board in wooden construction (Khedari et al. 2003). Natural fibers have many remarkable advantages over synthetic fibers. Nowadays, various types of natural fibers (Mohd Yuhazri et al. 2010) have been investigated for use in composites including flax, hemp, wheat, jute straw, rice husk, wood, barley, oats, rye, (sugar and bamboo) cane, grass, reeds, kenaf, ramie, sisal, coir, oil palm, water hyacinth, penny-wort, pineapple leaf fiber, kapok, banana fiber, paper mulberry, and papyrus.

Natural fibers show a lot of advantages in its properties as reinforcement for composites (Sabeel Ahmed and Vijayarangan 2008). Some of the natural fibers have low-density materials that can yield relatively high specific properties with lightweight properties. Natural fibers also offer significant benefits and cost advantages associated with the processing process, as compared to synthetic fibers such as glass, nylon, carbon, etc. Unfortunately, the mechanical properties of the natural fiber composites are much lower than those of synthetic fiber composites. Another drawback of natural fiber composites that make it less attractive is the poor resistance to moisture absorption (Brahmakumar et al. 2005). Hence, the use of standalone natural fiber in polymer matrix is inadequate to satisfy all the technical needed for a fiber to be reinforced with composite. Thus, to develop a superior, but economical composite, a synthetic fiber can be combined with a natural fiber in the same matrix material so as to take the best advantage of the properties of both fibers (D’Arcy 1986).

2.2 Natural Fibers

Due to noise pollution in our surroundings, there are need and demand to find alternative materials that are capable to reduce the noise level at various frequency ranges. The common acoustic panels are those made from synthetic fibers, which poses hazardous substances to the environment and human health and sometimes very expensive for small need. Researches on natural fibers and composite materials were done on acoustical panels. From the view of environmental protection, natural bamboo fibers were alternative materials that can use for sound absorbing purposes. By using impedance tube measurement, the bamboo fiber samples show similar properties to those of glass wool. Enclosing the surface of the bamboo material fiberboard yields a superior sound absorption property when compared to plywood material of similar density (Koizumi et al. 2002). Composite boards of random cut rice straws and wood particles were found to demonstrate higher sound absorption properties than particleboard, fiberboard and plywood in 500–8000 Hz frequency range (Mehta and Parsania 2006). Composite materials made from plant fibers are receiving a great deal of today attention since they are considered environmentally friendly options.

Among all the reinforced fibers, natural fibers have gained its importance, especially for load bearing applications. Natural fiber reinforced polymer composites have a superior properties than those synthetic fiber reinforced composites with certain properties, such as enhanced lightweight, biodegradability, combustibility, ease of recyclability, and etc. These advantages place the natural fiber composites, among those high performance composites that having good physical properties, while maintaining the economic and environmental advantages (Avella et al. 2000). Thus, the interest arises toward polymer composites filled with natural organic fillers. In recent years there has been an increasing interest in the use of fiber-reinforced polymers (FRP) in the sound absorption measurement field. In recent years, bio-composite materials based on natural fibers as reinforcements and biodegradable polymer matrices have received a significant scientific attention (Maldas and Kokta 1989).

A lot of researchers have redirected their research work towards the use of numerous combinations of natural fibers and biodegradable matrix polymer in order to create new types of biodegradable composites with improved mechanical properties with lower cost production. Among the research investigated, especially those natural fibers within its own area, different fillers have its own significant importance. For instance, the development of wood flour composites has been actively pursued (Lee et al. 2004). With the increasing usage of wood-based raw materials, its substitutions are inevitably needed. Recently, usage of agricultural waste as a substitute for wood-based raw materials is fast growing in interest. Among the various agricultural waste, rice straw could be very interesting material to be used as filler in biodegradable polymers due to its high thermal stability compared to other agricultural waste. Mainly, the rice straw is comprised of carbohydrate constituents such as cellulose, hemicellulose, and lignin (Pan et al. 1999).

The content of carbohydrate may vary, as well as other components, such as ash and silica. The character of the rice straw that is hydrophilic is one of the reasons for relatively high moisture content, which is approximately 60% is wet base, or/and 10–12% is dry base. The ash may contents as high up to 22% and low protein content may result in readily material decomposing which is not the same with other type of straws (Yang et al. 2004). In composite materials for building, the rice straws have an advantage and suitable resistance to bacterial decomposition, which makes it a good material to be used as fillers. On the other hand, high content of silica up to 20% represents an additional potential benefit posed for flame retardant usage when used in building industry. From this point of view, various studies showed that the rice straw has a potential as filler in various thermoplastic matrices. Recently, a report of the World Commission on Environment and Development prepared by the United Nations, has examined the potential used of polypropylene filled rice straw composites (Khedari et al. 2003). They reported improved mechanical properties, such as increased tensile modulus of the PP/rice straw composites with the increase of filler content.

In the late 1987, the World Commission on Environment and Development developed a definition of sustainability which became widely known as the Brundtland Report (United Nations 1987). It stated that sustainable development needs to meets the present without compromising the ability to meet future generation's needs. Green technology is widely used to manufacture materials from agricultural based, either as a substitute to synthetic fibers and wood-based materials for acoustics absorption purposes. For example, Malaysia has plenty of agricultural waste such as coconut coir (*Cocos nucifera*), rice husk (*Oryza sativa*) and oil palm frond (*Elaeis guinnesis*) fiber which are anticipated to increase in the future. Coconut coir fiber has good sound absorption at higher frequencies, but then, less for the lower frequencies, which is the same with oil palm fiber. Higher noise absorption of oil palm is due to its higher density (Zulkifli et al. 2009).

Agricultural lignocellulose fibers such as wheat straw, rice straw, or oil palm frond can be easily crushed into chips or particle size. It is almost similar to wood fiber or particle, and may be used as substitutes for wood-based raw materials (Nick et al. 2002). Besides, kenaf can be properly seen as an alternative, especially for thermo-acoustic applications and sound barriers. This shows that natural fibers have high potential to be applied as raw material of sound absorbing materials. Amongst the advantages of these fibers are renewable, non-abrasive, cheaper, abundance, less effect on health problem and safer while handling and processing. Therefore, it is important to increase research on materials acoustical based on the renewable resources that can lead to viable alternatives to conventional materials for current and future applications (Saheb and Jog 1999). Recently human hygiene and environmental protection have turned into another major requirement, which resulting in more environmentally benign, natural materials to be used in certain applications. Among the technologists and scientist, natural fibers have gained much interest for applications in civil, industrial, spacecraft, military, and biomedical sectors (Taj et al. 2007).

In the late 1970s, a series of events that related to the public health concerns made sound-absorbing materials makers to change their main components of their products which have contained of asbestos-based materials to new synthetic fibers. These new fibers are much safer and posed fewer problems to human health. As developed into new industrial ages, the issues related to global warming caused by the emission of greenhouse gases into the atmosphere produced by the materials and manufacture industry may give a lot of impact in the change of course in the acoustical materials market. Therefore, the research on acoustical materials is important and need to be increased, especially those based on renewable resources that can lead to viable alternatives than the conventional materials for future and current applications. These advances include the use of natural fibers, recycled and bio-based polymers, porous metals, surplus materials, new composites, and smart materials.

2.3 Recycled Materials

Great interests were showed by some researchers by trying to make an alternative sound absorber from recycled materials (Mediastika 2008). Use of recycled rubber material results comparable sound absorption properties. Composite material of recycled rubber particles and perforated polymer panel exhibits a sound absorption property dominated by rubber particles when the particle size is too small and where polymer porous material is dominant when the recycled rubber particle size is larger. However the continuing increase and environmental considerations strives the need to develop alternative materials for sound attenuation purposes. Several researchers have succeeded in developing particle composite boards using agricultural wastes. Rice straw wood particle composite boards have properties that tend to absorb noise, preserve the temperature of indoor living spaces and able to partially or completely substitute for wood particleboard and insulation board in wooden construction.

Many studies focused on developing natural fibers, such as palm, kenaf, coconut, coir and many other fibers that have potential to be used as raw or waste material for sound absorption and sound insulation applications (Ersoy and Kucuk 2009). The effect of perforated size and air gap thickness on acoustic properties of coir fiber on sound absorption was investigated and reported suitable for acoustic panel because of its high elasticity and hollow space (Zulkifli et al. 2009). Porous materials used for sound absorption may be fibrous or cellular. Fibrous materials may be in the form of mats, board or preformed elements manufactured of glass, mineral or organic fiber (natural or man-made) and include felts and felted textile (Conrad 1983). Using bio-fibers can address the ecological and economical concerns of the industrial materials (Stahl and Ramadan 2007).

Cotton and jute are very important fibers. Wool also is one of the most widely used textile fibers that are often blended with less-expensive fibers to reduce the cost of the fabric or to extend its use. Synthetic fibers such as polyester and polypropylene have great uses in the industry. Their staple forms can be blended with many other fibers contributing desirable properties to the blend without destroying those of the other fibers (El-Sayed and El-Sammi 2006). Lignocellulosic fibers from agriculture wastes such as rice straw and wood fibers have also great uses in the industry which help in reducing the negative impacts on the environment. In many parts of the country after harvest of the rice crops, the fields must be cleaned and prepared for the next winter cultivation. The rice straw is usually burned soon after threshing. The uncontrolled burning of huge amounts of rice straw causes severe air pollution and leads to the formation of the "Black Cloud".

Wood fiber wastes such as sawdust are mostly used in the thermoplastics industry. The scrap wood sourced for species certain purity and usually it is grounded to certain specific particle size distributions. The specific but broad particle size distribution in commercial sawdust varies among manufacturers (Stark and Rowlands 2003). Non-woven fabric technology is the most modern branch of the textile industry and it embodies both old and very new processing techniques and materials (Turbak 1993). Since 1970, the non-woven industry has observed a phenomenal growth mainly because of a close alliance among non-woven producers, fiber producers, binder producers and machinery manufacturers. There are many non-woven manufacturing processes and products that have been developed and commercialized in recent years (Turbak 1993). Non-woven is used in a variety of purposes due to their advantages, such as versatility, light weight, flexibility, efficiency in sound, and easily tailored properties, recyclability, low process and materials costs (Balasubramanian 2009).

3 Recent Developments in Composites for Sound Absorption

For the study of the multi-layer acoustic absorber, three-layer assembly consisting airspace, perforated plate, and porous material are studied respectively. The results indicated that the density of the porous material and the porosity of the perforated plate have considerably changed the acoustic impedance and absorption coefficient of the acoustic absorber. Some researchers provided a simple but almost accurate analytical acoustic transmission analysis for evaluating the acoustic absorption of multi-layer acoustic absorber which utilized several sections including the layers of airspaces, perforated plates, and porous materials together but only for normal sound incidence. From the results demonstrations, it is reported that the acoustic absorption is generally more broadband and better for the assembly with three layers of perforated plate backed with airspaces than that with single layer of perforated plate backed with airspace (Randeberg 2000).

Micro perforated panels are increasingly used for reverberation control. Micro perforated panels are panels of arbitrary material with perforations of very small dimensions. The perforation diameter is typically less than a millimeter (Stankevicius et al. 2007). A study of acoustical characteristics and physical-mechanical properties of plaster with rubber waste additives was done (Poulain 2006). The sound absorbent material made from scrap tires with small grains showed better sound absorption (Mediastika 2008). A single layer acoustic panel made of paddy husk reinforced sodium silicate showed the optimum sound absorption coefficient at higher silicate content in high range frequencies (Sabri 2007). Then, industrial tea-leaf-fiber waste material also has sound absorption properties at high frequencies *Arenga pinnata* is one of the natural fibers that is abundantly available from the palm sugar tree. Since the last decade, it is widely used for many applications like roof, rope, water filter, and sound proof in the recording studio. Ceiling boards from agricultural wastes, such as rice husks and sawdust, and tested ceiling boards and commercial samples for moisture content, rate of water absorption, and tensile strength. Dimensional stability and mechanical properties of particleboards made from coir pith with average particle sizes of 0.4–2.1 mm, using phenol–formaldehyde and urea–formaldehyde (UF) resins were confirmed and water absorption and swelling were lesser and mechanical properties were best for boards made from the larger particles and phenol–formaldehyde resin (Ajiwe et al. 1998).

Particleboards made of waste tea leaves bonded with UF resin adhesives in three densities. As density increased, internal bonding strength and bending strength also increased (Yalinkilic et al. 1998). More recently, the use of active noise control has been combined with passive control to develop hybrid sound absorbers (Galland et al. 2005). The use of a piezoelectric actuator as a secondary source and wire meshes as porous material has allowed the design of thin active liners composed of several juxtaposed cells of absorbers to be used to reduce noise in flow ducts. Some research has been aimed at producing a broadband sound absorber known as smart foam, which is a hybrid active-passive sound-absorbing material. The absorber is made of melamine foam (made of melamine resin, a thermoset polymer) with Poly-vinyl-dene fluoride (PVDF) piezoelectric-film-embedded actuators (Leroy et al. 2008). Optimization of the sound absorption properties of the smart foam has been developed using three dimensional, finite-element techniques. So a lightweight, thin, efficient sound absorbing material can be produced.

Another approach involves combining active and passive control is using micro perforated panels. This has given promising results when applied in absorber systems (Allard 1993). Porous materials such as foams and fibers are used as sound absorbers. Viscous losses convert acoustic energy into heat as sound waves travel through the interconnected pores (or fibers) of the material. Recently, two very similar analytical formulations have been developed to describe the sound propagation of porous elastic materials. One theory is the Biot-Allard theory and the other is the Bolton-Shaiu theory (Bolton 1984). Though independently developed, these two theories are very similar and yield similar predictive results. The theories predict three types of propagating wave in a porous elastic material–the airborne wave, the structured-borne wave, and the shear wave (which is also structured-borne). The theories demonstrate how the participation of the different types of waves is a function of the boundary conditions (Nae-Ming 1991).

4 Conclusions

The uses of composites have rapidly evolved over the last decade primarily due to the issue of the shortage of commonly used sound absorbing material. This overview outlines the significance of the research and development that has been undertaken in the field of polymer matrix composite for sound absorption. The four general classifications of this material group includes the composites made of synthetic fibers, made of natural fibers, made of recycled materials, and made of bio based matrix and fibers. Due to various environmental concerns natural fiber reinforced with polymer matrix composites has been gaining special attention of technologist, engineers, industrial and manufacture for its enormous potential for application in sound absorption applications. Natural fibers are of basic interests since natural fibers have the ability to be manipulated and functionalized.

Furthermore, it also has advantages from the point of view of weight and fiber-matrix adhesion, specifically with polar matrix materials. Further, natural fiber composite is cost effective, renewable material, low density, environment friendly and reduces CO_2 evolution. In this respect, polymer composite materials are particularly attractive because of their easy of manufacturing, and properties comparable to those of other materials used for sound absorption. Innovations in the composite material design and fabrication processes are increasing the possibility of realizing composites for sound absorption applications. The future growth and sustainability of polymers and composites from renewable sources is reliant on continued research.

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Okra Fibers: Potential Material for Green Biocomposites

Gazi Md Arifuzzaman Khan, Nazire Deniz Yilmaz and Kenan Yilmaz

Abstract Okra bahmia (*Abelmoschus esculentus*) plant is considered as one of the abundant sources of natural fibers. Huge amount of okra plant stem is discarded on the field annually after collecting vegetable, without proper utilization. However, this biomass from the okra plant is a renewable, biodegradable, cost efficient and low-density source for production of bast fibers, and other industrial cost-efficient eco-friendly materials. The research on okra bast fiber has started in 2007. After that, the fiber extraction process, composition of fiber, morphology and performance properties of fiber, fiber modification techniques, and some important applications of the fiber etc. have been established. It was found that the okra bast fiber contains high cellulose content, excellent mechanical strength and stiffness, and good thermal resistance which are comparable to some traditional bast fibers like jute, hemp and ramie. Some okra bast fiber reinforced biocomposites were successfully fabricated with different matrices including biodegradable corn starch, Poly(lactic acid), P(vinyl alcohol), urea formaldehyde resin etc. via application of various processing methods. These studies revealed that the okra bast fiber biocomposites exhibited better mechanical properties, water resistance and thermal properties at optimized processing conditions. Therefore, by suitably optimizing the fiber, matrix, processing conditions, the future expectations of the okra bast fibers can be dramatically enhanced and its usage in composite field can be widened.

Keywords Okra bast fibers · Green composites · Biocomposite processing · Properties of biocomposites

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1 Introduction

Over the past few decades, scientists have been trying to replace non-biodegradable synthetic materials with their environmentally-friendly counterparts. The development of bio-composite materials is the outcome of those innumerable research efforts. The attention in biocomposite is growing fast in different industrial applications including transportation vehicles, aerospace, furniture, construction, packaging as well as biomedical applications due to their notable benefits (renewable, cheap, recyclable, and biodegradable) (Puglia et al. 2004; Müssig et al. 2006; Zah et al. 2007; Yilmaz et al. 2013; Khan et al. 2016b). Biocomposites are mainly composed by combining biodegradable fillers/reinforcement (e.g., lignocellulosic fiber) and the matrix material which may be or not be a bio-degradable polymer. Lignocellulosic fiber reinforced polymer bio-composite systems have become increasingly important in a diversity of engineering fields. The fibers which are used in such application should have sufficient mechanical properties and thermal resistance. As like some traditional fiber such as jute, sisal, hemp, etc., some agro-residual fibers like coir, banana, okra, pineapple leaf fiber etc. are also proved their potentiality in the field of biocomposite (Mir et al. 2012; Raghavendra et al. 2013; Khan et al. 2014b; Asim et al. 2015; Yilmaz et al. 2016a).

Okra (*Abelmoschus esculentus*) has been utilized as a nutritious vegetable and pharmaceutical material for humans (Yilmaz et al. 2015), as well as fodder for livestock for a long time. Sometimes it is considered as an oilseed crop and its durability against drought emphasize its growing importance in sustainable agriculture especially when the global warming is taken into consideration. This economically important crop is cultivated in tropical and sub-tropical regions of the world. Okra plant can be grown as a garden crop or cultivated on large commercial farms (Dhande et al. 2012). It is commercially grown in various countries including India, Nigeria, Sudan Iraq, Coote d'Ivorie, Pakistan, Egypt, Cameroon, Ghana, Saudi Arabia and Benin (according to Factfish database 2013) (FAOSTAT 2015) most of which are developing countries. India ranks the first in the world with 6.35 million tons (70% of the total world production) of okra produced from over 0.35 million hectors land (Dhande et al. 2012; FAOSTAT 2015). Hence, large amounts of plant stems are generated through agricultural processing each year. Unfortunately, this biomass is still commonly discarded by incineration, not only in developing countries, but in some developed countries as well, which is also an environmental problem in global scale. Nevertheless, the abundant okra stems that are found in vast regions of the world can potentially be converted into a various value-added products (Khan et al. 2009b; De Rosa et al. 2010; Yilmaz et al. 2016b).

Recently, a number of researchers have been involved in investigating the exploitation of bast fibers from okra stems as load bearing constituents in composite materials. In 2007, Alam and Khan were the first to determine the composition of okra bast fiber (Alam and Khan 2007). The fiber was reported to consist of great amount of cellulose (67.5%) together with low lignin content (7.1%).

Morphological, thermal and mechanical properties were studied by De Rosa and coworkers (De Rosa et al. 2010). The fiber was found to possess great mechanical strength and modulus. The improvement of different properties by surface modification of okra fiber via chemical treatments (Khan et al. 2009a, b; De Rosa et al. 2011; Yilmaz et al. 2016b) as well as enzymatic treatments (Yilmaz et al. 2016b) were also studied by others studies. The dyeability of the fiber with industrial biowaste and the possibility of its utilization in heavy metal ion removal from aqueous solutions were also among the subjects of studies related to okra bast fiber (Yilmaz et al 2014b, 2016b).

The composites of okra bast fibers were fabricated with various polymer matrices viz poly(lactic acid) PLA, poly(vinyl alcohol) PVA, polyester, urea-formaldehyde resin, starch etc. (Moniruzzaman et al. 2009; Srinivasababu and Rao 2009; Fortunati et al. 2013a, b; Khan et al. 2014a; Guleria et al. 2015).

Studies related to the effect of different fabrication techniques, treatment and material parameters such as fiber fraction, size and orientation on the performance of okra bast fiber based composites are reviewed in this chapter.

2 Okra Plant and Its Fiber

Okra (*Abelmoschus esculentus*) is a summer-time vegetable that grows 4–7 feet long. It is also called as “lady’s fingers”. The geographical origin of okra is thought to be South Asia, Ethiopia or West Africa. But it is now grown all over the world. It is an annual renewable crop. Like other hibiscus plants (kenaf, roselle etc.), okra also contains bast fibers which corresponds to 10–25% of the weight of plant (dry basis). The fiber is found at the outer side of the plant core. The okra bast fiber is bright, shiny and strong similar to conventional bark fibers of jute, kenaf, flax and hemp fibers. The okra fibers form clusters with pectin of plant cell wall. The fiber can be separated from pectin and plant core by various retting or degumming processes. In a retting process, the chemical bonds which hold the stem together are broken and separation of the bast fibers from the woody core takes place due to microbial activity or chemical effect. Different retting/degumming processes can be given as dew retting, cold water retting, hot water retting, mechanical separation, chemical extraction, enzymatic extraction, bacterial degumming, ultrasonic separation, steam-explosion etc. (Bismarck et al. 2001; Evans et al. 2002; Wang et al. 2007; Yu and Yu 2010; Jankauskienė and Gruzdevienė 2013; Martin et al. 2013; Yilmaz et al. 2014a). Most of the researchers extracted fibers from okra stem by water retting because more uniform and high-quality fibers can be obtained by water retting (Yu and Yu 2010). Approximately 10–15 days is needed to complete the water retting process of fiber. The retting period may depend on some parameters like weather conditions, water quality and quantity. Hot humid weather and sufficient amount of water is suitable for retting because microorganisms can grow faster in such conditions. Excellent high-quality okra fibers are separated from the stalk and washed several times with water to remove adhering impurities. Before

Fig. 1 Image of Okra fiber with permission from De Rosa et al. (2010); Copyright 2010 Elsevier

further processing, the extracted fibers are dried well and stored away from water and sunlight (De Rosa et al. 2010). The image of okra bast fibers extracted via water retting are shown in Fig. 1.

The cross sectional and longitudinal microstructure of okra fibers are represented in Fig. 2a and b, respectively. Generally, plant fibers are constructed as a bundle of microfibrills which are bonded tightly by non-cellulosic components including pectin providing strength to the fiber. The region at the interface of two microfibrils is called middle lamella Fig. 2a. In particular, the cross-sectional shape of okra fiber shows a polygonal shape. The longitudinal view of the fibers at Fig. 2b, which shows the surface of the okra fiber and that the fibers are cemented in non-cellulosic components (De Rosa et al. 2010).

The chemical composition of water retted okra fibers are given as 60–70% cellulose, 15–20% hemicellulose, 5–10% lignin, 3.4% pectin, 3.9% fats and waxes and 2.7% water-soluble compounds (Khan et al. 2009b) which is very close to some bast fibers (jute, flax, hemp, ramie etc.) widely used as reinforcement in natural fiber composites. The values of density, diameter, moisture content, tensile strength, young modulus and elongation of okra fiber and some traditional fibers are given in Table 1. No great differentiation of the properties of okra fiber is seen from others. However, the properties of the okra bast fiber show changes based on the species of okra, place of cultivation, plant age, fiber location (main stem or branch) as well. It has also been found that the onset degradation for the okra fibers occurs at a high temperature, 220 °C, whereas that of jute, kenaf and hemp are 205, 219 and 250 °C, respectively (De Rosa et al. 2010). The XRD diagram of okra fiber shows diffraction peaks at 15.6°, 21.8° and 34.0°, which are correspond to cellulose I

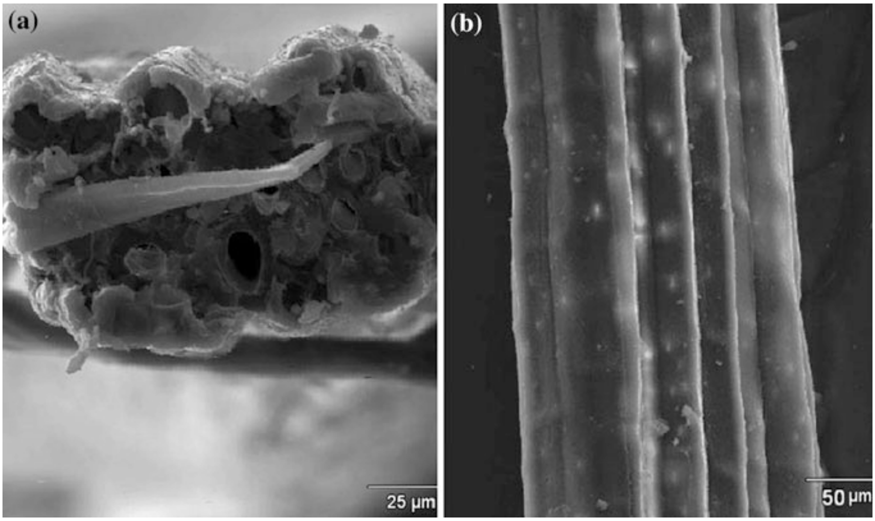


Fig. 2 SEM images of Okra fiber **a** cross-sectional and **b** longitudinal views with permission from De Rosa et al. (2010); Copyright 2010 Elsevier

Table 1 Properties of several conventional natural fibers and Okra bast fiber

Fibers	Density (g/cm^3)	Diameter (µm)	Moisture content (%)	Tensile strength (MPa)	Young modulus (GPa)	Elongation at brake (%)	Source
Flax	1.5	40–600	8–12	345–1500	27–39	2.7–3.2	Bledzki and Gassan (1999), Koronis et al. (2013), Yilmaz (2014), Khan et al. (2016a)
Hemp	1.47	25–250	6–12	550–900	38–70	1.6–4	
Jute	1.3–1.49	25–250	12.5–13.7	393–800	13–26.5	1.16–1.5	
Kenaf	1.5–1.6	2.6–4		350–930	40–53	1.6	
Ramie	1.5–1.6	34–49	7.5–17	400–938	61.4–128	1.2–3.8	
Sisal	1.45	50–200	11	468–700	9.4–22	3–7	
Curaua	1.4	7–10	–	500–1100	11.8–30	3.7–4.3	
Abaca	1.5	10–30	–	430–813	31.1–33.6	2.9	
Okra	1.15–1.45	40–180	4–6	234–380	5–13	2.5–8.6	(De Rosa et al. 2010; Yilmaz et al. 2014b)

(Fortunati et al. 2013a). Peaks at 21.8° and 34.0° relate to 002 and 040 lattice planes of cellulose I, whereas the crystalline peak with a maximum at $2\theta = 15.6°$ correspond to the overlapping of the characteristic 101 and $10\bar{1}$ peaks of cellulose I (placed at 14.7° and 16.6°, respectively) (Ford et al. 2010).

