

Bio-based Wood Polymer Nanocomposites: A Sustainable High-Performance Material for Future

Ankita Hazarika, Prasanta Baishya and Tarun K. Maji

Abstract Numerous studies are underway on the preparation and applications of petroleum-based polymer nanocomposites. The depletion of world oil pool, non-biodegradability, and raising cost of petroleum-based materials are some of the disadvantages allied with these polymers-based products. The utilization of renewable materials has attracted researchers because of its easy availability and low cost. They can potentially remove the harmful effects of petroleum-based materials and thus show a greener path in the fields of application of composites. The biocomposites developed by using renewable polymers such as furfuryl alcohol, poly(lactic acid), gluten, starch, soy flour, etc., and naturally available fibers have been gaining considerable attention because of their environment-friendly nature. Wood is a biologically derived biodegradable raw material which requires minimum processing energy. Wood polymer composites (WPC) have tremendous advantageous properties and it rapidly improves the mechanical, physical, chemical as well as other properties of the composite suitable for different outdoor and indoor applications. The properties of the WPC can be improved to the desired level through the application of nanotechnology, cross-linking agents, flame retardants, grafting, etc. Nano-based wood polymer composite provides versatile advantages in their properties compared to the conventional WPC. Flame retardants obtained from renewable resource such as the gum of the plant *Moringa oleifera* can efficiently improve the flame retardancy along with other properties of the composites. This chapter discusses the various properties of renewable polymer-based wood polymer nanocomposites as a potential, sustainable, green composite to attain durability without using harmful chemicals.

Keywords Wood · Bioresins · Bionanocomposites · Properties

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1 Introduction

Polymer nanocomposite (PNC) is a promising multidisciplinary research activity in the field of material research that might expand the utilization of polymers for various industrial applications (Hussain et al. 2006; Paul and Robeson 2008; Leszczyńska et al. 2007). Generally, the desirable properties including low gas permeability, good transparency, high thermostability, high mechanical strength, light weight, high chemical resistance, etc., required for many advanced applications, are not found in case of commercial polymers. The service of polymers has been extended in different fields as PNC enhance the properties of polymer to obtain a product with essentially new set of properties.

The raise in the environmental awareness has led governments to make more stringent regulations. This assists in evolution of simpler chemical processes or innovative designed product for future generations by the chemical industries that should create least environmental impact. An interest in naturally available renewable materials has been developed due to the global environmental concern. Therefore, there has been attempt to develop high-performance new materials at reasonable expense in recent years. Wood is one of the renewable resources with an outstanding strength-to-weight ratio. It is one of the preferred construction materials because products manufactured from wood require much less energy compared to those produced from competitive materials like concrete, plastic, or steel. It has an extensive sort of applications which include construction of materials, paper, pulp, and as source for energy (Giudice and Pereyra 2007; Wegner et al. 2010). Woods are of two types—hard- and softwoods. The softwoods remain as a biowaste and are mostly used for fuel purposes because of their poor properties, whereas the hardwoods are used for construction applications. These soft woods can be designed as a value-added product by forming wood polymer composite (WPC) (Hetzer and Kee 2008; Ashori 2008). Wood polymer composites prepared from a variety of renewable matrix and their properties are included in this chapter.

The most important disadvantage associated with the synthetic composite materials is that they are derived from nonrenewable resources. However, other disadvantageous properties of these materials include nonbiodegradability, high cost, etc. Thus, natural fibers like silk, wood, keratin biofibers obtained from chicken feather, etc., are acquiring more priority over the materials obtained from nonrenewable sources. The keratin biofiber can be found in hair and feathers. The advantages of keratin biofibers obtained from feathers are its biodegradable, eco-friendly, nonabrasive properties. They possess a very high mechanical strength as they are insoluble in organic solvents. Moreover, they are hydrophobic in nature, have low density, and low cost. Thus, keratin fibers obtained from chicken feather can be suitable for using as a high structural reinforcement material in polymer composites (Martinez-Hernandez and Velasco-Santos 2012). The keratin biofiber extracted from chicken feathers were used as short-fiber reinforcement for a poly (methyl methacrylate) matrix and can significantly improve the dynamic mechanical and thermal properties of the composites (Martínez-Hernández et al. 2007).