3 Okra Fiber Reinforced Biocomposites

Very few studies have been carried out relating to reinforcement of plastic composites with okra bast fibers. Fibers were used in different forms such as short fiber, nano and woven, for composites preparation. To date, a variety of manufacturing techniques have been employed in production of biocomposites of okra fiber, such as hand lay-up (Moniruzzaman et al. 2009), compression molding (Khan et al. 2014a), solvent casting (Fortunati et al. 2013b) and injection molding (Fortunati et al. 2013a). The manufacturing technique and the parameters including fiber size, fiber weight fraction, and surface treatment for fiber are given in Table 2. The fiber length or size has a great impact on the processing techniques of biocomposites as well as their properties. Generally, long fibers have lower tensile properties than the short fibers (Yan et al. 2014). The fiber weight fraction influences the performance of natural fiber reinforced composites. Generally, higher fraction of fiber results in better mechanical performance of the composites (Ku et al. 2011).

Table 2 Process parameters and fabrication methods of okra fiber biocomposites

Matrix	Fiber treatments	Fiber size	Fiber content (wt%)	Biocomposite processing methods	Source
Poly lactic acid (PLA)	Combined 0.7% $NaClO_2$ and 17.5% NaOH	5–10 mm	10, 20, 30	Twin screw microextruder & injection molding (165–200 °C)	Fortunati et al. (2013a)
Polyvinylalcohol (PVA)	Wax removal, bleaching, alkalization	Nano	1, 2, 5, 10	Solvent casting (room temperature)	Fortunati et al. (2013b
Phenol-formaldehyde resin (PFR)	1–15% NaOH	Short	10–40	Compression molding (150 °C)	Khan et al. (2014a)
Phenol-formaldehyde resin (PFR)	Acrylonitrile grafting copolymarization	Short	9, 19, 29, 38	Compression molding	Khan et al. (2014b)
Phenol-formaldehyde resin (Bakelite)	Sodium chlorite bleaching ($NaClO_2$), acetylation, alkalization, sodium sulphate	Short (2–3 mm)	5, 10, 15, 20	Hand lay-up (170 °C)	Moniruzzaman et al. (2009)
Polyester	Combined NaOH and $KMnO_4$	long	10–21	–	Srinivasababu and Rao (2009
Epoxy	Hybridization by glass fiber	Short 10–50 mm	15	Hand lay-up	Sule (2014)
Corn starch	Acetone	Short 1 mm	5, 10, 15, 20, 25	Compression (hot press) molding (95 °C)	Guleria et al. (2015)

3.1 Biocomposites Processing

Compression molding is the most widely used manufacturing technique of natural fiber composites. This technique is a combination of hot-press and autoclave processes. Khan et al. fabricated short okra bast fiber reinforced phenol-formaldehyde (PF) resin composites by compression molding (Khan et al. 2014a). The fibers were used in the chopped form. Various weight fractions of okra bast fiber such as 10, 20, 30 and 40 wt% were mixed with PF resin in a stainless steel closed mold. Composites were prepared at 150 °C and then post-cured at room temperature for 24 h. After the completion of the curing process, the composite was taken from the mold (Sathishkumar et al. 2013).

Hand lay-up is a labor-intensive process which is simple and cost effectively, it is widely used in civil infrastructure to retrofit and strengthen structure with carbon or glass fiber reinforced composites. Moniruzzaman et al. prepared okra bast fiber-reinforced Bakelite composites by the hand lay-up technique (Moniruzzaman et al. 2009). Before fabrication, the molds (male and female die) were sprayed with silicon mold release agent for easy releasing once the composite has been cured. The short randomly oriented okra fibers (2–3 mm) were added with the matrix material (phenol formaldehyde resin). The resin was then cured at 80 °C for 2 h and at 170 °C for 3 h in a closed matching mold under 0.5 MPa pressure, then cooled and post-cured for 18 h at room temperature. Fortunati et al. produced PLA/okra composites in a co-rotating twin screw micro-extruder (Fortunati et al. 2013a). The process parameters were maintained as screw speed 50 rpm, mixing time 1 min and temperature profile 165–185–200 °C. The composites were prepared with several weight fractions of okra fibers: 10, 20 and 30 wt% respect to the polymer matrix. The mixture was then transferred into injection molding machine.

In another study, Fortunati et al. (2013b) prepared 100–200 μm thick okra nano-crystal-reinforced polyvinyl alcohol composites film using a different method: solvent casting method. The researchers used water as the solvent. Nano-crystal structure was prepared by several steps like scouring, dewaxing, bleaching, alkali treatment and acid hydrolysis of okra fibers. PVA was dissolved at 80 °C for 2 h under mechanical stirring. Then cellulose nano-crystals were added and dispersed in PVA solution finally mixture was sonicated for 2 min. The mixture was casted onto a glass Petri dish. The weight factions of nanocrystal in composites were 1, 2, 5, and 10 wt% respect to PVA.

In order to produce a durable okra fiber reinforced composite, the hybrid of okra fiber with glass fibers has been considered (Sule 2014). The pre-calculated amount of epoxy and hardener in the ratio of 5:1 by weight were mixed in a plastic cup and stirred for 10 min. The mixture was then poured into the mold. Brush was used for uniform distribution of filler and matrix. The sample was cured at room temperature for 24 h.

Okra bast fiber was also blended with cornstarch in aqueous medium at the presence of urea–formaldehyde cross-linking agent at a temperature of 60 °C (Guleria et al. 2015). The mixture was pre-cured at room temperature for 24 h.

Then the pre-cured sample was taken in hot press molding machine. Fabrication process was performed in an iron mold at 95 °C for 1 h under the load of 100 kg/cm^2. Various fiber fraction (0, 5, 10, 15, 20 and 25%) and cross-linker urea–formaldehyde concentration (3, 6, 9, 12, and 15%) were practiced in this study.

3.2 *Properties of Okra Fiber Reinforced Biocomposites*

3.2.1 Mechanical Properties

The properties of natural fiber composites are not only depended on processing techniques but also other parameters, namely, fiber size, fiber content, fiber treatment, matrix type, compatibilizer etc. have great effect on the properties. The mechanical properties of various resin composites reinforced with okra bast fibers (OF), are presented in Table 3. Natural fibers can act as reinforcement element in various forms, namely, short fiber, long fiber, woven fabric and nano-crystalline forms. In case of okra fiber reinforcement, most of the investigation was carried out with short fiber form. Short okra fiber can be easily penetrated into polymer matrix which gives homogeneous composites. In addition to this, short fiber length and random orientation leads to easier wetting of the fiber with the matrix polymer (Arbelaiz et al. 2005; Raghavendra et al. 2013). Most of the studies investigated the effect of fiber loading which ranges between 0–40% in different matrix systems. In most of the studies the mechanical properties of the composites improved with the increase in fiber loading u to a point then the trend got reverse (Khan et al. 2014b; Guleria et al. 2015). The chemical treatments of okra fiber usually improved the properties of their properties (Khan et al. 2014b). In general, chemical treatments increase surface roughness or hydrophobicity of fiber which enhance better interlocking of fiber with polymer matrices (Yilmaz 2015).

Table 3 Properties of okra fiber reinforced biocomposites (Fortunati et al. 2013a; Fortunati et al. 2013b; Sule 2014; Khan et al. 2014b; Guleria et al. 2015; Srinivasababu 2015)

Property	Short of/PLA	Short of/PFR	Short of/epoxy	Short of/corn starch	Okra fiber NC/PVA	Okra/glass hybrid fiber/epoxy	Woven of/polyester
Tensile strength (MPa)	56.1–58.8	9–16	2–12	11–18	–	10.7–12.4	23–35
Tensile modulus (GPa)	4.03–4.63	0.27–0.49	0.14–0.69	0.24–1.61	0.68–1.92	0.7–0.75	0.52–0.80
Elongation at break (%)	1.9–2.2	0.6–3.4	8.9–25.6	2.6–5.1	2–130	–	–
Flexural strength (MPa)	–	10.1–13.2	–	33.5–60.1	–	–	–
Flexural modulus (GPa)	–	1.92–2.09	–	–	–	–	–
Water absorption (%)	–	1.55–2.98	4–19	8–46	–	2.6–4.3	–

Short okra fiber/phenol formaldehyde (OF/PF resin) composites was prepared with fiber loading 10–40% on the basis of weight of composite (Khan et al. 2014a). The tensile strength and flexural strength was found maximum at 30 wt% short fiber loading. In addition, 30 wt% OF loaded composites showed 95, 168, 200, 111 and 159% higher tensile strength, tensile modulus, elongation at break, flexural strength and flexural modulus, respectively in comparison to unreinforced PF resin. The study attributed that fiber has great reinforcing effect, resulting in a uniform stress distribution from a continuous polymer matrix to a dispersed fiber phase. This study also showed that alkali treatment has great influence to enhance the mechanical properties by removal of hemicelluloses; hence, fiber surface become rough which provide better interlocking with matrix polymer. Similar findings were reported by Gassan and Bledzki (Gassan and Bledzki 1997). However, at intensive alkali digestion (15% and 10 h), the treatment caused reduction in the mechanical strength of the fiber as well as the composite. This might be due to the degradation of cellulosic chain at longer time treatment as well as higher concentration of alkali (Yilmaz 2013).

Fortunati et al. investigated the morphological and mechanical properties of untreated and treated OF-reinforced PLA composites. They also studied the effect of various fiber fractions on the mechanical properties (Fortunati et al. 2013a). The fibers were reported to be homogeneously distributed in PLA matrix during the extrusion process for both pristine and alkali-treated okra fibers Fig. 3. It was observed that, the stiffness of the composites significantly increased with the increment in fiber fraction, while all composites show substantial decrease in the plastic deformation for both untreated and treated fibers. The tensile modulus of all composites samples are higher in comparison to neat PLA, which might be due to the constraint of the matrix by the fiber at low loads. By adding short OF to PLA, the ability of crystallization of PLA might have increased because of the nucleation effect of the okra fiber and this effect was more prominent for the composites which produce with alkali treated fibers. From the fiber/matrix interface observation, different results from other studies was found i.e. the untreated okra bast fibers have stronger adhesion with PLA compared to alkali treated fibers. The researchers attributed this situation to the phenomenon that the untreated fibers possess rougher surfaces compared to alkali treated fibers leading to more intense physical bonding with the matrix.

Fortunati et al. also investigated the OF nano-crystal (NC) reinforced PVA composites that were prepared by solution casting method with differing fiber contents of 1, 2, 5 and 10 wt%. The result revealed that elongation at break varied in a wide range (Fortunati et al. 2013b). For 1 and 2 wt% NC loaded composite, elongation at break is decreased 86 and 57%, respectively while for 5 wt% NC loaded composites showed 130% improvement with respect to neat PVA. The reduction in breaking elongation with incorporation of fibers into the polymer matrix is commonly observed for thermoplastic polymer matrices due to formation of stress concentrations (Colom et al. 2003). At 5 wt% NC loading may develop

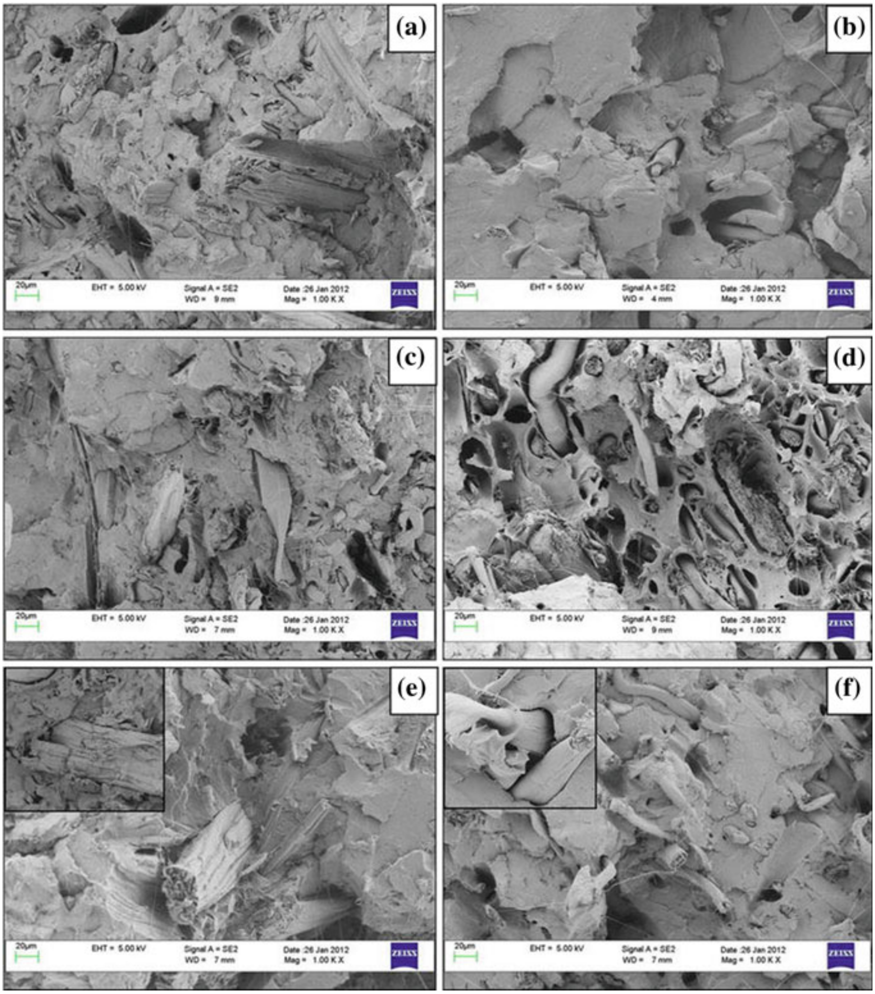


Fig. 3 Fracture surface images of PLA composites reinforced with 10 wt% **a** untreated Okra fiber and **b** alkali treated okra fiber; 20 wt% **c** untreated Okra fiber and **d** alkali treated Okra fiber; 30 wt % **e** untreated Okra fiber and **f** alkali treated Okra fiber with permission from Fortunati et al. (2013a); Copyright 2013 Springer

chemical or physical interactions/bonds between the PVA and cellulose structures. However, the change of Young modulus of 5 wt% NC loaded composite is not significant whereas it shows a substantial increase at 10 wt% NC loading (Fig. 4).

Sule et al. investigated the epoxy composites reinforced with okra bast fibers and glass fibers with various fiber lengths (10, 20, 30, 40, and 50 mm) and okra: glass hybridization ratios (90:10, 80:20, 70:30, 60:40 and 50:50) at 15 wt% total fiber loading (Sule 2014). The better tensile strength and modulus of elasticity for the short okra fiber reinforced epoxy composites were found at 20 mm fiber length.

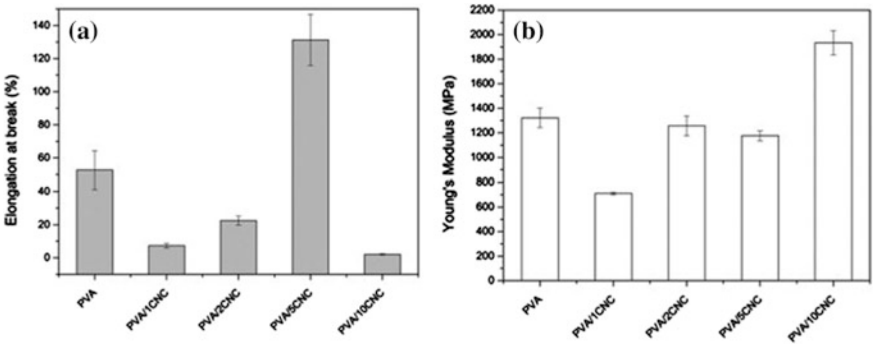


Fig. 4 Elongation at break **a** and Young's Modulus values **b** for polyvinyl alcohol (PVA) and PVA/cellulose nanocrystal (CNC) nanocomposites with permission from Fortunati et al. (2013b); Copyright 2012 Wiley Periodicals, Inc

50:50 (okra:glass) hybridization ratios exhibited the optimal properties for the tensile strength, modulus of elasticity, elongation at break and water absorption characteristics.

Guleria et al. (2015) prepared biodegradable short okra fiber (90 μm dimensions) reinforced corn-strach with fiber loading rates ranging from 5 to 25 wt%. The mechanical properties by means of tensile, compressive, and flexural strength of the composites were measured. It was found that all strength and modulus values of the composites increased with the increase in fiber content up to 15% loading and thereafter show decrease. They explained that the increase in mechanical properties with an increase in proportion of reinforcement was due to enhanced load transfer between matrix and fiber interface. However, above 15% fiber loading, fibers were agglomerated which caused in weak bonding between fiber and matrix and; thus, insufficient load transfer leading to deterioration of mechanical properties.

3.2.2 Water Absorption Property

Water absorption is a very important and undesirable property of composite materials based on the intended application. The mechanical properties and usability of composites materials are directly related to water absorption. Natural fiber reinforced composite can absorb water by three major mechanisms (Karmaker 1997; Espert et al. 2004; Dhakal et al. 2007; Ahmad et al. 2011) such as diffusion, capillary, and transport of water molecules. Diffusion phenomenon occurs inside the micro-channels of the polymer chains. Capillary transport phenomenon takes place within the gaps at fiber-matrix interface space, if proper impregnation of fiber with matrix was not obtained during fabrication of composites. Inside the composites, the transportation of water molecules through the micro-cracks towards the matrix occurs and leads to swelling of the composite. These mentioned mechanisms of water absorption are known as Fickian diffusion model, anomalous or non-Fickian, and an intermediate case between Fickian and non-Fickian respectively (Munoz and Garcia-Manrique 2015).

In order to measure the water absorption percentage, okra bast fiber reinforced phenol formaldehyde resin composites were kept at cold water (20 °C) and hot water (50 °C) for 24 h (Khan et al. 2014a). As expected, it was found that the percentage of water absorption is higher in hot water than cold water which might be caused by the increase in the mobility of the water molecules. Similar trends of moisture absorption were also observed previously (Khan et al. 2015). In the same study it was found that the treated fiber composites exhibited lower water uptake, compared to the untreated fiber composite for the same conditions. This finding might be due to better wettability of the treated fibers with the matrix polymer in comparison to untreated fibers. Sule (2014) reported that the fiber length is another important factor for water absorption rate. The author reported that the relatively higher length fiber composites absorb less water. Another study shows that extent of water absorption is increased with the increment of fiber content in composites. This phenomenon is probably due to the fact that the moisture absorptivity of the fibers is greater than the matrix. The presence of more hydrophilic fiber content can also accelerate the biodegradation properties of composites (Sule 2014). On the other hand, water uptake is reduced with the increase of fiber content in okra fiber reinforced corn-starch composites. This was attributed to the cellulosic structure of the fibers, which is less hydrophilic compared to cornstarch (Guleria et al. 2015). Figure 5 shows that water uptake percentage increases with increase of immersion period up to 6 days thereafter remains constant. It was pre-established that the moisture absorption increased with the increase in the immersion duration up to a certain time period where it reached saturation (Khan et al. 2015).

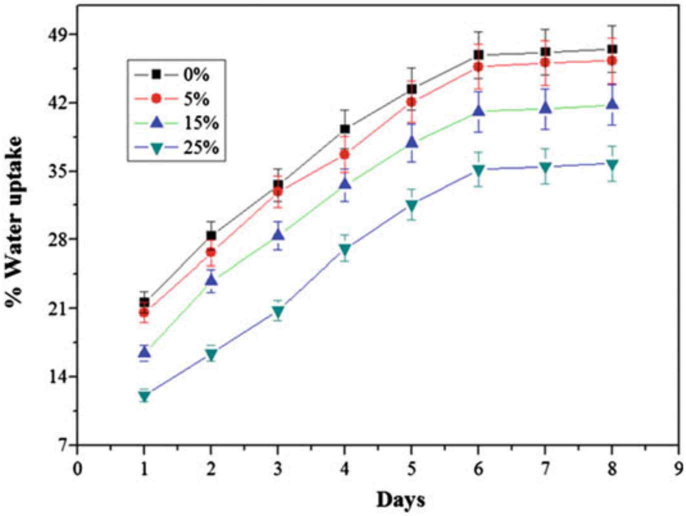


Fig. 5 Water uptake of okra bast fiber - cornstarch composites with different fiber loading rates with permission from Guleria et al. (2015). Copyright 2016 Wiley Periodicals, Inc

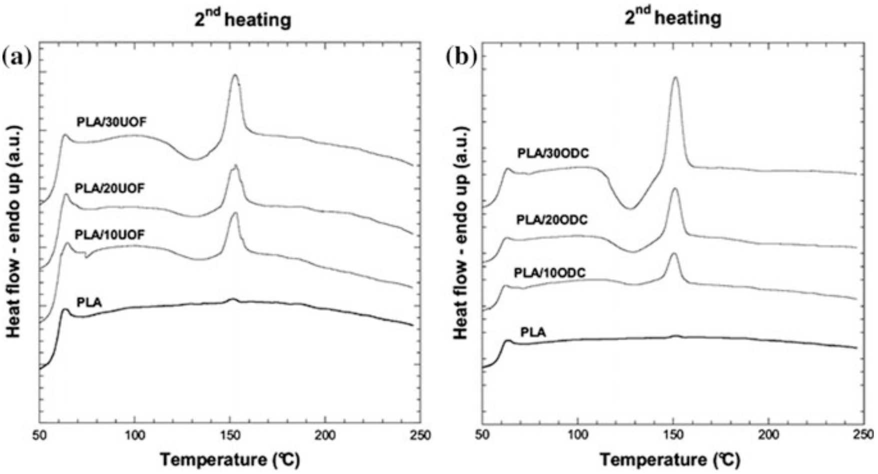


Fig. 6 Dynamic DSC scans (second heating) of PLA composites reinforced with **a** untreated Okra fiber and **b** Okra derived cellulose at different fiber loading rates with permission from Fortunati et al. (2013a); Copyright 2013 Springer

3.2.3 Thermal Properties

Thermal properties of various okra bast fiber based composites were performed by DSC, TGA and DTA measurements. The DSC thermograms for the PLA/okra fiber composites of untreated okra fiber and okra derived cellulose with different loading ratios (0–30 wt%) were studied by Fortunati et al. (2013a). The glass transition temperature, melting endotherm temperature and an obvious cold crystallization exotherm temperature (Tcc) changed with the variation of fiber content Fig. 6. The highest values of cold and melting enthalpies, with respect to the amorphous PLA matrix, were observed for PLA composites with 30 wt% fiber loading rate both with untreated and treated okra bast fibers.

Fortunati et al. (2013b) also analyzed TGA of okra cellulose nano-crystal (CNC)/PVA nanocomposites (PVA, PVA/1%CNC, PVA/2%CNC, PVA/5%CNC, PVA/10%CNC,) in nitrogen atmosphere. The derivative thermogravimetric curves (DTG) shows three degradation steps of the weight loss profiles (Fig. 7). All curves show similar trends. The low initial weight loss at below 100 °C caused by the loss of moisture. After 200 °C, two large decomposition steps were found in the DTG curves for the neat PVA and nanocomposites. The second and third degradation steps happened due to the degradation of PVA together with pyrolysis of cellulose (Frone et al. 2011; Khan et al. 2012a; Li et al. 2012). The peak temperature related to the second step of decomposition for the neat PVA matrix was very close to the PVA/CNC nanocomposites up to 5 wt% CNC content. The decrease of to the second step of decomposition temperature is easily seen for 10% CNC containing composite. This phenomenon is due to the increased crystalline material content, as a shoulder on the left side of the main peak was seen based on the early crystal thermal degradation

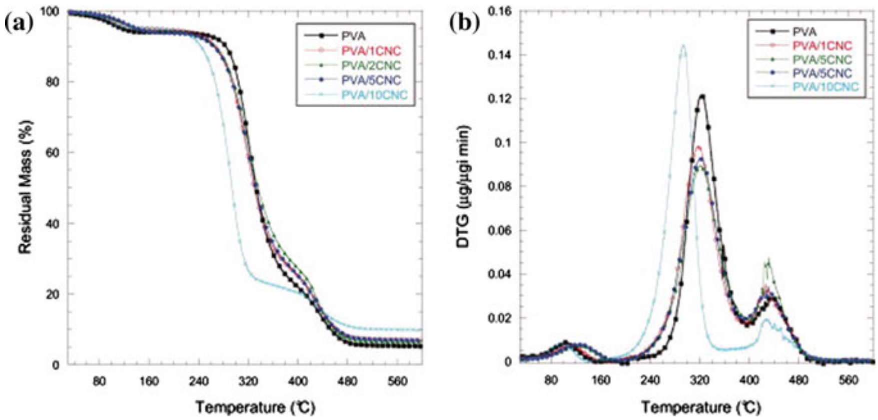


Fig. 7 TG **a** and DTG profiles **b** for neat PVA and PVA/CNC nanocomposites in nitrogen atmosphere with permission from Fortunati et al. (2013b); Copyright 2012 Wiley Periodicals, Inc

(Qua et al. 2009; Frone et al. 2011; Khan et al. 2012a; Li et al. 2012). DSC analysis of PVA/CNC nanocomposites also demonstrated that the okra cellulose nano-crystal does not have great effect on glass transition temperature (Tg), whereas it notably changes the melting temperature of the PVA and the crystallization temperature, due to the nucleating effect of the CNC (Wan et al. 2006).

Guleria et al. (2015) investigated the TGA of native cornstarch (CS), urea–formaldehyde crosslinked (UF) cornstarch matrix and 15% okra fiber–reinforced CS-UF composites as a function of weight loss with increase in temperature at a constant heating rate of 10 °C/min. CS was degraded in two steps: the initial decomposition temperature (IDT, 74.5% weight loss) occurred at 277 °C and final decomposition temperature (FDT, 24.5% weight loss) was found at 525 °C. It was also found that the addition of cross-linked UF resin decreased the IDT (200 °C) and increased the FDT (637 °C). The IDT and FDT for okra fiber–reinforced CS-UF composite were found to be 200 and 657 °C with corresponding weight losses are 51.2 and 37.4% respectively. It is evident that FDTs of okra fiber–reinforced CS-UF composite are higher as compared to CS as well as to cross-linked UF-CS. The improved thermal durabilitye of cross-linked polymer and composites were caused by the introduction of covalent bonds by cross-linking and addition of reinforcing modified fibers (Guleria et al. 2015).

3.2.4 Biodegradation Properties

Most of the biodegradation tests of okra fiber biocomposites were conducted by applying the soil burial method. Fortunati et al. (2013b) studied disintegration rate of PLA and PLA/okra composites according to ISO 20,200 standard. The effects of gradual disintegration of neat PLA and PLA/okra composites with different fiber

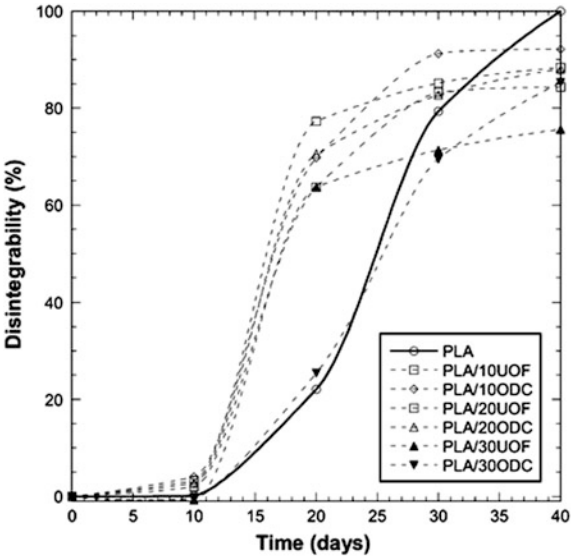


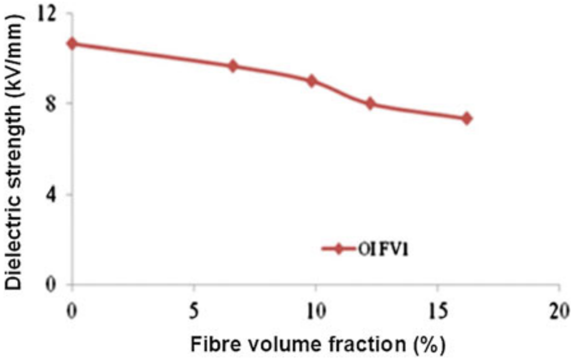
Fig. 8 Disintegration curves of neat PLA and PLA/Okra composites with permission from Fortunati et al. (2013a); Copyright 2013 Springer

loading rates (10, 20 and 30%) during their soil burial test for incubation times up to 40 days were identified by weight loss, FTIR spectroscopy and FESEM. It was found that the addition of higher contents of fibers into the composites leads to accelerated biodegradation due to preferential degradation of the fibers. The introduction of 10 and 20 wt% of fibers increased the disintegration rate of PLA matrix (Fig. 8) due to the hydroxyl groups of the cellulose which act as a catalyst in the hydrolysis of the ester groups of the matrix polymer. This finding suggests that accelerated PLA biodegradation via natural fiber introduction might be useful for the environmental impact of these composites after their useful service life. On the other hand, increasing the okra bast fiber content in the cornstarch based composites decreases the degradation rate, which might be due to the slower degradation of cellulosic okra bast fibers in comparison to the cornstarch (Guleria et al. 2015). In their study, the cornstarch based composited loaded with 15% okra bast fiber showed 40% weight loss for a seven-week duration, whereas the cross-linked corn starch matrix exhibited 60% weight loss by the sixth week and completely vanished in eight weeks. The researchers also observed that the matrix undergoing biodegradation possessed a rough and heterogeneous surface topology compared to non-degraded matrix.

3.2.5 Dielectric Properties

Srinivasababu investigated the insulation property of the okra bast fiber reinforced polyester composites (Srinivasababu 2015). They plotted dielectric strength of the composites against fiber content (volume basis) which is shown in Fig. 9. It is

Fig. 9 Dielectric strength of Okra fiber reinforced polyester composites Adapted from Srinivasababu (2015)



evident that dielectric strength slightly decreased with the increase in the okra bast fiber volume fraction in composites. Among the okra bast fiber reinforced composites, the greatest dielectric strength (9.67 kV/mm) was found at 6.59% fiber volume fraction. Therefore, the okra fiber reinforced polyester composites have been found to have opportunity on the application of the light weight insulating materials.

4 Effect of Chemical Modifications of Fiber in Biocomposites

Natural fibers possess attractive properties, nevertheless, their industrial applications remain limited. Because of their highly hydrophilic nature, natural fibers can readily absorb moisture which leads to the degradation (Bismarck et al. 2001; Khan et al. 2012b; Rashid et al. 2016) and swelling of the fiber which in return deteriorate the dimensional stability and mechanical properties of the biocomposites (Yilmaz 2015). In addition, these hydrophilic fibers are not compatible with hydrophobic polymer matrices. Thus improper impregnation of fiber inside polymer matrix takes place. Chemical treatments of natural fibers are powerful methods to recover these problems (Rong et al. 2001; Dányádi et al. 2010; Kabir et al. 2012; Khan et al. 2013; Pickering et al. 2016). Chemical treatments can also improve the surface properties as well as mechanical strength of fiber which are also important in terms of attaining better properties of composite materials. Effects of some treatments on the morphology of okra bast fibers are shown in Fig. 10. Till now, very limited work has been performed of the effect of chemical treatments on lady's finger (okra) fiber reinforced composites. Moniruzzaman et al. incorporated bleached and untreated okra bast fibers in Bakelite matrix (Moniruzzaman et al. 2009). Appreciable improvement was achieved by $NaClO_2$ bleaching of fiber. Fortunati et al. used alkali treatment to modify okra fiber for PLA composites (Fortunati et al. 2013a). They found that the addition of alkalized okra fiber to the PLA matrix

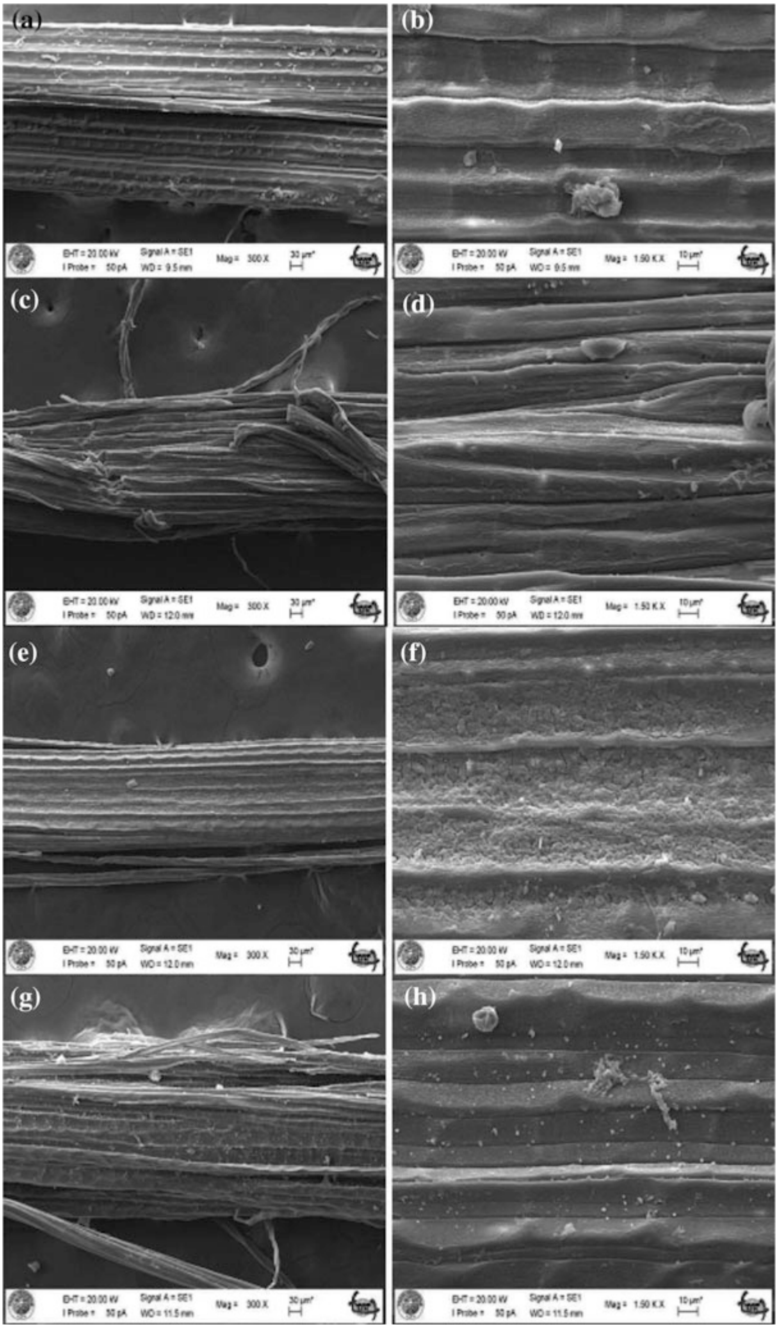


Fig. 10 Scanning electron microscopy images of **a** ×300, **b** ×1500 of untreated, **c** ×300, **d** ×1500 of alkalized, **e** ×300, **f** ×1500 of bleached and **g** ×300, **h** ×1500 of 2% enzyme treated Okra bast fibers with permission from Yilmaz et al. (2016b); Copyright 2016 ICE Publishing

pronounced nucleation effect, which in turn improved the ability of the polymer to crystallize. The results also show that the alkali treatment removes non-structural matter on okra fibers, and increased the stability of the cellulose structure. Besides chemical treatments, the properties of okra fiber reinforced corn starch biocomposites can be improved by using coupling agents including urea formaldehyde resin (Guleria et al. 2015).

5 Potential Applications of Okra Fiber for Green Biocomposites

Strict environmental regulations, social concerns, and growing awareness of the community have fueled the search for new products and processes those are compatible with the ecological environment (Yilmaz et al. 2012). Composites from renewable resources are now moving into the mainstream and the biodegradable composites based on renewable "feedstock" may be competing with conventional plastics in the near future. Okra bast fiber is now considered as an important material extracted from agro-residual biomass. From the technical point of view, okra bast fiber reinforced composites are suitable for use in applications requiring high stiffness at low weight. For transportation applications this leads to extra environmental gains since the lighter construction leads to the reduction in petrol consumption during service life of the vehicle as well as lower emission of greenhouse gas and other toxic fumes (Yilmaz and Powell 2015; Yilmaz 2016). Okra bast fiber reinforced composites have similar properties as composites reinforced with other natural fibers. Some potential applications of okra fiber composites are recommended by a previous researcher. Srinivasababu mentioned that okra bast fiber bacomposites can be utilized in the preparation of various automobile, structural parts (Srinivasababu 2015). Okra bast fiber reinforced polyester composites have shown reasonable insulation ability i.e. dielectric strength. Therefore it might be used in electrical or electronics industries. The properties of the hybrid composite made it suitable for applications in the building and architectural sectors (Sule 2014). The composite can be used as a substitute for hardwood, which is currently used as architectural features in buildings, hence preserving the environment. They can also be used as architectural landscaping, public and private constructions due to their minimal water absorption, walkway paths, and panels for partitioning. Recent works on okra fiber biocomposites with PLA also reveal that the composites completely compost after 40 days in soil. The use OF composites can reduce construction waste and increase energy efficiency would provide a solution to immediate infrastructure needs while promoting the concept of sustainability. As like other natural fibers, okra may possess sound absorbing efficiency and shatter resistant ability and have better energy management characteristics than glass fiber reinforced composites (Table 4).

Table 4 Comparison of some biocomposites reinforced with okra bast fibers and other conventional natural fibers in terms of mechanical properties

Fiber type	Fiber size	Matrices	Fiber loading (wt%)	Coupling agent	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Sources
Untreated okra	Short fiber	PLA	30	NA	58.8 ± 1.4	4.6 ± 0.28	1.9 ± 0.2	(Fortunati et al. 2013a)
Untreated okra	Short fiber	Corn starch	15	UF resin	17.78 ± 0.89	5.14 ± 0.26	1.61 ± 0.08	(Guleria et al. 2015)
Okra nanocellulose	Nanocrystal	PVA	10	NA	–	1.9	<5	(Fortunati et al. 2013b)
Untreated flax	Short	PLA	30	NA	53 ± 3.1	8.3 ± 0.6	1.0 ± 0.2	(Oksman et al. 2003)
Untreated hemp	Short random	PLA	30	NA	44	10.6	–	(Islam et al. 2010; Pickering et al. 2016)
Untreated banana	Short	PLA	30	NA	29	2.67	<5	(Lee and Wang 2006)
Untreated jute	Nonwoven	PLA	30	NA	41 ± 11.6	1.02 ± 0.027	6.08 ± 1.9	Khan/bioresources
Abaca	–	PLA	–	–	74.0 ± 0.7	8.0 ± 0.34	1.44 ± 0.1	(Faruk et al. 2012)
Jute	–	PHBV/ecoflex			35.2 ± 1.3	7.0 ± 0.26	0.8 ± 0.0	(Faruk et al. 2012)
Flax	Short random	PHB	30	NA	~40 ± 2.5	~4.7 ± 0.3	~7 ± 1.5	(Bodros et al. 2007)
Hemp	–	PTP®	25		~62 ± 2	7.2 ± 0.3	n.a	(Müssig et al. 2006)
Alkali treated ramie	Short	PLA	30	Silane	66.8 ± 1.7	n.a	4.8 ± 0.2	(Yu et al. 2010)
Date palm Leaf fibers	short	PVA	30	na	19.6 ± 1.42	1.15 ± 0.05	1.854 ± 0.09	(Mohanty et al. 2013)

6 Conclusions

This chapter confers extraction and chemical modification of okra bast fibers, okra bast fiber based composite processing techniques, and discusses the properties of these composites as well. Okra fibers in short, long and nanocrystal forms were blended with thermoplastic, thermoset and biodegradable polymer matrices which exhibit promising mechanical properties. Chemical modifications of the fiber promoted the mechanical properties of composites. Therefore, it can be concluded that the renewable okra bast fiber has great scope to produce high-quality biocomposites in industrial scale that can form job opportunities, save the environment and increase the incomes of farmers and workers. However, more attention should be given on quicker, cheaper and environmentally friendly methods of modification, as well as reduction of moisture absorption and biodegradation of composites. Future work on okra bast fiber based biocomposites should focus on understanding the environmental assessment, durability, further improvement of the mechanical properties and moisture resistance. Additionally, novel manufacturing processes and surface modification methods should be further developed.

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Interface Interaction of Jute Fiber Reinforced PLA Biocomposites for Potential Applications

Anika Benozir Asha, Ahmed Sharif and Md Enamul Hoque

Abstract Green composites recently have attracted the attention of the researchers due to the advantages of low cost, renewable resource usage and biodegradability. In general, natural fibers being highly polar and hydrophilic have low interfacial shear strength (IFSS) with polymer matrix which is nonpolar and relatively hydrophobic in nature. The surface modification of natural fiber is necessary to improve the fiber/polymer compatibility and their interfacial adhesion. Natural fibers without surface modification embedded in a polymeric matrix generate unstable interfaces and the stress applied to the fiber/polymer composite is not efficiently transferred from the matrix to the fiber. Thus the beneficial reinforcement effect of the fiber remains under exploited. Among the available biopolymer, polylactic acid (PLA) is the most established biodegradable polymer. Surprisingly jute is the second most widely used natural fiber for reinforcing polylactide. Several chemical and physical treatments are performed to improve the fiber–matrix adhesion by reducing the difference between hydrophilic/hydrophobic characters of jute fiber and PLA matrix. Conventional chemical modification methods are alkalization, acetylation and bleaching. These methods are more frequently used due to their relative simplicity, low cost and efficiency. Permanganate treatment, silane treatment, peroxide treatment, shellac resin treatment are also commonly used as chemical treatments. However physical treatments such as plasma treatments, corona discharge treatments, UV treatments etc. are reported as more eco-friendly than chemical treatments. In this chapter a brief summary of all physical and chemical treatments of jute fiber reinforced PLA composites has been presented and the resulted mechanical properties are also discussed.

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1 Introduction

Green composites refer to biocomposites of which both matrix and reinforcement material are from biological origin. Search for alternatives of petroleum resources, ignites the research on renewable materials. Green composites are completely biodegradable and environment friendly. Green composites are the combination of natural fiber and biodegradable polymer matrices. Recently due to the advantages of low cost, renewable resource usage and biodegradability, green composites increasingly attracted the attention of the researchers (Goda and Cao 2007). In biocomposites a variety of natural fibers are used as an alternative of synthetic and glass fiber. There are six basic types of natural fibers. They are classified as follows: bast fibers (jute, flax, hemp, ramie and kenaf), leaf fibers (abaca, sisal and pineapple), seed fibers (coir, cotton and kapok), core fibers (kenaf, hemp and jute), grass and reed fibers (wheat, corn and rice) and all other types (wood and roots) (Faruk et al. 2012). In fully ecocompatible "green" composites biodegradable polymer matrices are used instead of petroleum derived ones. Polysaccharides (starch, chitin, collagen, gelatines, etc.), proteins (casein, albumin, silk, elastin, etc.), polyesters (e.g. poly (hydroxyalkanoate), poly (hydroxybutyrate), polylactic acid), lignin, lipids, natural rubber, some polyamides, polyvinyl alcohols, polyvinyl acetates, and polycaprolactone- are usually known as natural-derived biodegradable polymers (Khalil et al. 2012; La Mantia and Morreale 2011). Although these green composites are not as strong as the traditional GFRP, their moderate mechanical properties and biodegradability make them suitable for applications in housing sectors, secondary and tertiary structures, automotive sector (e.g. Door panels, instrument panels, armrests, etc.), textile (geotextiles and nonwoven textiles), packing materials, entertainment accessories (archery bows, golf clubs and boat hulls), etc. (Goda and Cao 2007; Satyanarayana 2015). Advantages such as low cost, light weight, high specific property, outstanding insulation properties and biodegradability have made green composites widely acceptable. However, the main drawback of green composites is hydrophilic property of natural fibers which lowers their compatibility with the hydrophobic polymeric matrix during composite fabrications. Consequently, the poor fiber-matrix adhesion engenders low mechanical properties. The other disadvantages are the high cost of biodegradable resins and the low processing temperatures that must be used because of the possibility of fiber thermal degradation. As the composite properties significantly depends on fiber/matrix interface properties, it is necessary to improve mechanical and other properties in natural fibers before the fabrication of composites. That's why recent research is particularly focused on the modification of filler surface in order to improve the interfacial adhesion between filler particles (hydrophilic) and polymer macromolecules (generally hydrophobic) and their dispersion in the matrix. The type of fiber used, fiber length, fiber orientation, fiber-volume fraction, and fiber surface treatment also plays an important role in fiber/matrix adhesion and thereby affects the mechanical performance of the biocomposites.

Several physical and chemical treatments of natural fiber have recently been conducted to improve interfacial adhesion (Sirvaitiene et al. 2013; Ragoubi et al. 2012). Incompatibility between hydrophilic natural fibers and hydrophobic matrix, adversely affects stress transformation from the matrix to load bearing fibers. Surface treatments not only improve the reinforcing efficiency of the fiber however also enhance environmental durability (moisture and temperature) and wear resistance of the composite (Goriparthi et al. 2012).

Among the available biopolymer poly(lactic acid) (PLA) is the most established biodegradable polymer which is produced at a large scale of over 140,000 tonnes per year (Mukherjee and Kao 2011). And jute is the second most widely used natural fiber is used for reinforcing polylactide. In recent decades, to improve the fiber–matrix adhesion by reducing the difference between hydrophilic/hydrophobic characters of jute fiber and PLA matrix several chemical and physical treatments are practiced. In contrast to chemical techniques physical treatments are more eco-friendly (Ragoubi et al. 2012).

1.1 Jute as a Fiber

The growing environmental concern leads to rise in the demand of the natural fibers as a substitute of synthetic fibers. The natural fibers such as jute, hemp, sisal, flax, bamboo etc. are renewable and biodegradable in nature. Besides, they can compete with glass fiber in terms of specific strength and modulus. After cotton, jute is the second most abundantly available and relatively inexpensive natural fiber. Jute has already proved to be effective and good reinforcement in the thermoplastic and thermoset matrices (Gowda et al. 1999). Jute is the cheapest vegetable fiber with golden and silky shine and hence called ‘The Golden Fiber’. Because of the high specific modulus of jute fiber, it is now used as a partial substitute of glass fiber (Sever et al. 2012). A key feature of jute is its ability to be used either independently or blended with a range of other fibers and materials. Apart from this, jute fiber has many other inherent advantages like low thermal conductivity, moderate moisture retention, biodegradability, high tensile strength, moderate fire and heat resistance and long staple lengths (Islam and Ahmed 2012; Ghosh and Jethi 2013). Jute fiber can be used as reinforcement in polymer composites in various forms such as short jute fiber, woven jute fiber, unidirectional jute fiber, needle-punched nonwoven fiber mat etc. Jute is also used for the manufacturing of traditional products such as carpets, curtains, bags, packages, handicrafts etc. Jute fiber based composites are also used in semi-structural applications in an automobile. These typical applications are door panels, insulations, headlining, carpets, door pad etc. (Sathaye 2011).

1.2 Compositions of Jute Fiber

Jute is a lignocellulosic bast fiber which is one of the most promising natural fibers. Jute fiber is primary composed of cellulose, hemicellulose, lignin, pectin and waxy substances which play a key role in imparting properties of jute as a fiber. For instance cellulose imparts fiber stiffness, stability and strength. The major constituents of jute fiber are cellulose (58–63%), hemicellulose (20–24%) and lignin (12–15%) (Rajesh and Prasad 2014). This cellulose content of jute is responsible for poor interfacial adhesion between the fiber and polymer matrix. Cellulose is a semicrystalline polysaccharide made up of D-glucosidic bonds. A large amount of hydroxyl groups in cellulose (three in each repeating unit) imparts the hydrophilic properties to the jute fibers. Besides, hemicellulose is the cell wall polymer with the highest water sorption which is responsible for high moisture absorption and results poor mechanical properties (Agu et al. 2012). However, lignin is amorphous and aromatic with the least water absorption. Other components such as fats and waxes (0.4–1%), pectin (0.2–1.5%) and ash (0.5–1.2%) also present in jute fiber.