The natural fiber like wood possesses certain advantages like low cost, low density, light weight, high specific properties, corrosion protective, and the most significant is its biodegradability and nonabrasiveness (Raj et al. 1989).

The various properties of wood like appearance; pulp quality; strength properties, resistance to penetration by water and chemicals, decay, etc., are influenced by the chemical and anatomic composition of wood (Panshin and de Zeeuw 1980; Haygreen and Bowyer 1982). The cellular structure of wood consists of cellulose, lignin, hemicelluloses, and minor amounts (5–10 %) of extraneous materials. The quantity and distribution of these constituents of wood lead to variations in the characteristics of wood and the nonconformity in cellular structure causes wood hard or soft, bulky or light and stiff, rigid or flexible. The major constituent of the wood cell wall is cellulose, normally 40–50 % by mass of the dry wood. The cellulose is a polymer of glucose residues attached by 1, 4- β -glucosidic bonds. Hemicellulose is a combination of nebulous branched-chain polysaccharides containing a few hundred sugar residues. Lignin is very difficult to separate in a natural state and is an insoluble, amorphous organic polymer. Chemically, lignin is a methoxy-substituted propylphenol moiety which is bonded asymmetrically by ether and carbon–carbon linkages (Rowell et al. 1997). It consists of 18–30 % by weight of the dry wood. It is mainly centralized in the layered cell wall and compound middle lamella of wood. The rigidity in the structure of the cell wall of wood occurs due to the presence of lignin and imparts a woody, rigid structure to the cell walls. It differentiates the fibrous plant of minor lignin content from wood. There is presence of abundant free hydroxyl groups in the structure of cellulose that can form hydrogen bonds with the moisture present in the atmosphere without any difficulty (Xie et al. 2011). The swelling and shrinking of wood is the consequence of bond formation of wood with the water molecules depending upon its moisture content. Besides, the properties of wood are destructed and deteriorated by biotic agents which include decay, mold, fungi, bacteria insects, etc., and abiotic agents which include sun wind, water, and certain chemicals. The sapwood of wood has very low durability. Since wood is an organic compound, it is a nutritional product of the degrading fungi and assist in its decay. The hydrophilic –OH group of wood participates in chemical bonding with the polymers on formation of wood polymer composites and thus gets converted to hydrophobic groups (Hill et al. 1998). This prevents wood from shrinking and swelling and the bacteria and fungi can no longer recognize wood as their food source within their service life (Li et al. 2013).

The use of synthetic polymer-based composites has led to disposable problems because of their nonbiodegradable nature. Naturally available water-soluble polymer can be used in the different application as a substitute of the synthetic polymers due to scarcity of petroleum resources and environmental awareness. Water is the best solvent among all the green solvents because it is nonpolluting, inexpensive, and renewable.

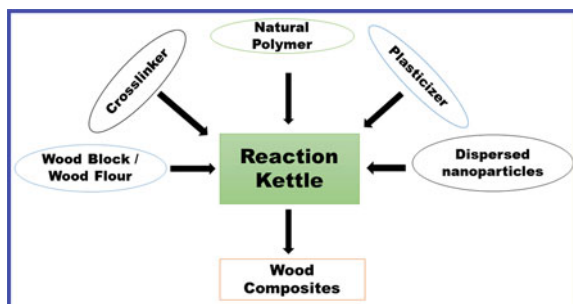
There are several limitations associated with the conventional composites, although they have higher mechanical and other properties. To overcome the limitations, the concept of nanocomposite arises. Nano-dimensional particles-based WPC are reported to improve fire retardancy, moisture barrier, UV protection, etc.,

(Hazarika and Maji 2013a, b, 2014a, b, c, d). Dimensional stability, UV protection, and weather resistance are very significant properties for wood-based materials used in exterior applications. Bio-based wood polymer nanocomposites will have superior properties and can be regarded as high-performance material for the future generation.