1.3 PLA as a Matrix

In the last decade, to compete with non-renewable petroleum based products natural fiber reinforced PLA based biocomposites are widely investigated by the polymer scientists. Increased availability of PLA and the competing petroleum costs are the key driving factors for the polymer scientists to produce novel PLA based biocomposites. Poly(lactic acid) (PLA) is a hydrolytically degradable aliphatic polyester which is obtained by polymerization of lactic acid. Lactic acid is the naturally occurring acid which is derived by fermentation of sugars from carbohydrate sources such as corn, sugarcane or tapioca. Most commercial routes utilize ring opening polymerization of lactic acid (Auras et al. 2011). Because of the advantages such as: biodegradability, high degree of transparency, and prominent mechanical properties PLA has become one of the most promising thermoset biopolymers (Adomavičiūtė et al. 2015). However, the poor thermal and mechanical resistance and limited gas barrier properties compared to petroleum-based polymers limit the widespread application of PLA in packaging industries (Abdulkhani et al. 2015). PLA is brittle, chemically inert and hydrophobic in nature and it is therefore necessary to add fibers or filler materials to improve the elongation and impact properties of PLA (Huda et al. 2008). Due to low degradation rates PLA act as matrix material for natural fiber composites to enhance thermal stability of fibers.

2 Fiber Surface Treatment

The performance of any fiber reinforced composites is largely dependent on the fiber matrix compatibility and bonding. Incompatibility between hydrophilic fibers and hydrophobic matrix, leads to poor adhesion of the fiber with the matrix. Weak fiber/matrix interface is responsible for reduced reinforcement efficiency of the fiber (Goriparthi et al. 2012). A weaker interface leads to lack of stress transfer from the matrix to the load bearing fibers and consequently the strength and stiffness are not high. Long fiber pull-outs and clean fiber surfaces in the fracture surface indicates poor adhesion between fiber and matrix. Improper adhesion also leads to debonding and premature failure of composites (Renner et al. 2010). However, the interfacial properties between natural fiber jute and aliphatic polyester polylactic acid are inadequate, because jute fiber contains numerous hydroxyl groups that are strongly hydrophilic (Mukhopadhyay and Fangueiro 2009). Surface modification of natural cellulosic fibers such as jute is conducted to remove surface components such as wax, pectin or hemicelluloses from the amorphous region. This primary treatment is attempted to increase the concentration of oxygen related functional groups on the fiber surface and to make the fiber hydrophobic which imparts better compatibility between hydrophilic fiber and hydrophobic matrix PLA. A number of chemical and physical treatments on a variety of natural fibers have been investigated to enhance interfacial adhesion between fibers and the polymer matrix. Conventional chemical modification methods are alkalization, acetylation and bleaching. These methods are more frequently used due to their relative simplicity, low cost and efficiency (Sirvaitiene et al. 2013). Permanganate treatment, silane treatment, peroxide treatment, shellac resin treatment are also commonly used chemical treatments (Goriparthi et al. 2012; Royse 2012; Li et al. 2007). However physical treatments such as plasma treatments, corona discharge treatments, UV treatments and so on are more eco-friendly than chemical treatments (Kafi et al. 2011).

3 Physical Treatments

Limited thermal stability and higher moisture absorption of natural fiber lead to incompatibility and poor wettability in a hydrophobic polymer matrix. This fact attributes to poor adhesion at the interface of fiber matrix and poor mechanical property of composites. To modify fiber surface for composite applications several physical treatments are done on natural fiber. The objectives of physical treatment are to remove surface contamination, to enhance the contact area and to facilitate mechanical interlocking (Mukhopadhyay and Fangueiro 2009). Physical treatment includes cold plasma treatment, atmospheric pressure plasma, corona discharge treatment, UV treatment, thermo mechanical process etc. These electric discharge methods are very effective for non-reactive polymers (Adekunle 2015). Gibeop et al. (2013) conducted plasma polymerization for surface modification of jute fiber to improve the mechanical properties of Jute fiber/PLA composites. Researchers also studied oxygen plasma treatment, atmospheric pressure plasma treatment, corona discharge treatment and UV radiation for enhancing reinforcement property of jute fiber.

3.1 Plasma Treatment for Jute/PLA Composites

Physical treatments of natural fiber change the structural and surface properties of fiber. Plasma treatment is a dry process, cost effective and environment friendly. To achieve better interfacial bonding of the fiber to matrix plasma polymerization is most effective than other physical methods. Plasma treatment changes the structure and surface property of jute fiber either through activation of the surface or grafting with suitable monomers. Physical modification of fiber is achieved by this treatment through roughening of fiber and produces a large contact area which increases the friction the fiber and the polymer (Mukhopadhyay and Fangueiro 2009). Generally atmospheric pressure plasma and oxygen plasma treatment are widely used for surface modification of jute fiber without affecting the bulk properties. Plasma is defined as gaseous environment contains the mixture of reactive species such as heavy particles, ions, free radicals, electrons and neutral species. Plasma is generated through the ionization of gas or gas mixture. A number of gasses such as argon, nitrogen, helium, oxygen etc. are used. Plasma modification may result in surface cleaning, ablation or etching, cross linking and modification of surface introducing free radicals to the surface (Mukhopadhyay and Fangueiro 2009; Kafi et al. 2011). Ionized gas bombards the surface and causes chemical and topographical changes of the surface. Chemical changes involve the interaction of free radicals through crosslinking and generation of polar groups to the surface to activate the fiber surface. Topographical changes occur through the ablation or etching which involve removal of surface molecules and thus leave the fiber surface rough which improves its adhesion. Plasma surface modification is shown in Fig. 1.

Gibeop et al. studied the effects of plasma treatment (PT) on mechanical properties of jute fiber and jute/PLA composites and compared the study with NaOH treated and untreated fibers (Gibeop et al. 2013). They have found that etching effect of plasma treatment increased surface friction coefficient value which indicates surface roughness. As surface roughness leads to increase of (IFSS), the IFSS of plasma treated jute fiber/PLA composite was found higher than both untreated and Alkali treated (AT) jute fiber/PLA composites. Figure 2 shows that plasma treated jute fiber/PLA composites have 90% greater IFSS than untreated jute fiber/PLA composites which were observed by Gibeop et al. SEM micrographs of plasma treated fiber also revealed that plasma treatment of jute increased the surface roughness (Fig. 3). This surface roughness helps to improve mechanical interlocking through the better interfacial adhesion between the fiber and PLA matrix. Due to good contact of plasma treated jute fiber with PLA matrix Gibeop et al. observed higher tensile strength of plasma treated jute fiber/PLA composites than

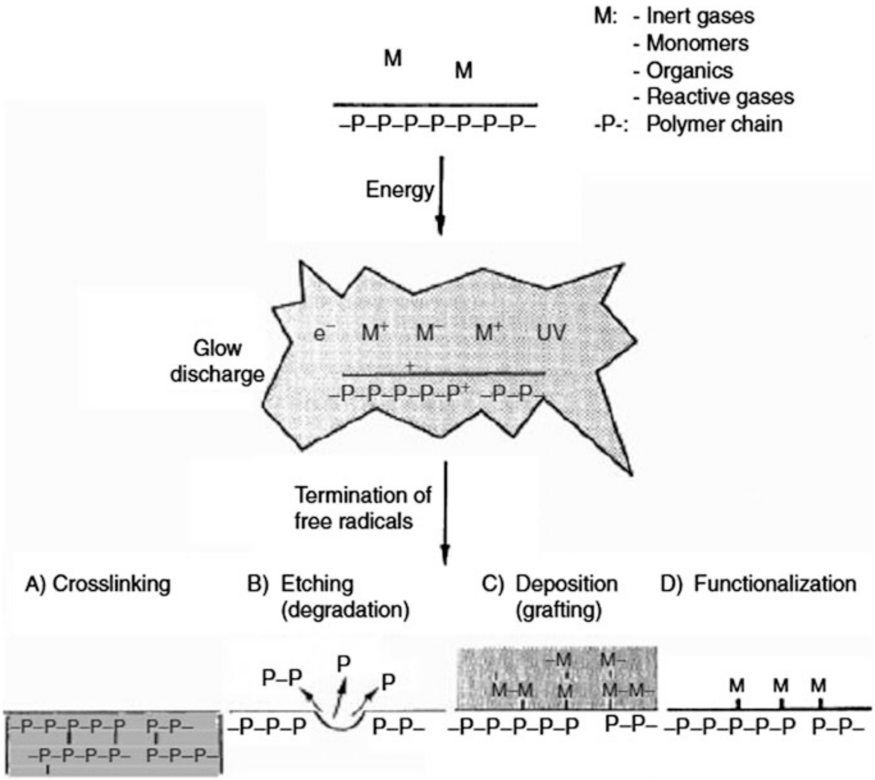
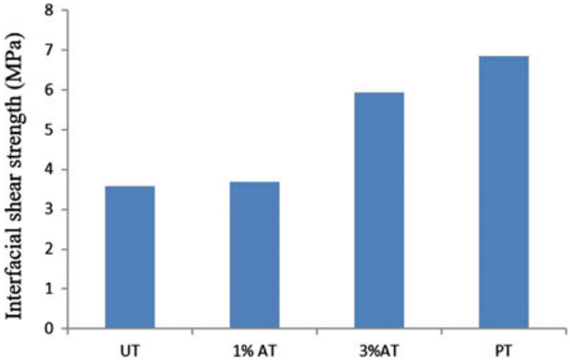


Fig. 1 Schmatic representation of the mechanism of plasma surface modification (Huda et al. 2008)

Fig. 2 Effect of various surface treatments on interfacial share strength (IFSS) of jute fiber/PLA composites (Khalil et al. 2012)



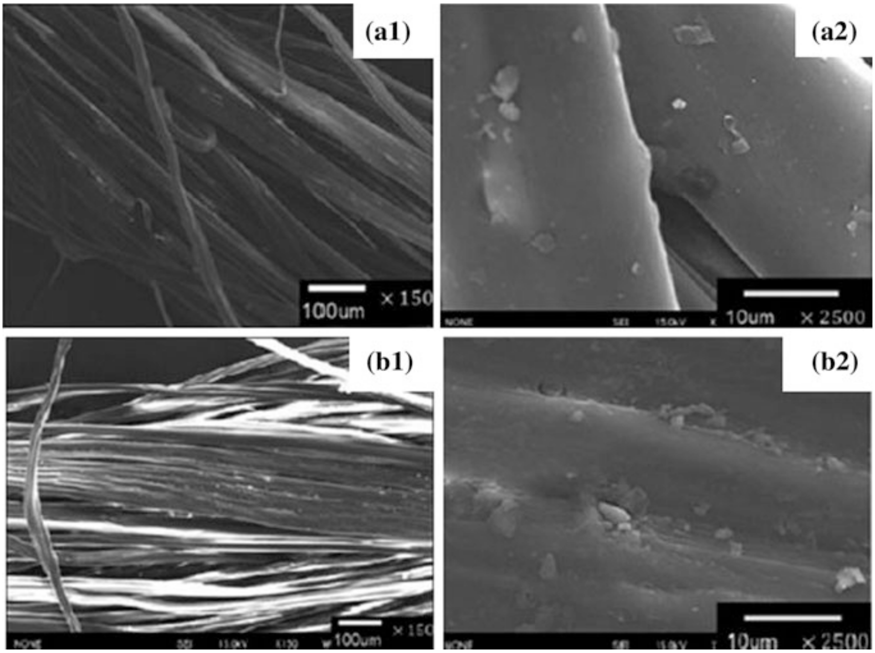


Fig. 3 Surface morphology of jute fiber **a** untreated, and **b** plasma treated (Khalil et al. 2012)

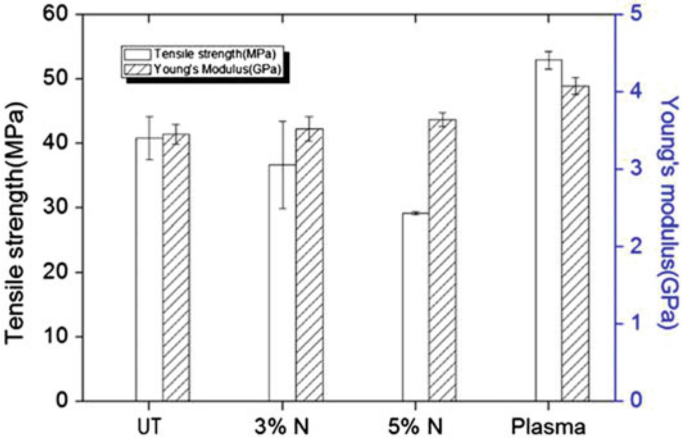


Fig. 4 Tensile strength and tensile modulus of jute/PLA composite (Khalil et al. 2012)

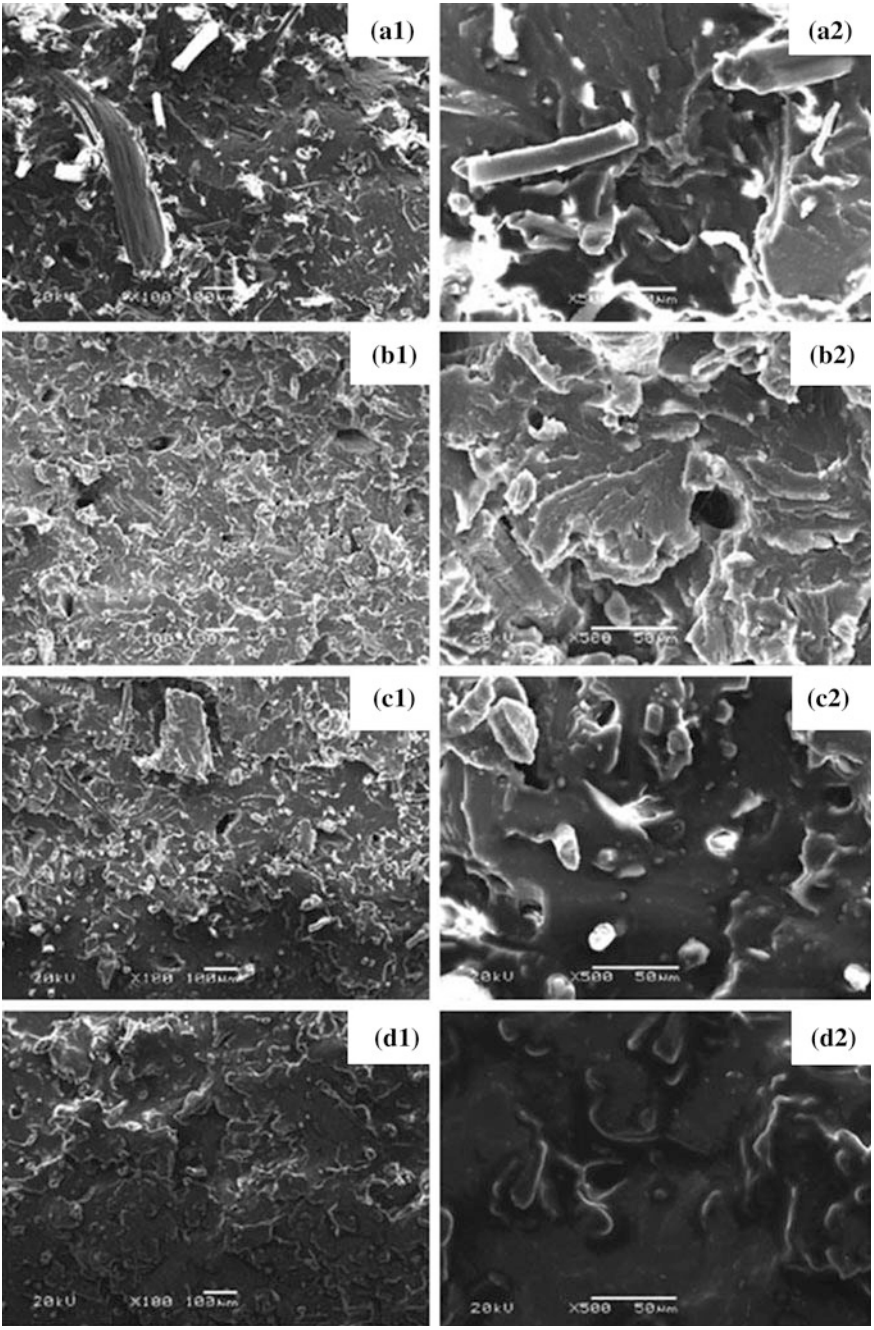


Fig. 5 SEM micrographs of tensile fracture surfaces of jute/PLA composites: Untreated (**a**), 3% AT (**b**), 5%AT (**c**), and plasma treated (**d**) (Khalil et al. 2012)

the untreated or alkali treated composites (Fig. 4) (Gibeop et al. 2013). This tensile property result was also supported by SEM micrograph of tensile fracture surfaces (Fig. 5). Due to poor interfacial adhesion untreated and 3% alkali treated fiber composites showed fiber pull out holes in the PLA matrix. Whereas plasma treated fiber composites hardly showed any hole in the PLA composites due to the etching effect of plasma treatment which led rough surface of the fiber and enabled good adhesion between fiber and matrix. Comparing all the results with alkali treated composites Gibeop et al. (2013) concluded that plasma treatment (physical method) improves the composite's performance more effectively than alkali treatment (chemical method).

3.2 Other Physical Treatments

3.2.1 Corona Discharge Treatment

Corona treatment is a kind of pretreatment to activate the cellulose to improve the efficiency of a grafting process. Corona discharge treatment is an eco-friendly solvent free route which acts on lignocellulosic fiber surface without changing the bulk properties. Gassan and Gutowski (2000) studied the effect of corona treatment on tossa jute fibers. Corona treated jute fibers showed significantly higher polar components of free surface energy with increasing corona energy output. They observed improved polarity of the jute fiber surface, better adhesion and wettability after corona treatment. Corona discharges are relatively low power electrical discharges that take place at or near atmospheric pressure. The corona is generated by strong electric fields associated with small diameter wires, needles, or sharp edges on an electrode. Corona discharges exist in several forms, depending on the polarity of the field and the electrode geometrical configurations. Corona treatment changes the morphology of lignocellulosic fiber depending on the corona energy output. Corona treatment, though, is difficult to use on 3D objects. This limitation applies not only to 3D shaped products, but also to fibrous materials, particularly in the form of woven fabrics or strands. The awareness of the existence of these limitations has highlighted the need for alternative, more 3D 'compliant' surface modification techniques such as ultraviolet radiation (e.g., UV) light.

3.2.2 Ultraviolet Treatment

Ultraviolet energy has also been used to modify the natural fibers. UV light cannot penetrate beyond the surface fibers and leaving the bulk materials unaffected. When the fiber surface is exposed to UV radiation to modify the surface, UV radiation produces large numbers of highly reactive free radicals. Surface modification is particularly useful on natural fibers such as jute, wool and cotton etc. In the presence of air and free radicals, oxidation on surface of the fibers occurs which alters their physical, chemical and mechanical properties. Surface of the fibers form a sacrificial layer beyond which a brief exposure to high-intensity UV is unable to penetrate. This protects the bulk fibers responsible for fabric strength. Almost every chemical constituent (cellulose, hemicellulose and lignin) of wood and natural fibers is sensitive to UV radiation with a consequential deterioration effect. Of these chemical constituents, lignin (as the surface constituent of a natural fiber) appears to be oxidized and degraded very rapidly by UV light. UV treatment increases the wettability of hydrophobic fibers to improve better adhesion with polymer matrix. Gassan et al. treated tossa jute fibers by ultraviolet and studied its effect compared with corona treatment (Gassan and Gutowski 2000). The UV treatment of the jute yarn led to higher polarity (up to 200% increase) with increased treatment time and constant bulb-substrate distance. Furthermore, the treatment distance was showed to have a significant effect on the polarity as well as to the tenacity of the yarn and 30% increased flexural strength was achieved.

3.2.3 High Pressure Steam

High pressure steaming is one of the best pretreatment which is mainly a combination of both physical and chemical method. Steam treatment process separates the lignocellulosic material into its main components, namely cellulose fibers, amorphous lignin, and hemicellulose. Wang et al. studied the structural change of jute fiber exposed to high pressure steam after mercerization, acid steam and alkaline treatment (Wang et al. 2009). They carried out the treatment by a pressure cooker with pressure of about 0.078 MPa for 30 min. This treatment split the fibers along fiber axis which created micro- and nano-fibrils which is beneficial to better adhesion.

4 Chemical Treatments

Jute fiber is composed of small units of cellulose surrounded and cemented together by lignin and hemi-cellulose. Large cellulose content of jute fiber leads to hydrophilic property which results poor adhesion with polymer matrix. Chemical treatments including alkali, silane, acetylation, benzoylation, acrylation, permanganate etc. are conducted to improve the adhesion between the fiber surface and the polymer matrix. The chemical modification aims to improve natural fiber hydrophobic nature, interfacial bonding between matrix and fiber, surface roughness and wettability, and also decrease moisture absorption, leading to the enhancement of mechanical properties of the natural fiber reinforced composites. To improve adhesion of jute fiber with PLA matrix researchers have investigated the effect of chemical treatments including alkali, permanganate, peroxide, shellac resin and silane treatments.

4.1 Alkali Treatment (Mercerization)

Alkali treatment or mercerization is one of the most commonly used chemical treatments of natural fibers. It cleans fiber surface removing impurities, lignin, waxy substances and natural oils, depolymerizes cellulose, and exposes the short length crystallites. It also produces a rough surface topography, facilitating mechanical interlocking which leads to an improvement in fiber-matrix adhesion. Mercerization increases the number of free hydroxyl groups in the fiber surface, which improves the adhesion with polymer matrix. Addition of aqueous sodium hydroxide (NaOH) to natural fiber promotes the ionization of the hydroxyl group to the alkoxide.

$$\text{Fiber} - \text{OH} + \text{NaOH} \quad \text{Fiber} - \text{O} - \text{Na} + \text{H}_2\text{O}$$

In this structure, the OH groups of the cellulose are converted into O–Na groups, expanding the dimensions of molecules. Sodium hydroxide (NaOH) is used in this method to remove the hydrogen bonding in the network structure of the fibers cellulose and thus to increase surface roughness of the fiber. This process consists of soaking of natural fibers into NaOH solution for a certain range of time. Here concentration of NaOH is in the range of 1–25% and processing time of 1–60 min. Then the fibers are neutralized with acetic acid to remove any absorbed alkali and finally washed in distilled water thoroughly and then dried in an oven. Rajesh and Prasad (2014) studied jute fiber/PLA composites with different concentrations (5, 10 and 15%) of NaOH and successive H_2O_2 treatments on jute fiber. It was reported that composite with 10% NaOH treated jute fiber showed a 7.5% increase in tensile strength. They had shown that tensile fracture surface of untreated fiber reinforced PLA composites showed large fiber pullout which indicated the poor adhesion of fiber–matrix. They also observed that lower concentration of NaOH was not so effective to improve the fiber matrix adhesion. Moreover higher concentration of NaOH of alkali treatment led to fiber damage which was also responsible for less stress transfer between fiber matrix. For 10% NaOH treated jute composite they observed fiber breakage rather than fiber pullout which is the evidence of better stress transfer between fiber matrix (Fig. 6).

4.2 Permanganate Treatment

Permanganate treatment is one of the chemical treatments used for jute fiber surface treatment in jute/PLA composites. This treatment is usually conducted by using potassium permanganate ($KMnO_4^-$) solution (in acetone) in different concentrations with soaking duration from 1 to 3 min after alkaline pre-treatment. Permanganate is a compound that contains permanganate group $KMnO_4^-$. Permanganate treatment leads to the formation of cellulose radical through $KMnO_3^-$ ion formation.

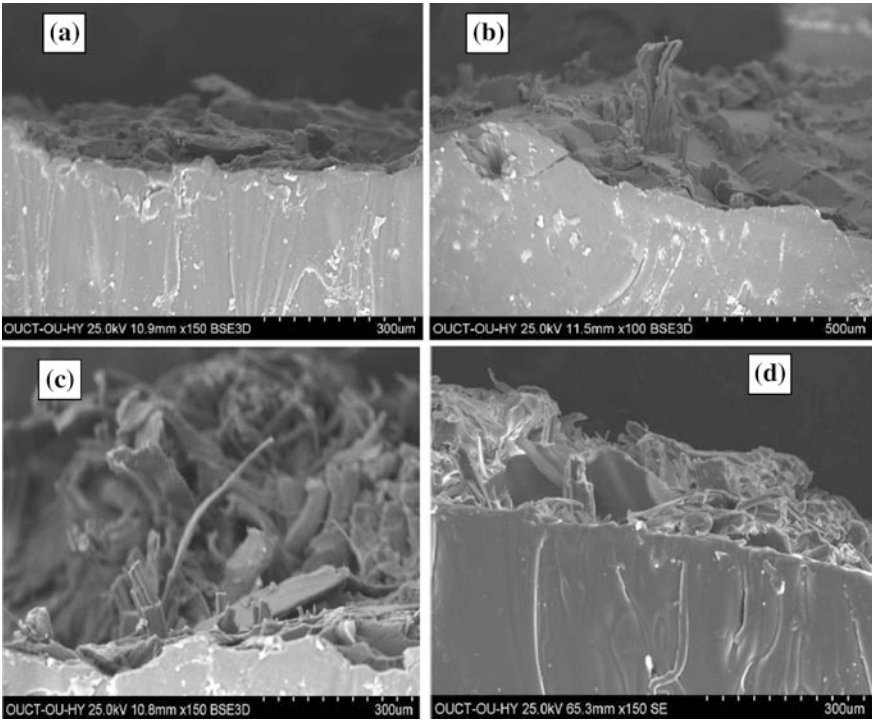
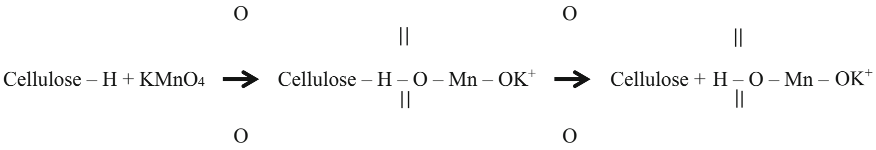


Fig. 6 SEM images of tensile fracture surface of jute/PLA composite **a** untreated, **b** 5% NaOH treated, **c** 10% NaOH treated, **d** 15% NaOH treated (Gassan and Gutowski 2000)

Then, highly reactive Mn^{3+} ions are responsible for initiating permanganate induced grafting of PLA into jute fiber as shown below:



$$\text{Cellulose} - \text{H} + \text{KMnO}_4 \rightarrow \text{Cellulose} - \text{H} - \text{O} - \underset{\underset{\text{O}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{Mn}}} - \text{OK}^+ \rightarrow \text{Cellulose} + \text{H} - \text{O} - \underset{\underset{\text{O}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{Mn}}} - \text{OK}^+$$

However, in a permanganate treatment, mechanical interlocking between the rougher fiber and the matrix is a dominant interfacial bonding mechanism than that of the chemical bonding. The hydrophilic tendency of natural fiber decreases with the increase of $KMnO_4$ concentrations (Paul et al. 1997). Goriparthi et al. (2012) in their permanganate treatment dipped alkaline treated fibers in 0.125% permanganate acetone solution for 1 min and then dried the fibers at 80 C for 5 h to remove excessive solvent and moisture. Permanganate treatment showed better flexural property than alkali treatment.

4.3 Peroxide Treatment

Peroxide treatment is one of the easiest chemical treatments to improve natural fiber surface properties. Peroxide is a specific functional group or a molecule with the functional group ROOR containing the divalent ion O–O. Organic peroxides tend to decompose easily to free radicals of the form RO, which further reacts with the hydrogen group of the matrix and cellulose fiber. In peroxide treatment, nature of bonding is chemical bonding with little mechanical interlocking. Benzoyl peroxide [BP, $(C_6H_5CO)_2O_2$] and dicumyl peroxide [DCP, $\{C_6H_5C(CH_3)_2\}_2O_2$] are chemicals that are usually used in natural fiber surface modifications. Goriparthi et al. (2012) in their study used 6% benzoyl peroxide for peroxide treatment of jute fiber. Jute fibers were immersed in 6% BP acetone solution for about 30 min after alkali pre-treatment. As a result, of peroxide treatment of jute fiber, the hydrophilicity of the fibers decreased and the tensile as well as flexural properties of jute/PLA composites increased more than alkali or permanganate treatment.

4.4 Silane Treatment

Silane with chemical formula SiH_4 is a chemical compound which are used as coupling agents to reduce the number of cellulose hydroxyl groups in the fiber–matrix interface. Silane treatment may contribute hydrophilic properties to the interface especially when amino functional silanes are used as primers for reactive polymers. The primer may supply much more amine functionality than can possibly react with the matrix at the interphase. Goriparthi et al. (2012) used two kinds of silane coupling agent's namely 3-amino propyl trimethoxysilane (silane 1) and trimethoxy methyl silane (silane 2) to modify the jute fiber surface of jute/PLA composite. Jute fibers were soaked in a solution of acetone/water (50/50 by volume) with a 1% silane concentration for 2 h and then cleaned with acetone and dried in the hot air oven at 80 °C for 5 h. In silane treatment, silane reacts with water to form silanol and alcohol (John et al. 2008).

$$\text{Silane 1}: NH_2(CH_2)_3Si(OCH_3)_3 + 3H_2O \rightarrow NH_2(CH_2)_3Si(OH)_3 + 3(CH_3OH)$$
$$\text{Silane 2}: CH_3Si(OCH_3)_3 + 3H_2O \rightarrow CH_3Si(OH)_3 + 3(CH_3OH)$$

The silanol then reacts with the hydroxyl group of the fiber and forms a stable covalent bond.

$$\text{Silane 1}: NH_2(CH_2)_3Si(OH)_3 + H_2O + \text{Fiber} - OH \rightarrow NH_2(CH_2)_3Si(OH)_2 - O - \text{Fiber} + 2H_2O$$
$$\text{Silane 2}: CH_3Si(OH)_3 + H_2O + \text{Fiber} - OH \rightarrow CH_3Si(OH)_2 - O - \text{Fiber} + 2H_2O$$

Other functional group on the silane molecule, such as NH_2 for silane 1 and methyl group for silane 2, would react with hydroxyl group of the PLA matrix,

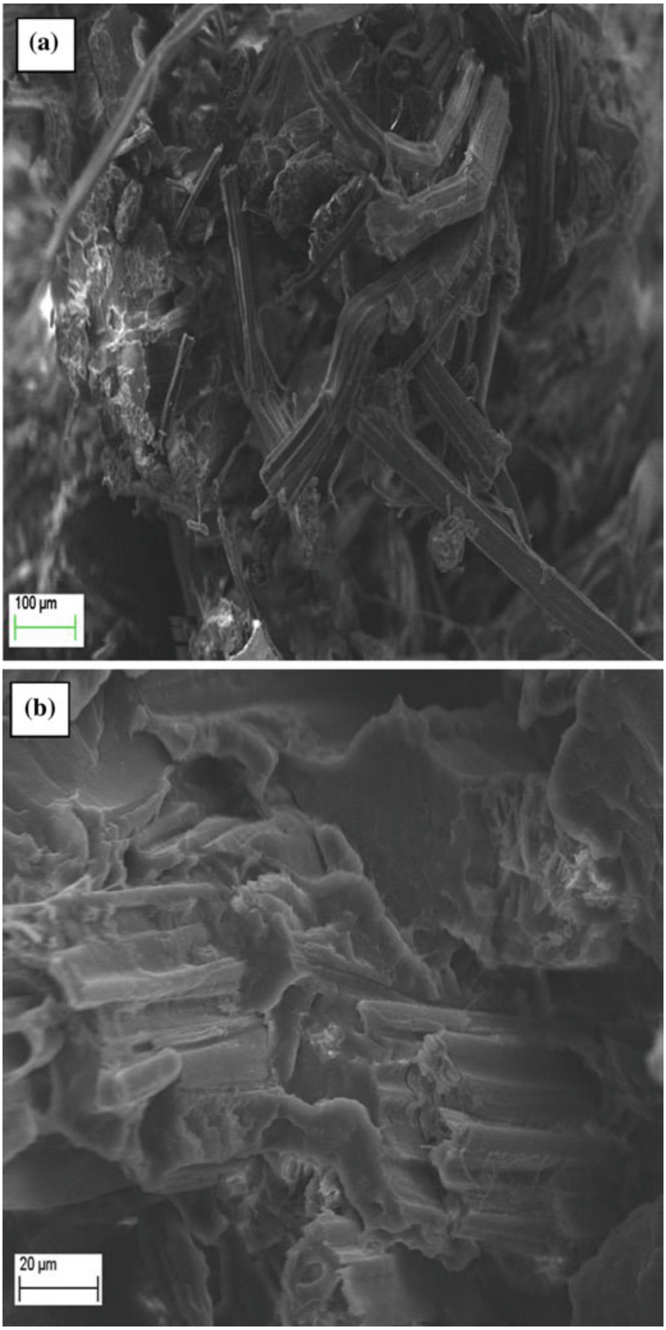


Fig. 7 SEM image of tensile fracture surface of jute/PLA composite **a** untreated, **b** Silane 2 treated (Asim et al. 2015)

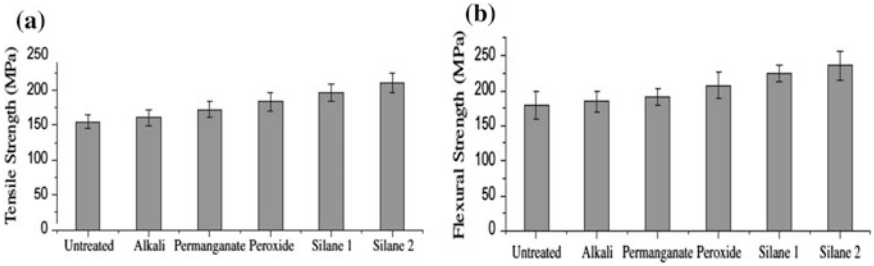


Fig. 8 Variations of **a** tensile strength, and **b** flexural strength of different chemical treated jute/PLA composites (Asim et al. 2015)

when the silane treated fiber is combined with combined with the PLA matrix. Goriparthi et al. (2012) found that silane 2 is more effective than silane 1 in improving the tensile and flexural properties, which may be due to the strong bond formed between organo functional group of silane 2 and PLA matrix. This was also confirmed from the SEM image (Fig. 7) of tensile fracture surface of silane 2 treated jute fiber/PLA composite. A large number of fiber pullouts was observed at fracture surface untreated jute/PLA composite, which is an indication of poor fiber matrix adhesion. Whereas silane 2 treated composite exhibited fiber breakage rather than pull out which indicates a strong interface between the fiber and matrix. Goriparthi et al. (2012) observed the maximum tensile and flexural properties (Fig. 8) for silane 2 (trimethoxy methyl silane) treated jute fiber/PLA composite. They compared the result with other chemical treatments and showed the order of increment of tensile properties as: silane 2 > silane 1 > peroxide > permanganate > alkalization > untreated. They got a maximum 35% increment of tensile strength for silane 2 treated jute fiber reinforced PLA composite. In case of silane 2 treated composites, flexural strength and flexural modulus were improved by 24 and 41% respectively. The tensile and flexural strengths of composites fabricated in that study were much higher than those of PLA/unidirectional jute fiber composites fabricated through non solvent techniques (Goriparthi et al. 2012; Khondker et al. 2006). Silane 2 treated jute fiber/PLA composite has the strongest interfacial adhesion, which was also proved by its abrasive wear behavior. Goriparthi et al. (2012) observed the highest wear resistance of Silane 2 treated jute fiber/PLA composite among all other chemically treated jute/PLA composite.

4.5 Shellac Resin Treatment

Shellac resin is one of the thermosetting resins of animal origin secreted by the lac insect. This shellac resin was used for surface treatment to improve the interfacial properties between jute fiber and polylactic acid (Nakamura et al. 2009). Both jute fiber and shellac resin contains polar functional groups such as hydroxyl group. So it is expected to improve interfacial properties of jute fiber by using shellac resin treatment. Nakamura et al. (2009) treated the Jute spun yarn with aqueous solution of shellac resin and then dried at 80 °C for 2 h. The concentration of shellac resin was varied (2.0, 3.0, 4.0, 5.0, 10wt%). They studied the effect of shellac resin treatment of jute fiber on mechanical properties of jute/PLA composite. The interfacial strength between jute fiber and PLA matrix and resistance of crack propagation were improved by shellac resin. Tensile properties of the composite were also improved until 4.0wt% shellac resin treatment by increasing in interfacial strength and resistance of crack propagation. At higher concentration of shellac resin, PLA cannot impregnate through the resin treated jute fiber bundle. That's why tensile property decreased above 4% shellac resin treatment (Fig. 9). SEM photographs (Fig. 10) of the fracture surface of this study showed that interfacial adhesion of resin treated jute fiber and PLA matrix was improved in case of 4wt% shellac resin treatment than untreated. Moreover, resin was elongated and ductile fracture occurred compared to untreated. Shikamoto et al. also treated jute fiber with shellac resin of different concentration (0.5, 2.0, 5.0wt%) to improve the interfacial bonding between jute fiber and PLA matrix. They also observed improved tensile and bending properties for low concentration of shellac resin treatment. The bending and tensile strength of surface treated jute/PLA composite showed maximum at 2% shellac resin treatment than untreated or 5wt%. Jute fiber could not be dispersed when the amount of shellac on the reinforcement fiber was too much and consequently property degraded at higher concentration of shellac resin.

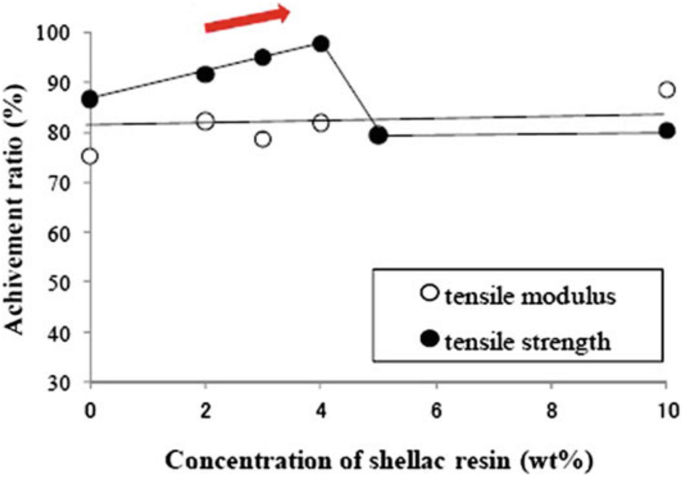


Fig. 9 Relationship between achievement ratios of tensile properties and concentration of shellac resin (Michael et al. 2016a, b)

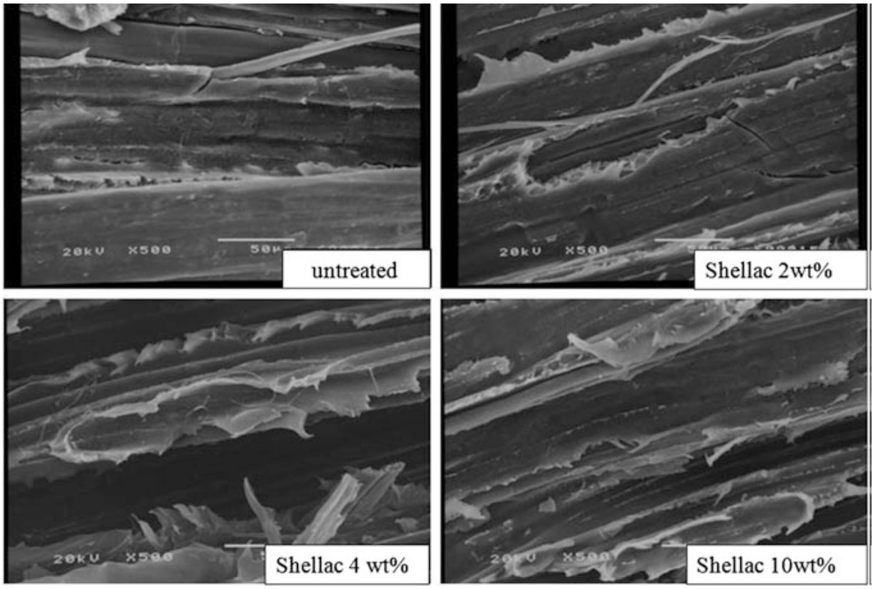


Fig. 10 SEM photographs of fracture surface of specimens **a** untreated, surface treated with, **b** shellac 2wt%, **c** shellac 4wt%, **d** shellac 10wt% (Michael et al. 2016a, b)

4.6 *Other Chemical Treatments*

Acetylation is one of the promising chemical treatments which are used to improve the hydrophobicity and fungal attack (Mitra 2014). Acetylation of jute fibers is a well-known esterification method causing plasticization of cellulosic fibers. The reaction involves the generation of acetic acid (CH_3COOH) as by-product which must be removed from the lignocellulosic material before the fiber is used. Al-Mobarak et al. treated jute with 2wt% acetic acid (CH_3COOH) solutions and found acetylated jute more hydrophobic than untreated (Al-Mobarak et al. 2012). Fluorocarbon treatment is a chemical treatment which uses fluorocarbon resin, one of the most popular chemical for improving the water and oil repellency of fibers. Sever et al. used fluorocarbon and micro-silicone to improve the surface characteristics jute fabrics for polyester matrix (Sever et al. 2012). The composites with fibers treated with silicone exhibited slightly higher stiffness and strength values than alkali-treated and acetylated fiber composites. Amino- and amido-functional polymers are among the most popular forms of silicones which have plasticizing effect on polymer matrix. They found that silicon treatment and fluorocarbon treatment of jute fabric after alkalization process brought about 47–43% increases in inter laminar shear strength of the composites, respectively. From yarn pull-out test, it was inferred that fluorocarbon treatment of jute fabric caused the best adhesion between jute fibers and polyester and better tensile and flexural properties.

5 Possible Areas of Applications

Although many biopolymer-based products are already developed and marketed, very few biodegradable composites have been developed recently. The technological aspects of PLA based composites are still in the research and development stages. This is despite the fact that the environmentally friendly composites, where biodegradability is important, provide designers new alternatives to meet challenging requirements. These include aquatic and terrestrial environments, municipal solid waste management and compostable packaging, while those for automobiles include for parcel shelves, door panels, instrument panels, armrests, headrests and seat shells (Bajpai et al. 2012). Unlike mineral-based materials, natural fiber reinforced composite materials offer high potential as next generation functional materials (AL-Oqla et al. 2015; Haniffah et al. 2015; Asim et al. 2015). It is useful to define suitable areas of application according to the characteristics of the composites. Several utilization alternatives have been considered, and the following four possible uses of PLA/jute composites are listed:

a. Construction materials
b. Automotive parts
c. Medical devices
d. Food packaging.

5.1 Construction Materials

Building materials comprise 60–75% of the total cost of construction (Dittenber and GangaRao 2012) that many of the cases is because of the high expenses involved in the extraction of the materials from mineral sources. The use of locally grown raw materials can reduce the construction materials cost efficiently. If jute/PLA based composites were used to create construction modules, then countries with rural regions to grow jute would be empowered to address their own poverty, employment, and housing issues with little or no outside assistance. As surface modified jute significantly increases tensile strength and Young's modulus of composites, these composites should be used for parts that need high tensile strength and stiffness. Examples are ceiling, floor, window, wall partition and ceiling of building components and shelving, cupboards and cabinets of furniture (Azwa et al. 2013).

5.2 Automotive Parts

Manufacturers are enhancing the biodegradable content due to increased social awareness of the environmental problems posed by the non-degradable, non-recyclable contents of salvaged automobiles (Koronis et al. 2013). PTAT or EastarBio from Eastman Chemical Company, BioPET or Biomax from Dupont, Ecoflex from BASF, PLA from Dow-Cargill and PHBV from Metabolix are instances of environmentally friendly material for automobiles (Bodros et al. 2007). A rich application of plant fibers are in Mercedes-Benz E-class. Many parts in this car like center console and trim, various damping and insulation parts, C-pillar trim, rear parcel shelf, seat cushion parts and door trim panels are made from plant fiber composites (Akampumuza et al. 2016). Jute-reinforced polymer composites are used in automobiles applications such as (door panels, seat backs, headliners, dash boards, trunk liners and parts in railway coach) (Bajpai et al. 2012).

5.3 Medical Devices

Like many other biopolymers (Michael et al. 2016a, b; Nainar et al. 2014; Pradeep et al. 2015) PLA has been well recognized as a good material with both biodegradable and bioresorbable properties that can be inserted into the human body without inducing any harmful effect. However, the low strength of the degradable polymers also limits the range of their applications. With jute fiber reinforcements the PLA composites, degradable polymers are of value in short-term applications that require only the temporary presence of a device. The most concern relating to the use of degradable implants is the toxicity of the implant's degradation products. The common types of medical devices include the substitute heart valves and artificial hearts, artificial hip and knee joints, dental implants, internal and external fracture fixators and skin repair templates, and so on (Satyanarayana et al. 1990).

5.4 Food Packaging

Regarding the potential applications of such full-biocomposites, they might be used for food packaging applications (Sorrentino et al. 2007). Certainly, the role of food packaging is the protection from physical damage and also to control the mass transfers responsible for food degradation. Biocomposites emerge as innovative and promising materials of future for the sector. The main drawbacks of biocomposites for their uses in the food packaging are mainly their limited processability, insufficient mechanical and barrier properties, high production cost (e.g., bio-polyesters), or controversial environmental claims (Johansson et al. 2012).

6 Conclusion and Future Perspective

In this study, it was focused to understand the effect of different treatments on the surface characteristics of jute fibers in terms of surface chemistry, roughness and adhesion. Further, the attention was paid to understand how these parameters affected the thermo-mechanical, flexural, and interlaminar shear properties of the corresponding composites. Chemical treatments of jute fiber not only provide roughness on fiber surface but also increase the surface area available for surface contact with polymer matrix. However, jute fibers may be prone to damage due to excessive chemical treatments. Especially, upon getting the cellulose damaged, natural fibers will lose some of its characteristics. Moreover, chemical treatments are not that eco-friendly process and involve high cost. In that sense, physical treatment such as atmospheric plasma treatment is the preferred solution for improving jute fiber interface properties which is environment friendly as well as cost effective. Development of new PLA based biocomposites with added functional properties will create further scope for expansion of materials technology.

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Reinforced Natural Rubber Nanocomposites: Next Generation Advanced Material

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Mohammad Reza Ketabchi and M. Enamul Hoque**

Abstract Undoubtedly, the advanced green composites have replaced the use of many conventional mineral based or naturally occurring single materials in wide spread industrial applications including aerospace, automotive, locomotive, chemical and biomedical industries. Specially, the reinforced natural rubber nanocomposites have drawn the attention of the research as well as industrial worlds greatly because of their superior thermal and mechanical properties without major compromise of transperancy/clarity. This chapter presents the preparation of rubber nanocomposites, characterization techniques, and the properties of the developed nanocomposites such as mechanical and thermal characteristics along with the recent applications of these nanocomposites. The rubber nanocomposite (RNC) have found their niche commercially in the tyre and sports industries providing reduced weight and energy dissipation, and enhanced air retention to the applied products.

Keywords Natural rubber · Carbon nanotube · Fullerenes · Graphene, functional material

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1 Introduction

Natural rubber (NR) is extracted from latex; a milky suspension of small rubber globules in water that is obtained by making incisions into the central bark of rubber trees. Crude rubber is obtained by coagulating the latex by using dilute acid. The coagulated latex is dried and passed through rollers to get sheets of NR. At this stage NR is soft, gummy, low in strength and elasticity, and also has minimum resistant to shape deformation. The property of NR alone is not sufficient for commercial applications. Even after being processed and vulcanized; it lacks the required physical and mechanical properties. Therefore, reinforecment of rubbers with the fillers is required to meet the commercial and industrial requirements. Reinforcing material such as carbon black (CB) and silica plays a significant role in enhancing the fatigue, impermeability, tear and abrasion resistance, while simultaneously increasing modulus and elongation at break the two antagonistic properties of reinforced elastomers. This paradox of elastomers rationalizes the ability of reinforced rubber to provide exceptional material properties and applications in numerous fields.

This chapter is devoted to various modified and unmodified nanofillers properties, rubber nanocomposites manufacturing methods, assembly, shape, and other nanocomposite properties. It will review the effect of shape/size of nanofiller materials, manufacturing methods and characterization, on reinforced rubber nanocomposites. Further, this chapter will examine the rubber-filler interaction with different types of nanofillers such as dispersion characteristics and matrix-filler compatibility. Finally, the current and future applications of rubber nanocomposites are underlined.

2 Fillers as Reinforcing Agents

Fillers have been employed as reinforcing agents for many years. Straws and branches have been used to reinforce adobe bricks and mud houses since the early part of human history. The word "filler" is very broad and encompasses a very wide range of natural and artificial materials. Fillers can be natural or synthetic solid materials (organic, inorganic) that may be spherical, irregular, flaky, rod shaped or fibrous and are used in varying amounts in the matrix following the product application. Depending on the activity they are generally categorized as "Inactive filler", also called "extenders or diluent", which increase the volume of an expensive material. "Active fillers" known as "reinforcing fillers" improve certain physical and mechanical properties. A clear distinction between reinforcing agent and diluents is not possible because the same filler could improve certain properties but deteriorate others. The significant factors for filler reinforcing ability are directed by its specific properties including the particle shape, size and agglomeration, surface properties and also degree of interaction between filler and matrix. An advanced reinforcing property can be achieved by increasing the contact area between the matrix and the filler particles. The bonding between the matrix and the filler is employed to define the elastomer reinforcement quality. The most widely used and most effective conventional reinforcing filler in the rubber industry is CB because it provides notable improvement in the properties of general-purpose elastomers. However, in some cases where coloured rubber compositions are required, non-black filler particles are needed. Among non-black fillers, silicon dioxide (SiO_2) is known to be the most effective reinforcing agent due to its high specific surface area. A number of new filler materials similar to silica compounds are identified as potential reinforcing systems such as kaolin clay (hydrous aluminium silicate), mica (potassium aluminium silicate), talc (magnesium silicate), limestone (calcium carbonate), and titanium dioxide. Recently, nanofillers, a new class of fillers have recently gained a notable attention both in scientific and industrial fields. These nanofillers have high specific surface area and often a high aspect ratio that can be dispersed in the elastomer matrix as individual particles. The distance between the matrix material and filler components are extremely small as a result, interactions at molecular level between matrix and the nanofillers provides extraordinary properties compared to conventional materials. Based on their dimensions in host matrices, nanofillers are classified into three categories. (1) Isodimensional nanoparticles: The three dimensions of the particle can be in the order of nanometers and hence appear as spherical particles. CB, silica, aluminium oxide, titanium dioxide, zinc oxide and silicon carbide are examples for nanoparticle fillers. (2) Elongated structure: only two dimensions are in nanometer scale and the third is larger, giving it as shape of tube, as in nanotubes, whiskers or nanofibers. (3) Layered structure: only one dimension of the filler is in the nanometer range giving it a layered appearance, a few nanometers thick but several hundreds of nanometers long. Layered silicates, layered graphite flakes and layered double hydroxides are examples for layered nanofillers. Due to the high adsorption surface energies associated with these nanofillers, they have a strong tendency to form aggregates and agglomerates.

2.1 Carbon Nanotube

Carbon is an incredible element that can form a number of morphologies through sp2 hybridization. It is capable of forming open and closed cages with a honeycomb atomic arrangement which was discovered by Kroto et al. (1985). Iijima (1991) reported the production of a new type of carbon structure consisting of needle-like tubes (with dimensions of few nanometres), commonly referred as multiwalled carbon nanotubes (MWCNT). Following this discovery, two years later, single atomic layer thick carbon nanotubes (SWCNT) (Fig. 1) were first synthesized independently (Iijima and Ichihashi 1993).

To fabricate multifunctional polymer nanocomposites, CNTs are optimal option to substitute the conventional nanofillers following their notable thermal, electrical and mechanical properties. These exceptional properties of CNT prompted huge

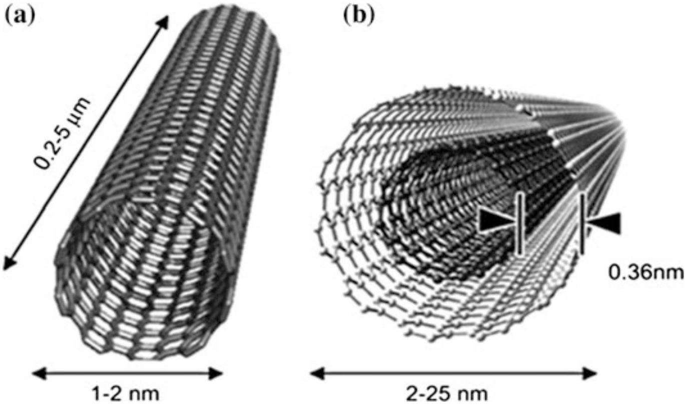


Fig. 1 Conceptual diagram of single-walled carbon nanotube (SWCNT) (**a**) and multiwalled carbon nanotube (MWCNT) (**b**) delivery systems showing typical dimensions of length, width, and separation distance between graphene layers in MWCNTs (Iijima and Ichihashi 1993)

interest in the production of CNT based nanocomposite. The first polymer nanocomposite reinforced using CNT was reported by Ajayan et al. (1994). Later, these nanocomposites have employed different polymer, ceramics and metals matrices, whereas more recent studies are devoted to nanocomposites based on elastomeric matrix. However, owing to the tendency of CNT to form agglomerates, the challenge of forming bonds between the tubes and matrix, and problems associated with the physical properties of CNT-matrix mixtures is a major challenge in preparing such nanocomposites. Also, to assess the success of utilizing the full potential of nanotubes and to provide a quantitative, accurate representation of the structure and properties of a nanocomposite is yet another grim task.

2.1.1 Preparation and Properties

Filler orientation and dispersion are two critical factors for optimal reinforcement in any particle-reinforced composite systems. Dispersion of CNTs into the host matrix has been one of the main challenges until today. Poor dispersion is due to agglomeration of nanotubes as a result of the van der Waals interactions between individual tubes. Uniform dispersion of the filler throughout the matrix will result in a uniform load transfer from the matrix to the filler. Moreover, uniform dispersion can further contribute in network formation for conducting electrical and thermal energy. CNTs have been believed by many researchers to be the ultimate filler for next generation high performance structural and multifunctional composite materials. Thostenson et al. (2005) reported uniform dispersion, CNT alignment in the matrix, wetting, and functionalisation of CNT for matrix/filler interfacial bonding as critical issues in processing of CNT/polymer nanocomposites. In addition to the dispersion quality, nanotubes orientation in the nanocomposite plays an important role as well. Alignment of nanotubes in direction of applied force can result in a larger load transfer from matrix to the filler. Also such arrangement allows easier transfer for either thermal or electrical energies. Consistent dispersion and orientation in nanocomposites allows ideal property improvements. Various methods have been employed to obtain an optimal dispersion quality; such techniques include solution chemistry to functionalize the nanotube surface (Chen et al. 1998; Mitchell et al. 2002; Bubert et al. 2003; Eitan et al. 2003; Jang et al. 2003), the use of polymers to coat the nanotube surface (Star et al. 2001), in situ polymerization (Jia et al. 1999; Deng et al. 2002), ultrasonic dispersion in solution (Qian et al. 2000; Safadi et al. 2002), melt processing (Potschke et al. 2002; Bhattacharyya et al. 2003; Tang et al. 2003; Broda 2003; Gorga and Cohen 2004; Siochi et al. 2004), the use of surfactants (Shaffer et al. 1998; Gong et al. 2000), electrospinning (Dror et al. 2003), electrode chemistry (Chen et al. 2000), and gelation/crystallization (Bin et al. 2003). Meanwhile, natural rubber nanocomposites have been successfully reinforced using CNT through different methods such as melt mixing (Lopez-Manchado et al. 2004; Shanmugharaj et al. 2007; Sui et al. 2007), solution blending (Bokobza and Kolodziej 2006; Fakhru'l-Razi et al. 2006; Kueseng and Jacob 2006; Kolodziej et al. 2007; Zhao et al. 2006) and latex compounding (Wang et al. 2006).

As mentioned earlier, compared to other CNT/Polymer nanocomposites, CNT/rubber nanocomposite is yet another emerging field and only few studies have been reported based on this subject. In specific case of NR, Bokobza and Kolodziej (2006) and Kolodziej et al. (2007) prepared MWCNT/NR nanocomposites at several filler concentrations (1.0–9.1 wt%) by solution blending. Later, the results were compared against the conventional CB filler. The authors reported an increase in reinforcing effect with increasing MWCNT loading, demonstrating the superior reinforcement capabilities of MWCNT compared to conventional CB filler. Furthermore, an unexpected decrease of the resistivity by several orders of magnitude (adding between 2.9 and 3.8 wt% of MWCNT) was also reported, indicating the formation of a percolated network. Based on an equivalent filler loading, samples containing MWCNT displayed a better conductivity than the samples filled with conventional CB, signifying that the filler-filler network in carbon-filled systems take place at a filler loading higher than 9.1 wt%. In addition dramatic decrease in storage modulus with increasing strain amplitude was recorded for composites containing more than 3.8 wt% of MWCNT. In general, dynamic properties of filled rubber system are amplitude dependent and decrease with increasing amplitude due to breakdown of a filler network formed by filler-filler interactions (known as the Payne effect). For the same filler loading, a greater Payne effect was observed in MWCNT/NR composites compared to samples filled with CB. To further improve the dispersion of MWCNT in rubber matrix surface modification was suggested by the authors. Peng et al. (2010) prepared CNT/NR composites with latex through a self-assembly method and observed 58% increase in both tensile strength and tensile modulus at different elongations by adding 1 wt% of CNT. A similar study reported reinforcement of NR with carboxylated CNTs dispersed with SDS shows a low percolation threshold (<1 wt%) and a major improvement in the mechanical properties at low strain in the rubbery state (Bhattacharyyaa et al. 2008). Anand et al.

(2010) added single walled CNT (SWCNT) to NR through a casting technique and observed 56% improvement in tensile strength and 63% improvement in elastic modulus. The composites displayed an electrical percolation threshold at a concentration of 1.5 wt%, while maintaining the thermal stability of the matrix. Lopez-Manchado et al. (2004) investigated the effect of SWCNT loading on mechanical and physical properties of NR. They prepared the SWCNT/NR blends at room temperature using an open two roll mill and later vulcanised using a hydraulic press at 150 °C. SWCNT behaved as effective accelerators, decreasing the time of the crosslinking reaction. Also, a strong filler-matrix interaction resulted in increase in storage modulus as well as a notable transition in the glass transition temperature (T_g) towards higher temperature. These effects were more pronounced in comparison with NR composites filled with CB. This shows the importance of filler-matrix interaction which can result in a more immobilised rubber shell as compared to the large CB particles. This can be explained based on shape factor which is larger for SWCNT than its counterpart CB, which explains the higher hydrodynamic reinforcing of CNTs.

In another study, addition of 0.25 wt% of SWCNT to NR resulted in 20% improvement in the composite modulus (Zhao et al. 2006). This enhancement was related to the physical crosslinks between matrix and filler. Grunlan et al. (2006) and Bhattacharyya et al. (2008) reported a notable increase in the mechanical properties of rubber latex film even at low concentrations of CNT. Bhattacharyya et al. (2008) linked the improvement to the formation of a MWCNT rigid network probably mediated by rubber or protein molecules adsorbed at the surface of oxidized MWCNT. Later, Fakhru'l-Razi et al. (2006) and Nazlia et al. (2007) also achieved significant reinforcement for NR with MWCNT. Kim et al. (2006) focused on the preparation of chloroprene rubber nanocomposites filled with 5–30 wt% of highly aligned CNT through conventional rubber blending and milling technique. The alignment of CNTs was possibly due to the shear force induced during the optimized milling process. The selective alignment of CNT led to enhancements in the elastic modulus, thermal conductivity, electrical conductivity, and electromagnetic shielding property, compared to neat rubber sheet.

Atieh et al. (2006) prepared MWCNT/SMR CV60 rubber nanocomposites by solvent casting method and reported that this technique was able to disperse MWCNT homogenously in the natural rubber matrix. In their study, through mechanical analysis, the initial modulus was increased by 12 times as compared to the pure NR.

Khalid et al. (2010) demonstrated the influence of electron beam irradiation on CNT/NR nanocomposites. Significant improvement in all mechanical properties with irradiation dosage including tensile modulus, tensile strength, and hardness were reported. The noteworthy improvement in mechanical properties was again attributed to the higher surface area of CNT in contact with the NR matrix; allowing the higher stress transfer from the rubber matrix to the CNT. Also, increase in tensile strength with increasing radiation was due to the radiation-induced crosslinking of the nanocomposites. The gradual increase in the gel fraction of the nanocomposites with irradiation indicated that the nanocomposites were crosslinked upon electron beam irradiation, hence, improved mechanical properties. Further, TEM and AFM studies confirmed the enhancement in the mechanical properties, showing uniform dispersion of the CNT. However, above 150 kGy, tensile strength increase was less remarkable possibly due to irradiation degradation. Irradiation degradation is result of oxidative crosslinking and chain scission, which are believed to be more prevailing reactions at high irradiation dosage. A similar study with application of irradiation at 150 kGy shows tremendous improvement in the mechanical properties of CNT/NR nanocomposites (Atieh et al. 2010). The irradiation resulted in almost six times increase in the tensile strength at 7 wt% CNT loading compared to non-irradiated samples. Sui et al. (2007) observed after acid treatment and ball-milling, CNT dispersed homogeneously in NR matrix and interfacial interaction between them also improved significantly. The maximum torque increased and at the same time, vulcanization, scorch and optimum cure time decreased using this method. Furthermore, the over-curing reversion of nanocomposite was notably improved. This method of treatment also improved overall performance of the nanocomposite compared to the pure NR and CB/NR nanocomposites.

Wang et al. (2006) fabricated powdered NR nanocomposites modified carbon nanotube using spray drying process. The acid modified CNT were fully dispersed in the NR matrix and had an improved interfacial interaction. However, NR powder with modified CNT showed more vulcanizer requirement when compared to the conventionally prepared NR materials. To fully vulcanize the nanocomposite at least 1.5 times or more as that of neat NR compound was required. Moreover, with the addition of vulanizer, the vulcanizing reversions phenomena did not occur and the mechanical properties were also significantly enhanced. In another research, both optimum cure and scorch time in the sulphur vulcanization system increased by using silane (3-aminopropyltriethoxisilane) functionalized CNT (Shanmugharaj et al. 2007). This improvement was linked to the absorption of basic accelerator by acid groups and also quinone-type oxygen atoms of the earlier oxidative treatment. NR/silane functionalized carbon nanotubes nanocomposites exhibited improved mechanical properties compared to NR vulcanisates due to the high rubber-filler interaction between the silanised carbon nanotubes and NR vulcanisates.

2.1.2 Characterization

The CNT nanocomposites demonstrate noteworthy potential enhancements in mechanical, electrical, and thermal properties of the nanocomposite. However, CNT/NR nanocomposites overall performance has fallen short of expected potential. The major reason is agglomeration of CNTs due to the inherent van der Waals' attraction, resulting in non-uniform dispersion of CNT into the matrix. Alignment, dispersion, aspect ratio and interfacial interaction are reported to be the main factors during such reinforcements and therefore, it is necessary to understand/analyse various aspects of nanocomposites (Coleman et al. 2006a). Several methods including AFM, XRD, Raman spectroscopy, SEM and TEM were used to analyse various structural properties of nanocomposites. Morphological observations using various microscopies are extremely important to comprehend the link between processing methods and nanocomposite performance, as both electrical and mechanical properties of NR nanocomposites intensely are dependent on the nanoscale reinforcement dispersion level. Such morphological observed information needs to be used for feedback to improve processing methods that will lead to optimize various properties of rubber nanocomposites. In order to fully confirm and characterize the morphological structure of the nanocomposite, it is essential to employ several characterization methods. For instance, optical microscopy enables access to micro sized agglomerates, whereas AFM is employed to screen nano scaled suspended CNT particles.

Figure 2a–d shows the CNT-reinforced nanocomposites SEM micrographs at increasing MWNT loadings. An excellent dispersion of CNT is observed through all MWNT loadings. The particles dispersed homogeneously in the hosting matrix implying complete nanotubes exfoliation in the polymer matrix. The CNT homogeneous dispersion can be simplified as colloids, wherein the matrix stabilizes the particles distribution and prevents bridging flocculation due to the free polymers (Shaffer and Windle 1999). Similar observations were achieved for MWCNTs/acrylic latex nanocomposites (Vandervorst et al. 2006; Masenelli-Varlot et al. 2009) and iron/iron oxide-filled CNT/NR nanocomposites (Matos et al. 2012).

Matos et al. (2012) used X-ray micrography to confirm the particles aggregation in the nanocomposite. Dissimilarities in contrast approve the variation in CNT concentration at the nanocomposite cross-section. The variations in the X-ray scattering results were related to the Fe-based CNT fillings which have a greater

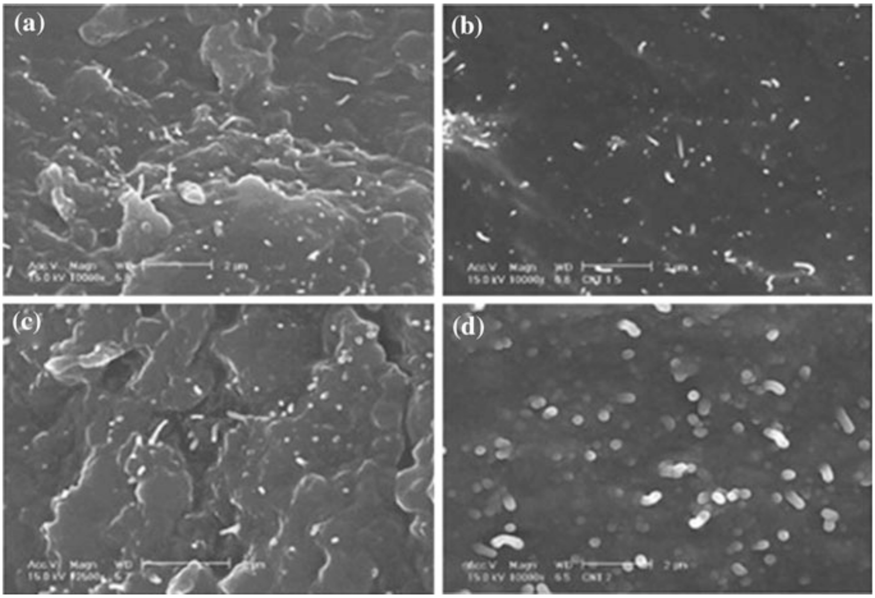


Fig. 2 Scanning electron microscopy of razor-cut section of MWNT-reinforced fluoroelastomer vulcanizates: **a** 1.5 phr, **b** 3 phr, **c** 4.5 phr, and **d** 6 phr (Shaffer and Windle 1999)

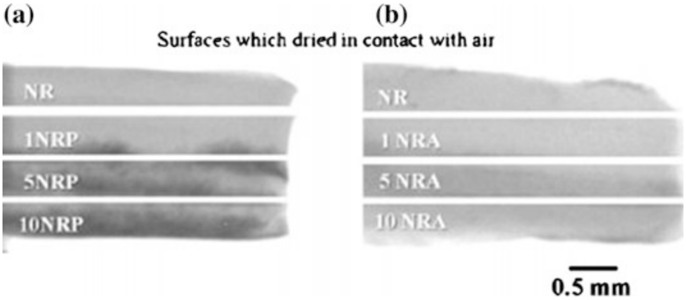
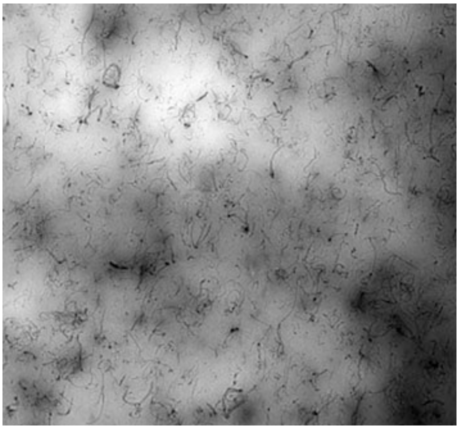


Fig. 3 X-ray microtomograph obtained from the cross-sections of **a** NRP (composites prepared using pristine MWCNT/SDS dispersions) and **b** NRA (composites prepared with acid-treated MWCNT dispersions) that contain 1, 5 and 10 wt% of CNTs. NR pure film of natural rubber (films are ~0.5 mm thick) (Matos et al. 2012)

Fig. 4 TEM images of 5 phr CNT/NR nanocomposites. Scale bar is 0.5 μm (Wang et al. 2010a)



electron density as compared to the hosting matrix (Fig. 3). It was reported that the increase in untreated filler concentration, decreased the homogeneity of the hosting film. Meanwhile, it needs to be noted that the acid-treated particles performed a more acceptable homogeneous dispersion in the matrix as compared to the untreated fillers (Fig. 3a).

Wang et al. (2010a) used TEM to observe the dispersion of the pristine CNT into NR matrix prepared using an open two-roll mill mixer. The TEM findings in Fig. 4 show the unmodified CNT are well dispersed in the NR matrix at 5 phr loading.

A homogeneous dispersion of unmodified MWCNTs in poly(styrene-b-butadiene-co-butylene-b-styrene) using an ultrahigh-shear processing extruder was achieved by Li and Shimizu (2007). The homogeneous dispersion of the CNTs can be attributed to the high shear stress that overwhelmed the electrostatic and van der Waals interactions between the nanotubes and peeled each nanotube apart, thread by

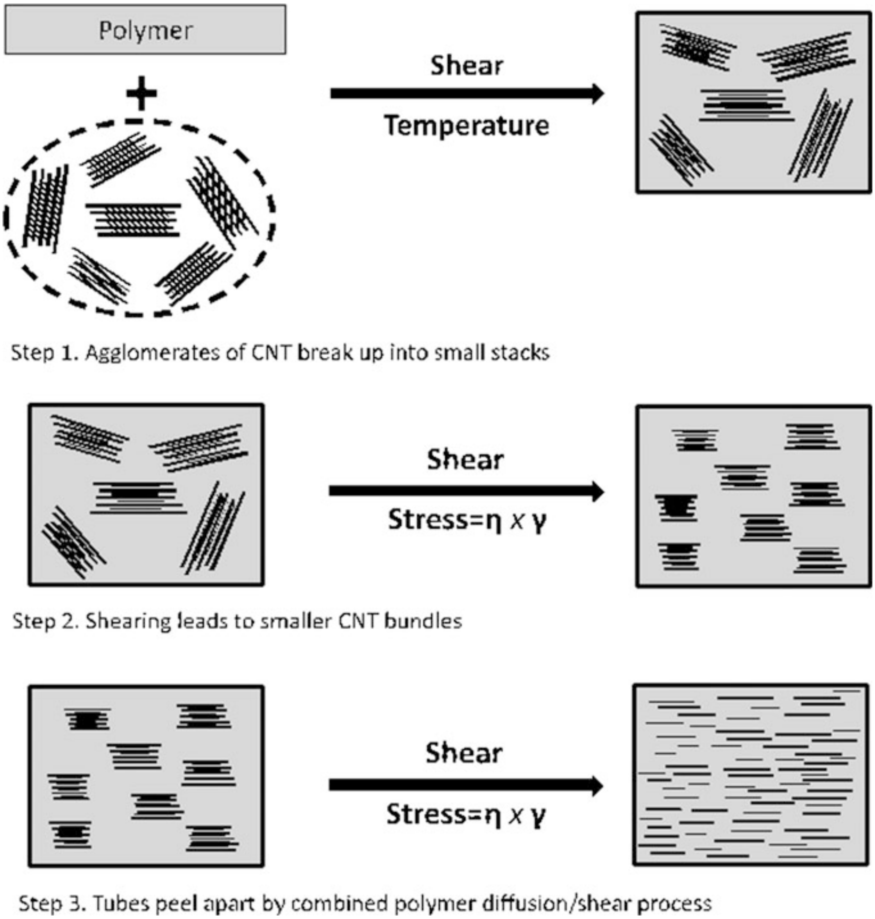


Fig. 5 Simplified diagram of the CNT dispersion states depending on the applied shear stress (Li and Shimizu 2007)

thread. Figure 5 shows a simplified diagram of the CNT dispersion states depending on the applied shear stress.

Using an AFM nanomechanical mapping technique, Wang et al. (2010a, b) investigated the topography, modulus, and adhesive energy distribution maps of the resulting nanocomposites in term of CNT loading. Those maps were successfully used to identify and characterize heterogeneity of such composites. The mechanical interfacial regions formed around CNTs together with CNT divided elastomer matrix into small "cells" in which the elastomer matrix was occluded. Figure 6 shows typical AFM tapping mode images of the CNT/NR composites fabricated by open roll mill mixer. It can be seen that the CNTs are well dispersed in the NR matrix, especially for the low CNT loading (⩽20 phr). Moreover, even at very high loading content (60 phr), the CNT showed relatively homogeneous dispersion.

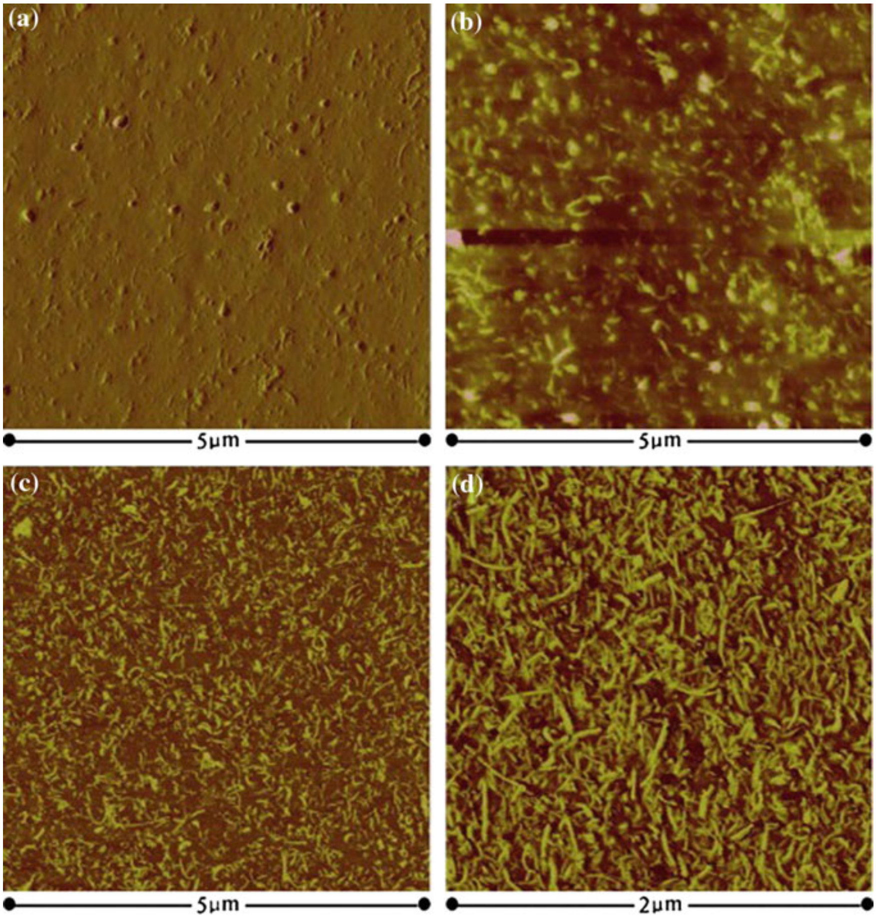


Fig. 6 Typical AFM tapping mode images of NR3, NR5, NR20, and NR60 composites. **a** Amplitude image of NR3, **b** height image of NR5, **c** phase image of NR20, and **d** phase image of NR60. Note the different scale in the images (Wang et al. 2010b)

The fair dispersion of the pristine CNTs was again attributed to the high shear stress exerted during mixing.

The authors also studied the nanocomposite deformation using the same technique. The deformation images (Fig. 7) reflect the relative stiffness of composites. They observed that with increasing CNT loading, the deformation of the nanocomposite decreased, which indicates the increase or improvement in composite stiffness.

Using the nanomechanical mapping technique, NR interfacial regions bound to CNT were visualized with intermediate modulus and adhesive energy. A number of studies suggest that interactions with CNTs may result in a region around the polymer with morphology and properties different from the bulk (Coleman et al. 2006a; Moniruzzaman and Winey 2006; Coleman et al. 2006b). However, Wang et al.

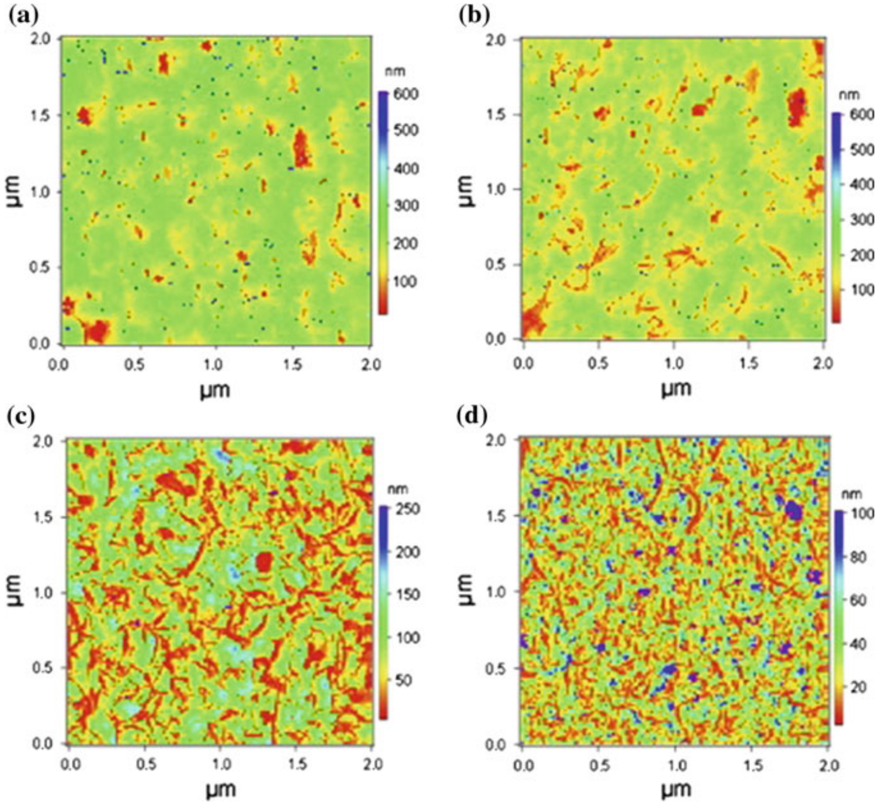


Fig. 7 Nanomechanical mapping deformation images of different NR composites. The images acquired under the same trigger deflection. **a** NR3, **b** NR5, **c** NR20, and **d** NR60. Scan size is 2 μm (Wang et al. 2010a)

(2010a, b) were the first to evaluate quantitatively the intermediate mechanical regions in real space. The mechanical interfacial region function as cell walls and the NR matrix is confined in the "cells". With the increase in CNT loading the CNTs as well as mechanical interfacial regions firmly connect to each other into a network and form a three-dimensional structure, termed "cellular structure". As a result, the NR matrix is considered to be divided into small units consisting of the mechanical interfacial regions and CNT itself. The cellular structure is formed when the CNT loading is high (Fig. 8). This cellular structure is responsible for the greatly increased mechanical properties. It is worthy to mention that a cellular structure formed promoted by 1-Allyl-3-methyl imidazolium chloride (AMIC) ionic liquid, is also observed at low CNTs loading (~ 3 wt%) in rubber/MWCNT composites (Das et al. 2009).

Lopez-Manchado et al. (2004) described the effect of SWNT on the physical and mechanical properties of NR. Raman spectroscopy was used to study the possible interactions between both materials as well as the dispersion of SWNTs in NR

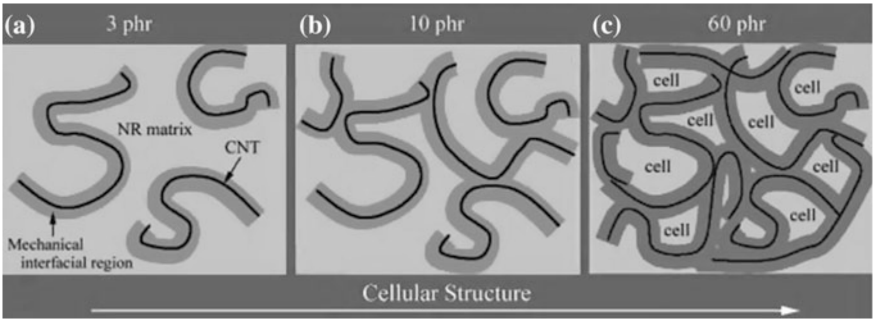


Fig. 8 Schematic diagram of the cellulation model formed in CNTs/elastomer composites. **a** Percolation, **b** partial cellular structure, and **c** three-dimensional cellular structure (Wang et al. 2010a)

matrix. The result indicates that SWNTs dispersion into the elastomer matrix creates residual strain on the nanotubes bundle and the load transfer predominantly occurs along the axis of the nanobundle in NR nanocomposites. The up-shift of the bands to higher frequencies in the presence of ionic liquid for MWCNT/styrene-butadiene polybutadiene rubber blend (Das et al. 2009) and MWCNT/polychloroprene rubber composites (Subramaniam et al. 2011) was also observed. This was due to the disentanglement of the MWCNTs, their subsequent dispersion and chemical interaction with the rubber polymer in the presence of ionic coupling agent during mixing process. Other study by Zhao et al. (2006) noted the relationship between SWNTs D wavenumber shift and the amount of sulfur added for various SWNT/NR composites. They observed that the D peak of SWNTs shift upwards as the extent of vulcanization is increased by increasing the amount of sulfur. Therefore, it might be possible that Raman Spectroscopy could be used to determine the degree of cross-linking in other rubbery materials also.

DMA is used to indicate the extent of filler–matrix interaction. In case of SWNTs incorporation in NR, it shows a noticeable decrease of the height of tan δ peak, as well as a profound shift of T_g towards higher temperatures Lopez-Manchado et al. (2004). For CNT/SBR and BR blend Das et al. (2009) observed that the incorporation of CNT affects the glass transition behaviour by reducing the height of the tan δ peak considerably. Above the T_g the storage modulus has been increased after incorporation of a small amount of CNTs. The 'Payne effect', an indication of filler-filler interactions, was observed at very low concentrations of CNT in the rubber matrix. Similar observations for NR/CNT nanocomposites were also reported by Bhattacharyya et al. (2008), Sui et al. (2008a). However, with high MWCNT loading the T_g drops owing to the phase separation/agglomeration of MWCNT, which allows the macromolecules to move freely. When the content of MWCNT is higher, they congregate, possibly because due to the intrinsic van der Waals forces which leads to bubbles and small aggregates. The conglomerations and matrix holes existing in the network of MWCNT may act as defects, which make the macromolecules move easily, and thereby decreasing the T_g of the matrix. In addition, other techniques such as differential scanning calorimetry (DSC) is used to study the effect of nanofiller on the melting and crystallization transitions of nanocomposite material as well as to obtain information on the extent of crystallinity from the area under the melting transition (melt enthalpy) (Subramaniam et al. 2011; Nair et al. 2012). TGA was used to determine the thermal stability of the nanocomposite material and also the purity of the material so as to use them in high temperature compounding or in in-situ polymerization processes (Sui et al. 2008a, b; Chen et al. 2009; Anoop et al. 2009). XRD was used to determine the increase in interlayer spacing of the fillers after compounding with polymers, which is related to the shifting of the diffraction peaks to lower diffraction angles. However, this method does not provide quantification of the extent of intercalation and exfoliation (Nair et al. 2012). FTIR is particularly well-suited for such analysis to study the changes in the infrared spectra occurring during the hydrolysis reaction (Sui et al. 2008a; Chen et al. 2009; Xiao et al. 2008; Aziz et al. 2012).

2.1.3 Applications

The possible applications of CNT based polymer nanocomposites range widely, from electrically conductive systems to sensors or biomedical applications. At present, polymer composites are the biggest application area for CNTs. These nanocomposites are being utilized in different fields including transportation, automotive, aerospace, defence, sporting goods, energy harvesting, flame retardation and infrastructure sectors. Wide range applications of such materials are due to their high durability, high strength, light weight, design and process flexibility. CNT/polymer nanocomposites are also used as electrostatic discharge, radar absorbing and electromagnetic interference shielding material because of high electrical conductivity of this material. Smart applications can be categorized into sensing (mechanical/chemical sensing) and actuation.

MWCNT reinforced rubber composites show significantly increased wear resistance, mechanical and thermal properties. Such nanocomposite is capable of operating under extreme conditions such as high temperature and pressure, and could be used in the fabrication of innovative seals, O-rings, high-performance tires, rubber bladder for tires and anti-static rubber belts or parts. Recently, CNT/SBR composites have attracted considerable attention due to the possibility to obtain improved properties at low filler loadings (Chen and Song 2004; Moniruzzaman and Winey 2006; De Falco et al. 2007; Girun et al. 2007; Kolodziej et al. 2007; Bokobza and Belin 2007). The first reported study on CNT/SBR compounds was carried out by Chen and Song (2004). The performances of MWCNTs/SBR compounds were better than those of carbon black (N330)/SBR composites. The authors suggest the likely application of carbon nanotubes for tires with rolling hysteresis and decreased fatigue loss. Wang et al. (2010a) studied the piezoresistivity of MWCNT/silicone rubber nanocomposite under uniaxial pressure. The experimental results showed that the active carboxyl radical on MWCNT can effectively improve the homogeneous distribution and alignment of conductive paths in the composite. As a result, the composite presented positive piezoresistivity with improved sensitivity and sensing linearity for pressure, both of which are key parameters for sensor applications. Kim et al. (2012a) prepared a highly stretchable and conductive silicone rubber nanocomposites by adding gels composed of SWCNTs and an imidazolium-based ionic liquid. They reported the nanocomposites exhibit higher elastic modulus and ultimate strength than pristine silicone rubber and also retained their high conductivity (18 S cm^{-1}) even after 20th stretch/release/stretch cycle. Thus, the authors proposed that the nanocomposite can be used as stretchable conductors that require a constant conductivity when a high tensile strain up to 200% is applied. Endo et al. (2008) demonstrated that carbon nanotubes homogeneously and randomly dispersed in rubber matrices using a low temperature roll mill are able to produce durable sealants that can operate satisfactorily at extremely high temperatures and pressures (e.g., 260 °C and 239 MPa). However, the application of CNTs in elastomeric polymer is still limited because of the dispersion problem in high viscous rubbery polymer. Although several publications and patents regarding rubber/CNT nanocomposites have appeared, to the best of knowledge, no one, so far has come up with mass production techniques for producing rubber/CNT nanocomposites. Therefore, practical applications for this particular nanocomposite will have to wait for a while.

2.2 Fullerenes

Carbon is one of the most fascinating and remarkable materials of all chemical elements. An accidental discovery by Kroto et al. (1985) led to the discovery of a spherical molecule of carbon called the fullerenes or buckyball or Buckminster fullerene. It resembles the 20 hexagons and 12 pentagons on a soccer ball as shown in Fig. 9. A similar structure was also identified by Iijima (1980) five years ago, from an electron microscope image, where it formed the core of a bucky onion. A few scientists have predicted fullerenes before Smalley's group however, due to communication gap and lack of evidence they were not accepted in the scientific community (Thrower 1999). It was also reported that C_{60} fullerenes were found in a carbon-rich Precambrian rock from Russia and was confirmed using high-resolution transmission electron microscopy (Buseck et al. 1992). Recently, the environment of T_c 1, a peculiar planetary nebula was studied in which the infrared spectrum showed emission from cold and neutral C_{60} and C_{70}. The two molecules amount to a few percent of the available cosmic carbon in this region, indicating that fullerenes can and do form efficiently in outer space (Cami et al. 2010).

Fullerenes are synthesized using graphite by a number of physical and chemical methods. Such methods include DC arc-discharge Kratschmer–Huffman method (Kratschmer 1990), resistive heating of graphite (Hare et al. 1991), laser ablation of graphite (Chai et al. 1991), ion sputtering and electron beam evaporation of graphite (Bunshah et al. 1992), inductive heating of graphite (Peters and Jansen 1992), carbon particle evaporation in a hybrid thermal plasma (Yoshie et al. 1992), and

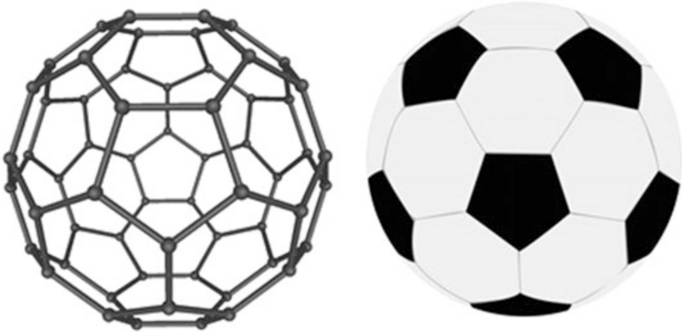


Fig. 9 Fullerenes resembles the 20 hexagons and 12 pentagons on a football (Kroto et al. 1985)

vaporization of graphite using highly concentrated solar heating (Chibante et al. 1993; Fields et al. 1993). Fullerenes have also been produced using non-graphitic raw materials by pyrolysis of naphthalene in an argon atmosphere at approximately 1000 °C (Taylor et al. 1993). The pyrolytic destruction of toluene in a radio frequency plasma and the laser-pyrolysis of benzene also produced fullerenes (Petcu et al. 2000). In 1991, Iijima reported the preparation of a new type of finite carbon structure consisting of needle-like tubes of few nanometers in solid deposits on the cathode of a graphite arc-vaporization apparatus operating under a pressure of 100–200 Torr (Iijima and Ichihashi 1993). Similar structures were synthesized using metal-doped graphite rods in arc-vaporization (Bethune et al. 1993). Moreover, some chemical methods were also used to produce fullerenes in the later stages (Scott 2004).

Physically, buckyballs are extremely strong molecules, able to resist the great pressure they will bounce back to their original shape after being subjected to over 3000 atmospheres. Fullerenes have some of the excellent properties, making it of the most desired material in several applications. Thin layers of fullerenes and solutions are coloured because of ππ* electron transitions. Buckminsterfullerene (C_{60}) is much more reactive because resonance structures that place double bonds in the pentagonal rings are energetically unfavourable and lead to restricted electron delocalization. C_{60} therefore, behaves as an electron-deficient ‘super-alkene’ rather than as a ‘super-aromatic’ (Birkett et al. 1992). Fullerenes form multiple-charged anions with electron donating species and thus electron-defficient molecules (Fowler and Ceulemans 1995). Studies suggest that C_{60} in general has good solubility while larger fullerenes (C_{72}) with trapped lanthanides have higher solubility (Ruoff et al. 1993). ICl-doped C_{60} was found to superconduct between 60 and 70 K (Iwasa 2010).

2.2.1 Preparation and Properties

Besides a number of areas the fullerenes have found its applications, rubber blends and rubber composites are one of the important applications. A method of using fullerenes to enhance the properties of rubber composites was proposed as early as 1994 (Chow 1994). The addition of small amounts of fullerene increases the elasticity, hardness and modulus of NR. Moreover, the degradation energies of the branching junctions grow and aging resistance of NR rises as the concentration of fullerene increases (Jurkowska et al. 2006; Al-Hartomy et al. 2012). It was identified that the fullerene-like nanostructures in carbon blacks play a key role in the formation of bound rubber phenomenon and in grafting natural rubber on carbon black surface (Cataldo 2005). Fullerene-like sites on carbon black surface was also explained as the formation of free radicals and diene sites during mixing by the mechanochemical degradation, which is caused by shear stresses (Cataldo 2000). It was observed that the ball milling is able to introduce a high concentration of defective sites in the pristine graphite including the fullerene-like structures. Upon mixing the natural rubber pristine and ball-milled graphite, it is shown by bound rubber measurements that the amount of rubber grafted (chemically linked) on the pristine graphite surface is negligible but reaches a very high level in the ball-milled graphite suggesting that the fullerene-like nanostructures in carbon blacks play a key role in the formation of the bound rubber phenomenon and in grafting natural rubber on the carbon black surface (Cataldo et al. 2003). This will help compounding technology when fullerene dispersed within carbon black is mixed with raw rubber on the available machines could be easily implemented in the industry.

2.2.2 Characterization

Perhaps, the most important aspect of the characterisation is to study the quality of filler dispersion in the polymer matrix and the interaction between filler and matrix. It is a well-known established fact that the dispersion of the filler has great effect on the bulk properties of the composites. The most common tool for investigating aggregates and filler dispersion is SEM and TEM. SEM is useful to reveal different morphologies of fracture and failure surface as well as the fillers aggregates on this surface. Figure 10 shows SEM micrograph of pure NR and NR containing 1.5 phr of fullerene. It was observed that the SEM resolution was not enough to visualize the structure and dispersion of filler particles, but a noticeable difference between the filled and unfilled rubber morphology was obvious (Al-Hartomy et al. 2012).

Further, the TEM micrographs (Fig. 11) have provided more clear insight on the distribution of the fullerene particles in the NR matrix. It was also reported that fullerene particles have undergone an additional disagglomeration during the compounding, and their size has further decreased.

DMA is one of many other techniques regarded as a highly informative characterization tool employed in industrial testing and in research and development. Generally, an increase in the storage modulus with increase in nanofiller loading is

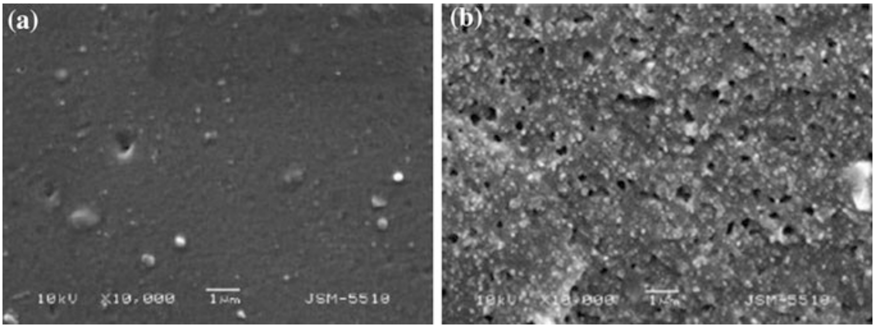
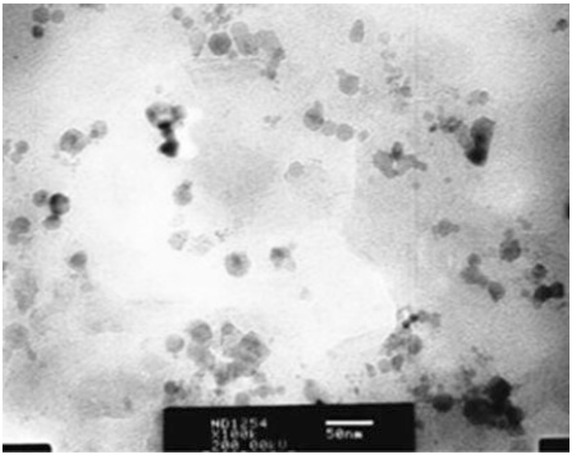


Fig. 10 SEM micrograph **a** non-unfilled composite and **b** composite, containing 1.5 phr of fullerene (Al-Hartomy et al. 2012)

Fig. 11 TEM micrograph of composites containing 1.5 phr of fullerene (Al-Hartomy et al. 2012)



reported, this can be related to the formation of strong bonds between the rubber macromolecules and to the formation of a three-dimensional network (Birkett et al. 1992; Jurkowska et al. 2006). In tyre manufacturing, DMA is often used to predict both rolling resistance and wet traction properties. Literature on DMA testing has shown that increasing the “tan δ at 0 °C” measure of the tread compound correlates to improved wet traction and lowering “tan δ at 60 °C” correlates to improved rolling resistance (Terrill et al. 2010). Therefore, by using different compounding techniques, varying filler level and filler and polymer type the tire tread could be tailored to its intended application for either high performance or normal applications. For example: The addition of fullerene tends to lower the intensity of tan δ peak and shifts the peak to lower temperatures (Al-Hartomy et al. 2012). Therefore, it would be reasonable to assume that the introduction of small fullerene amounts into the compounds for high performance tire treads would have a favourable on the traction properties of tires. In addition to above mentioned characterization techniques, TGA can be used to analyse the composition and thermal stability of the nanocomposite materials.

2.2.3 Applications

Although fullerenes are not yet used commercially, many applications have been speculated based on the research. The perspective application of fullerene, like other nanofiller in rubber-based nanocomposites are to achieve enhanced durability, lower heat-built up, and better fuel economy (Yadav and Kumar 2008). Fullerenes are chemically reactive and can be added to polymers and elastomers to create new copolymers with specific physical and mechanical properties. It was suggested that buckyballs would make great lubricants, rolling like little ball bearings between other molecules. Jurkowska et al. (2006) reported that adding a small amount of fullerene can improve the friction coefficient. It was anticipated that the introduction of fullerene in tread rubbers could reduce the tyre temperature at the service. Companies such as BuckyUSA are working with the tire industry to establish whether C_{70} would be a superior additive to carbon black. In polymer electronics, Organic Field Effect Transistors (OFETS) fabricated with C_{84} show greater mobility than C_{60} or C_{70} and exhibit greater stability. While more work is needed, the world of polymer electronics is opening up for both fullerenes and other carbon based nanomatrials.

2.3 Graphene

A series of fascination attempts resulted in the formation of various morphologies of carbon as shown in the Fig. 12, leading to the ultimate discovery of graphene (Terrones et al. 2010). Graphene is made of pure carbon, single layered two-dimensional crystal and is nearly a transparent material. Graphene is an allotrope of carbon, whose structure is a single planar sheet of sp^2-bonded carbon atoms which are densely packed in a honeycomb crystal lattice. Fullerene, diamond, multi or single-wall carbon nanotubes and graphite all of them are closely related to the graphene. At present, graphene is the hottest topics in condensed-matter physics and materials science research. This is because graphene possess not only unusual properties regarding extreme mechanical strength, thermal conductivity and 2-dimensional films, but also peculiar electronic characteristics such as Dirac-particles with a linear dispersion, transport energy gap and simply the absorption coefficient of lights (Geim and Novoselov 2007).

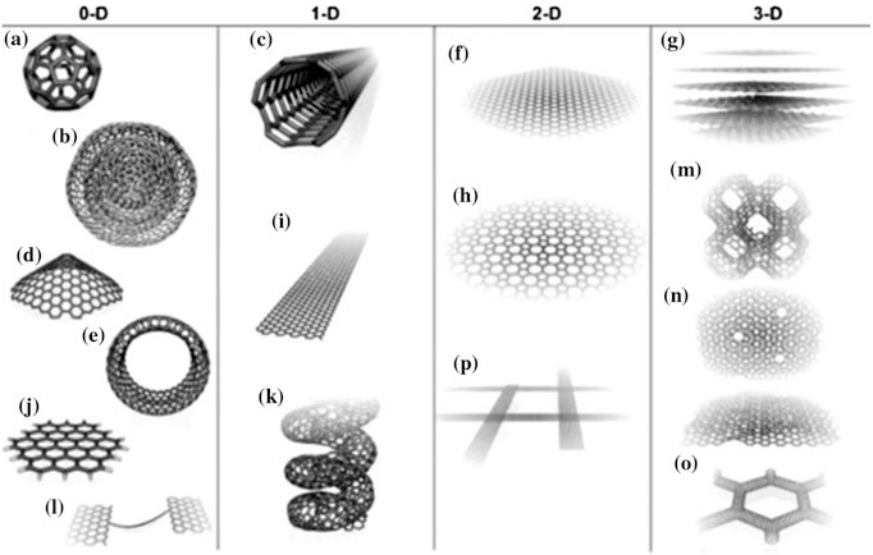


Fig. 12 Molecular models of different types of sp2-like hybridized carbon nanostructures exhibiting different dimensionalities, 0D, 1D, 2D and 3D: **a** C60: Buckminsterfullerene; **b** nested giant fullerenes or graphitic onions; **c** carbon nanotube; **d** nanocones or nanohorns; **e** nanotoroids; **f** graphene surface; **g** 3D graphite crystal; **h** Haeckelite surface; **i** graphene nanoribbons; **j** graphene clusters; **k** helicoidal carbon nanotube; **l** short carbon chains; **m** 3D Schwarzite crystals; **n** carbon nanofoams (interconnected graphene surfaces with channels); **o** 3D nanotube networks, and **p** nanoribbons 2D networks (Terrones et al. 2010)

2.3.1 Preparation and Properties

A number of attempts have been made to synthesise new carbon structures with sp^2 hybridization, such as single layer, bi-layer, few-layer graphene, and graphitic nanoribbons. The approaches to fabricate graphene broadly categorized into two methods: (1) top-down exfoliation of graphite into graphene by breaking π-bonding between graphite sheets and (2) bottom-up formation of sp^2 bonding between carbon atoms in a monolayer (Reina et al. 2009). The first method includes mechanical, chemical exfoliation of graphite (Novoselov et al. 2005; Geim and Novoselov 2007) and ionic liquid assisted exfoliation (Foelske-Schmitz et al. 2011; Kamath and Baker 2012; Shang et al. 2012; Wang et al. 2010b). The second one includes chemical vapor deposition (CVD) (Lv et al. 2011; Li et al. 2011), epitaxial growth on silicon carbide (Nomani et al. 2010; Park et al. 2011a, b; Emery et al. 2011; Baik et al. 2012), unzipping carbon nanotubes (Hirsch 2009), and self-assembly of surfactant molecules (Zhang et al. 2009) Although, pristine graphene (a single, sp^2 hybridized carbon layer free of heteroatomic defects) can be produced using micromechanical exfoliation of graphite but it does not yield large enough quantities for use in as fillers for nanocomposite applications. Therefore, it is essential to develop a high-yield and high throughput method for producing graphene. A much more scalable approach for producing graphene is the use of top-down chemical methods to exfoliate graphite. Such methods do not produce pristine graphene but rather graphene platelets-few-layer platelets or monolayer carbon sheets that may contain heteroatoms and topological defects, which resemble graphene on a local scale. The most common approach for the preparation of graphene platelets is the exfoliation and reduction of graphite oxide (GO). The first reported attempt to produce GO was by Brodie (1859). He obtained GO by treating graphite powder with an oxidation mixture of potassium chlorate and fuming nitric acid, repeatedly. Later, Staudenmaier (1898) presented a rapid and relatively safe method of accomplishing the oxidation by treating graphite with a mixture of concentrated sulphuric acid, sodium nitrate and potassium permanganate, which are most commonly used at the present time. Many other methods have also been developed for the large scale production of graphene based on the chemical reduction of GO using hydrazine (Stankovich et al. 2007; Park et al. 2009; Gao et al. 2010; Park et al. 2011b), hydroquinone (Wang et al. 2008; Gao et al. 2009), Sodium borohydride ($NaBH_4$) (Wang et al. 2008; Si and Samulski 2008; Muszynski et al. 2008), hydrohalic acid (Pei et al. 2010), iron nanoparticles (Fan et al. 2010), and ascorbic acid (Dua et al. 2010) as reducing agent. Although, these chemicals are promising reducing agents, they require elevated (80–120 °C) or low (−33 °C) temperatures, long reaction times (1–24 h) and sometimes require multi-step processes to achieve effective reduction. In addition to the drawback of these severe reduction conditions they can be sometimes poisonous and explosive and hence require great care. To overcome the extreme temperature limitations, considerable effort has been made to develop the room-temperature reduction reactions (Becerril et al. 2008; Tung et al. 2009; Fan et al. 2010; Kim et al. 2012a, b). However, reduction times at room temperature are generally longer (6–24 h) than those of elevated temperature reduction reactions. An ultrafast room-temperature reduction of graphene oxide to graphene using lithium naphthalenide has been proposed by Jung et al. (2013). This method is distinguished by the very fast (less than 10 min) and highly efficient reduction of graphene oxide, even under ambient conditions. Moreover, this new reducing agent produces reduced graphene oxide with enhanced hydrophilicity and a very stable dispersion in water. Eswaraiah et al. (2011) reported a novel chemical free and low temperature method for high throughput production of graphene by exfoliation of graphite oxide using focused solar radiation. This method claims high throughput production of exfoliated graphene with a simple and economical method with negligible oxygen functionality and high electrical conductivity.

For preparing polymer graphene nanocomposites, it is of significant interest to establish effective dispersion techniques in addition to a strong interfacial interaction between graphene and the polymer matrix. So far, very little work has been investigated on graphene-filled elastomers (Zhan et al. 2011) as compared to graphene/polymer nanocomposites. Moreover, to date, only a small fraction of work has studied the property enhancement in non-polar rubbers such NR which are of significant industrial and technological interest. Similar to nanofiller filled polymer matrix nanocomposites, elastomeric nanocomposites can be produced by three general routes: melt compounding, in situ polymerization, and solution/latex blending. As mentioned earlier, relative to solution mixing, melt mixing is often considered more economical (because no solvent is used) and is more compatible with many current industrial practices (Paul and Robeson 2008). Contrasting to layered silicate fillers where direct exfoliation can be achieved in the polymer or elastomer matrix using melt mixing, dispersing single- or few-layer GO-derived fillers without prior exfoliation have not been completely successful yet. Several studies reported melt mixing without the use of any solvents or surfactants using thermally exfoliated graphene oxide (TEGO) and graphite nanoplatelet (GNP) (Zhang et al. 2010) as filler. However, the very low bulk density of TEGO makes handling and processing of the dry powders difficult. Therefore, to avoid this problem Steurer et al. (2009) used solution mixing process to disperse the TEGO in the polymer prior to compounding. In a different approach, Kalaitzidou et al. (2007) used a sonication technique to premix the polymer and GNP in isopropyl alcohol such that polymer particles were uniformly coated with GNP prior to melt mixing, which was reported to lower the electrical percolation threshold of a GNP/polypropylene composite. Especially, for composites incorporating GO platelets as filler, melt processing and moulding operations may cause substantial reduction of the platelets due to their thermal instability (Jeong et al. 2009).

Zhan et al. (2011) reported a study on reduced GO/NR nanocomposites prepared using ultrasonic assisted latex mixing master-batch technique. The results show tremendous potential of graphene in NR reinforcement. However, their preparation method involved hydrazine reduction of a GO suspension without the aid of stabilization, which likely caused significant flocculation and re-stacking of the reduced GO platelets prior to mixing which would be disadvantageous to the filler dispersion. Moreover, their work considered nanocomposites only up to 2 wt%, and it is of interest to evaluate the performance of reduced GO/NR nanocomposites at higher filler loadings. It is expected that an analogous latex co-coagulation approach using GNP suspensions could yield similar results since both exfoliated montmorillonite and GNP are high aspect ratio platelets, although graphene-based materials tend to show more wormlike conformations when dispersed in a polymer matrix. Potts et al. (2012) reported on the formation of reduced GO/NR nanocomposites by coagulation of reduced GO colloidal suspensions and NR latex, which resulted in the exceptional multifunctional property enhancement of the NR. They also demonstrated that the processing approach had a tremendous impact on the nanocomposite morphology and thus the final properties. Solution treatment (implantation of peroxide curing agent by swelling the NR in toluene) preserved the segregated filler network morphology produced by the co-coagulation procedure, whereas the milling process destroyed this network and generated a homogeneous dispersion of reduced GO platelets in the NR matrix. In another study on TEGO/NR nanocomposite, Potts et al. (2013) observed the property improvements achieved by direct milling of TEGO into NR were small and comparable to those provided by carbon black; however, by pre-mixing TEGO with NR latex followed by milling, substantial property enhancements were achieved. Therefore, considering the ease by which kinetically stable aqueous suspensions of graphene-based materials can be prepared, water-based latex mixing could provide an effective means for production of graphene/rubber nanocomposites.

2.3.2 Characterization

Effective characterization techniques are important for establishing structure property relationships of nanocomposite materials as property enhancements is a strong function of nanocomposite microstructure, nanofiller dispersion and filler-matrix interaction. As both graphite and GO have layered structure similar layered silicate they exhibit similar states of dispersion into a polymer matrix, depending upon factors such as the processing technique and the affinity between the phases. Therefore, based on earlier studies, similar characterization techniques to those of CPNC and RNC could be employed to study the morphology and structure of nanocomposites of graphene/rubber nanocomposites. In this regard, TEM and XRD studies are the two most common used techniques by which the degree and state of dispersion can be assessed. TEM is useful in providing direct visualization of the morphology and degree of dispersion of nanofiller in the matrix. Potts et al. (2013) observed that the pre-mixing of TEGO with NR latex by an ultrasonically-assisted latex co-coagulation procedure followed by two-roll milling exhibited a more uniform dispersion with far fewer unexfoliated TEGO particles compared to direct melt mixing (Fig. 13). Stankovich et al. (2006) reported the

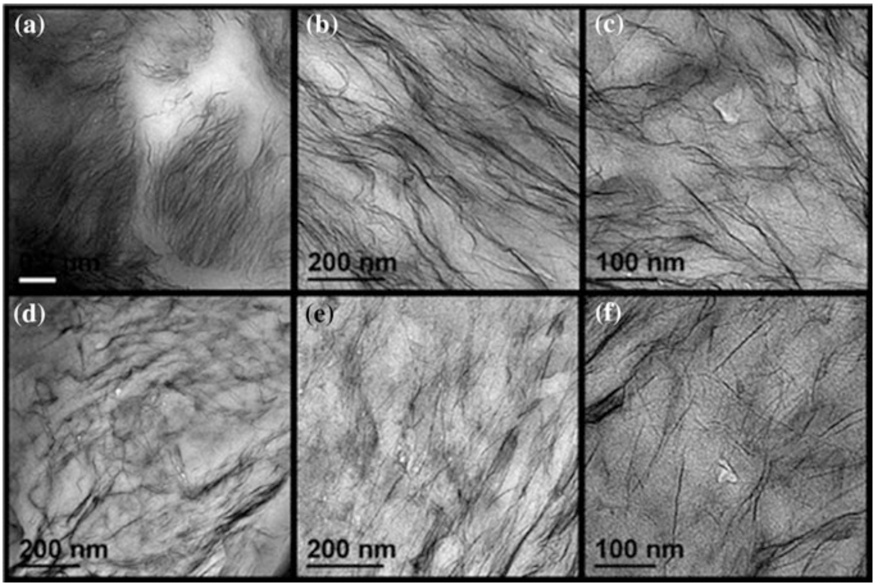


Fig. 13 TEM micrographs of **a**–**c**, TEGO/NR and **d**–**f** L-TEGO/NR nanocomposites. Scale bar in image **a** is 200 nm (Potts et al. 2013)

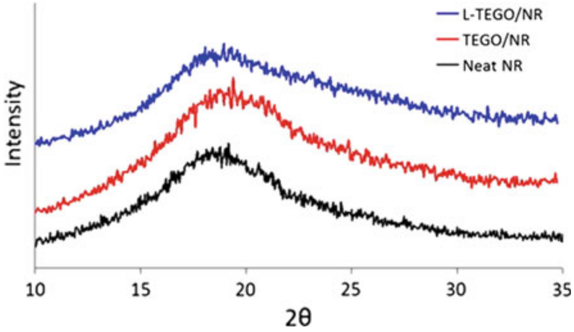


Fig. 14 Wide-angle X-ray scattering plots of TEGO/NR nanocomposites (Fu and Qutubuddin 2001)

TEM analysis to indicate the separation and delamination of EG within NBR matrix using an internal mixer. SEM studies have been used to examine the fracture surface of the nanocomposite for filler pullout, indicating the filler-matrix interaction and the strength of interfacial adhesion (Stankovich et al. 2006; Rafiee et al. 2009). It should be noted that SEM generally cannot resolve the degree of exfoliation of the platelets and is therefore best utilized as a complementary technique.

XRD can more rapidly provide insight into the state of dispersion over a larger volume of composite. It will provide (a) quantitative understanding of the degree of intercalation, as evidenced by a shifted diffraction peak from that of unmodified graphite or GO and (b) qualitative understanding of exfoliation as evidenced by the disappearance of the mean diffractive peak (Kai et al. 2008). An exfoliated morphology of GO is usually desired as it provides higher aspect ratio platelets relative to stacked or intercalated platelets (Fu and Qutubuddin 2001). However, Fig. 14 shows no evidence of graphite or a GO peak in the WAXS spectra, suggesting an exfoliated morphology in both types of nanocomposites. AFM and Raman spectroscopy (Gong et al. 2010) have been used to characterize the structure and morphology of graphene based nanocomposites. Other analytical technique such as dynamic mechanical analysis (DMA) is very useful in studying the changes in the dynamic moduli, determining the T_g and interfacial bonding of GNP and GO-derived polymer composites (Ganguli et al. 2008).

2.3.3 Applications

Graphene has a huge potential to influence major areas of science and technology mainly because of its outstanding properties. The research in the polymer composites has demonstrated graphene nanoplatelets to be ideal nanofillers which provide dramatic reinforcement and multifunction to the polymer matrix. However, looking into the vast literatures available on graphene nanocomposite, very limited work has been reported on rubber/graphene nanocomposite. Although it is known that the potential of rubber/graphene nanocomposite is undoubtedly tremendous and promising there are still many challenges that must be addressed for these nanocomposites to realize their full potential. Many researches are underway focusing on the mechanical, tribological, thermal, electrical, barrier, and other properties of graphene/rubber nanocomposites. Wu et al. (2013) observed that the functionalised graphene oxide effectively improved the mechanical and gas barrier properties of NR at significantly low filler loading. They found, incorporation of as low as 0.3 wt% of functionalised graphene oxide a 100% increase in the tensile strength, a 66% improvement in the tensile modulus and a 48% reduction in the air permeability can be achieved without sacrificing the ultimate strain. Calixto et al. (2007) reported that silicone rubber composite composed of 70 wt% graphite showed a good voltammetric response, making them a favourable material for preparing voltammetric sensor devices. Reznikova et al. (1992) developed electric-conducting rubber containing carbon black and graphite with a 3:1 ratio to prevent computer hardware being exposed to external electromagnetic waves. A recent patent on functional graphene/rubber nanocomposites describes fully exfoliated GO in the rubber matrix and exhibits excellent strength, toughness, modulus, thermal stability and electrical conductivity (Prud'Homme et al. 2010). So far no practical applications have been reported on graphene/rubber nanocomposite. To explore more into the novel properties of graphene/rubber nanocomposite, through investigations surrounding the complete exfoliation and dispersion of graphite fillers into matrix, improved compatibilities, the development of advanced functions, strategy optimization for improved mechanical and functional properties and other fundamental researches will be strongly required in the future.

2.4 Spherical Nanoparticles

The quality of reinforcement delivered by particular filler depends on a number of variables. The most important of which is the development of a large polymer-filler interface which can be enhanced based on the particles shape (Thomas and Stephen 2010). The filler material of a composite material can contain spherical particles as in the case of powders or of particles of uneven shapes, like fibers or flakes. As shown in Fig. 15, there are two types of spheroids; prolate and oblate spheroids. A prolate spheroid is obtained by rotating an ellipse about its major axis and a good example of this geometry is a football. An oblate spheroid is obtained by rotating an ellipse about its minor axis. A good example of this geometry is a disk. Spherical nanofillers or nanoparticles result when all the three dimensions are in the order of nanometers (isodimensional nanoparticles). The two most important fillers in this category are carbon black (10–30 nm) and precipitated amorphous silica (30–100 nm). Carbon black consists of chain-type or botryoidal aggregates that have coalesced during production from smallest, mostly spherical particles.

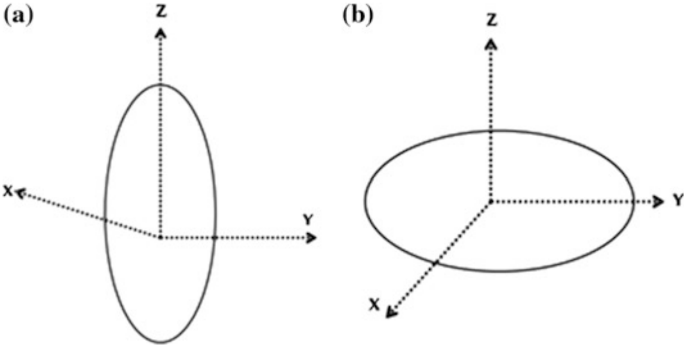
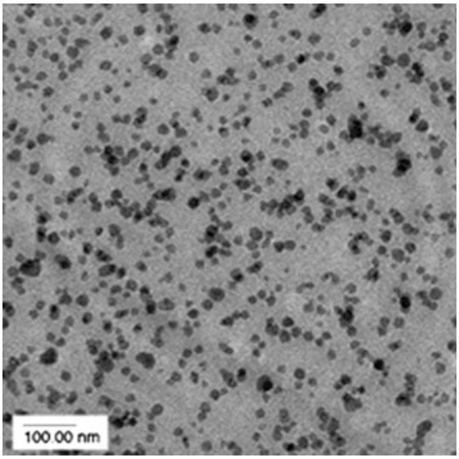


Fig. 15 Two different spheroids that can be used to model asymmetric filler particles **a** prolate spheroid, **b** oblate spheroid (Thomas and Stephen 2010)

Fig. 16 TEM results showing the dispersion of silicon dioxide nano particles in the epoxy resin (Kinloch et al. 2005)



2.4.1 Characterization

Various orientations of a sphere can yield the same impact, since the geometry of the sphere is uniform in all directions. In this regard, studies have shown that a suitable treated portion of the fly ash can be beneficially employed in various polymer matrices (Taguet and Cassagnau 2014; van der Merwe et al. 2014). To obtain a significant reinforcement for 1 μm in diameter spherical particles (considering the processablility, dispersibility, and serious loss of rubbery characteristics of the composites), a specific surface area within 6–300 m^2/cm^3 is recommended. Meanwhile, it should be noticed that finer reinforcing fillers require extra energy for their dispersion into rubber (Taguet and Cassagnau 2014). The fine diameter and excellent dispersion of the nano particles of silica are clearly shown in Fig. 16 (Kinloch et al. 2005).

The oldest, cheapest, and leading filler for rubber modification is indeed the CB. It is a form of amorphous carbon that has a high surface-area-to-volume ratio. CB means elemental carbon in the form of spherical particles of colloidal size (Barrie et al. 2004). As CB is obtained by the combustion or thermal decomposition of hydrocarbons, its particles are coalesced into aggregates and agglomerates (Jada et al. 2014). Carbon blacks do not exist as primary particles; during the preparation of carbon black the primary particles merge to form aggregates. The degree and shape of aggregation are referred to as structure. Increasing structure typically increases modulus, hardness, electrical conductivity and compound viscosity and improves dispersibility of carbon black. Structure measurement is done through an oil absorption experiment where a high value refers to a higher structure.

2.4.2 Applications

The application of reinforcing agent in rubber is nearly as old as the use of rubber itself. Nano-fillers have the ability to enhance the mechanical properties, electrical conductivity, flame resistance, and antibacterial effectiveness of polymers (Tian et al. 2006). Spherical fillers have numerous advantages over their unevenly formed counterparts correspondingly. As a result, man-made micro and nano spheres have found an increasing application in polymer composite manufacturing. Following the CB reinforcing capabilities, it is reported that about 90% of the worldwide production of CB is employed and applied in the tyre industry; enhancing tear strength, modulus, and wear characteristics of the tires (Praveen et al. 2009) and technical rubber products such as conveyor belts, flexible tubes, and sealing profiles. CB is also used as black pigment in printing inks, paints and varnishes, for dyeing and for UV protection of plastics as well as in special products such as mascara, flower soil, decor paper, and fibers. As conductive CB, it is used in the electrical industry to manufacture electrodes and carbon brushes. It is also used often in the Aerospace industry in elastomers for aircraft vibration control components such as engine mounts.

A study has been conducted to observe the role of filler particle shape on its reinforcing performance (Scotti et al. 2014). Through this study, a more homogeneous matrix has been observed using spherical or near spherical shaped particles compared to the rod shaped particles; following the anisotropic interaction between the elongated particles. Furthermore, scientists have prepared nano-calcium carbonates (NCC)/natural rubber nano-composites and have found a notable increase in mechanical properties of natural rubber using nano spherical shaped particles (Fanga et al. 2014). Also, in comparison to the chain and cubic shaped particles, the lowest damping factor value corresponding to energy loss has been observed through the samples containing spherical shaped particles.

2.5 Hybrid Materials

For many years, the scientists have devoted their studies to the mixture of inorganic and organic material (wood/rubber composites). The composition of two or more natural filler with a polymer matrix results in a hybrid bio-composite. The purpose of this composition lies in the use of the finishing product properties (Kohjiya and Ikeda 2014). Inorganic-organic hybrids can be employed in many fields of material production lines as they are simple to process and are amenable to design on the molecular scale. The inner interface of hybrid materials or nanocomposites is their fundamental feature which has a direct impact on the performance of the finishing product. There are three known procedures to develop hybrid materials; solid state, Sol-gel and hydrothermal reactions. Optimal hybrid composites are obtained when the fibers are highly strain compatible.

Presently in the synthesis of inorganic-organic materials there are four major areas as follows:

- Molecular engineering
- Nanometer and micrometer-sized structures
- The improvement from functional to multifunctional hybrids
- Combination with bioactive components

Hybridisation is used for enhancing the properties and usually for lowering the cost of conventional polymer composites. Their type of hybrid composite classification is based on the incorporated component materials. There are generally four main types of hybrid preparation; sandwich type, interply, intraply and intimately mixed.

2.5.1 Characterization

Hybrid structure combines organic and inorganic as well as soft and hard materials. Therefore it provides a natural link amongst natural rubbers and correlated matter. Studies are ongoing to enhance the processability characteristics and mechanical properties of hybrid composites. For instance, scientists have focused on reinforcement of natural rubber with sisal-oil palm hybrid fiber (Jacob et al. 2004). The application of sisal and oil palm fibers has increased tensile and tear strength of the natural rubber. Additionally, an alkali treatment on fibers has been recommended to exhibit better tensile performance as well as higher crosslink density and better adhesion properties.

As fillers, CB and silica possess their own advantages. The employment of hybrid filler or blends of silica and CB in natural rubber has given the benefits from both fillers (Rattanasom et al. 2007). Through another investigation, it is observed that the dielectric constant of natural rubber has increased with fiber loading (Jacob et al. 2006). Furthermore, bagasse fiber ash has been found beneficial as secondary filler in natural rubber compounds (Kanking et al. 2012).

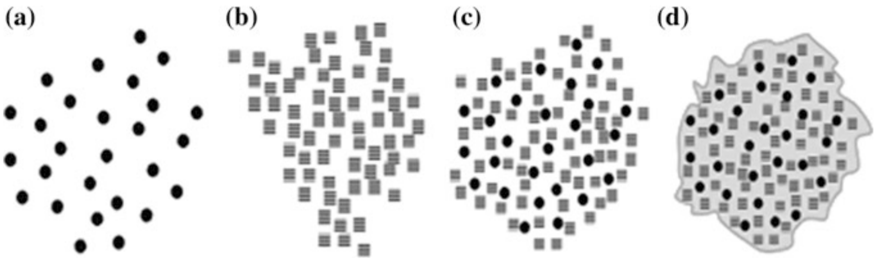


Fig. 17 Schematic diagram of the hybrid filler in the natural rubber matrix; **a** primary natural filler **b** secondary natural filler, **c** hybrid filler, **d** hybrid natural rubber based bio-composite (Bahl et al. 2014)

More recently, studies have recommended the blend of marble sludge with silica to reinforce natural rubber (Ahmed and Nizami 2014). Also to consume waste materials, rice husk has been introduced for extraction of silica. Similarly the mixture of marble waste powder with carbon black (CB), as a reinforcing material, has been presented to remarkably enhance the mechanical performance of natural rubber; particularly tensile strength, tear strength, modulus and hardness, and percentage elongation at break (Ahmed 2015). To decrease the viscoelastic loss in rubber compounds, hybrid filler of kraft lignin and CB has been introduced (Bahl et al. 2014). Following the TEM micrographs in this study, a clear insight on the distribution of the hybrid filler in the natural rubber matrix has been presented in Fig. 17.

2.5.2 Applications

In recent years, there has been a large increase in the use of polymers in engineering applications. More lately, to decrease the application of petrochemical based materials and more importantly to enhance the performance of such materials; the reinforcement of polymer materials with hybrid fillers has become the major focus of scientists. Following the reviewed studies, it is indicated that the addition of advanced silica into a blend of CB/rubber composite, can be applied to tyre treads, wire and fabric coating, conveyor belts, hoses, rubber-covered belts, carpet backing, bumper strips, cable jackets, oil well packing, bearings, diaphragms, engine mounts, and dock and ship fenders.

Hybrid composites have found their application in the automotive industry, truck tyres as well as auxiliary reinforcement with cord construction. Furthermore the metal braids can be stiffened using hybrid biocomposites and more importantly bridging the stress across weaker filaments can extend the hose life. Also power transmission belts, especially V-belts running over pulleys which are subjected to very severe stresses (when bent and flexed) are one of the most common applications of such materials. It is observed that tires with low performance can be reinforced with hybrid materials based on short fibers. Hybrid fiber reinforcement delivers an outstanding creep resistance to seals and gaskets at high temperatures.

3 Summary and Future Prospective

With the advent of manufacturing processes, the reinforced natural rubbers have demonstrated extended versatility as advanced functional materials, while the processing parameters and mutual miscibility of the constituents hold strong stands in ensuring ultimate blend properties and functionality. Nanoscale reinforcing elements have attracted great attention in the area of polymer science and technology. Because of their high aspect (surface/area) ratio and low density, they are many of the cases utilized as substitutes for traditional fibers as fillers in polymeric matrices. However, the homogeneous dispersion of the nanofillers throughout the matrix still remains a great challenge, which limits the scope of producing and/or utilizing the nanofiller reinforced rubbers. This issue needs to be addressed in the most accessible way that could further widen the applications of natural rubber nanocomposites in various areas.

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