2 Wood Polymer Nanocomposites

Nanobiocomposites obtained by incorporating nanofillers to biopolymers are extremely promising product because they provide better properties with conservation of the material biodegradability, avoiding eco-toxicity (Xie et al. 2013). WPC is a paradigm of a structured multiphase product. It is the amalgamation of wood with polymer that can be either polymer filled inside the void spaces of solid pieces of wood or polymer reinforced with wood fiber. Wood polymer nanocomposites (WPNC) are a novel class of wood products with significantly enhanced physical, biological, mechanical, and chemical properties (Deka and Maji 2011; Md. Islama et al. 2012). The impregnation technique is one of the preferred methods for the preparation of WPNC. Composites prepared through this technique can attain the desirable properties of wood completely (Devi and Maji 2011). In this method, the empty cell lumens of wood are occupied by the appropriate monomer or prepolymer, cross-linking agents, and nanoparticles under the influence of vacuum or high pressure, which is then polymerized inside the pores of wood. The wood samples are placed in the impregnation chamber at room temperature (30 °C) and vacuum is applied to eliminate air or water present inside the cavity of cell wall of wood. The prepolymeric mixture is poured to the impregnation chamber to completely immerse the samples. The samples are kept in the chamber for few hours (4–6 h) after attaining atmospheric pressure. The excess chemicals are wiped out from the surface of the samples after taking out of the chamber. They are wrapped in aluminum foil and cured in an oven at 90 °C for 24 h. The samples are further dried at 105 °C for another 24 h. To remove the homopolymers, the samples are Soxhlet extracted for 24 h. All the desirable properties of wood like water repellence, mechanical properties, and thermal stability can be achieved by the resultant wood polymer composite. Besides this, the wood fibers have also been used as reinforcing agents with the polymer for developing wood polymer composite (WPC). The wood fibers are added as reinforcing filler in the polymer matrix, pressed and molded in the presence of high temperature and pressure. The addition of various additives like coupling agents, plasticizer, flame retardant along with nanoparticles assist to obtain tailor-made the finished product as per end-use application (Deka and Maji 2012; Adeosun et al. 2012). Initially, the collected wood is chopped into small strips and washed with 1 % soap solution, followed by washing with 1 % NaOH solution and ultimately with cold water. It is dried at 105 ± 5 °C, ground in a mixer, and sieved at different mesh sizes. The polymer slurry is prepared by using suitable resin, plasticizer, coupling agents, nanofillers, etc., in a mechanical stirrer. The dried wood flour is added to the polymer solution

Fig. 1 Methodology for the preparation of wood polymer nanocomposites



and stirred for specified time period. It is oven dried and ground. The wood polymer nanocomposite in powder form is put into the compression molding press under pressure and temperature for certain period of time. It is then cooled at room temperature to obtain WPNC sheets (Deka and Maji 2013). The chemicals used in the formation of WPNC must be chosen appropriately. The prepared WPNC should not discharge any poisonous substances throughout service condition and can be recyclable or easily discarded at the termination of service life. Figure 1 shows the schematic diagram for the preparation of wood polymer nanocomposites.

3 Bio-based Polymers

Cellulosic polymers occupy a vital position in extensive variety of applications such as fabrics, apparel, food, molded goods, varnishes, and plastics. Among the different cellulosic polymers, starch is one of the most commercially significant class of bio-based materials and is being used for decades (Pandey et al. 2005; Yang et al. 2007; John and Thomas 2008).

Wood polymer nanocomposites are generally prepared using thermoplastics or thermosetting resin. The constant increase in the price of crude oil, problem of rising large-scale waste, and the exhaustion of fossil fuels have provoked attention in utilization of natural sources. A ‘greener’ solution to these issues lies in the utilization of renewable resources. The biopolymers obtained from renewable agricultural feedstock are easily available (Scott 2000; Johnson et al. 2003). Even though the biopolymers are derived from renewable resources, the extent of biodegradability of these polymers depends on its chemical structure. The higher the degree of cross-linking the lesser will be its biodegradability. These green polymers provide perceptible advantages over usual polymers regarding effluence of toxic gases during their service condition, energy consumption while synthesis and waste production. Biodegradability, high compatibility with other polymers, low melting temperatures are some of the attractive characteristics of the biopolymers. But the main drawback of the biopolymers is lack of mechanical properties which limits their applications. If the drawback is removed, it will be feasible to make wood-based green nanocomposites with adequate mechanical properties, durability, and

enhanced biodegradability. The bio-based composites are the eco-products that are obtained from natural sources with recycling capabilities (Mohanty et al. 2002).

3.1 Polyfurfuryl Alcohol

Furfuryl alcohol (Fig. 2) is a clear light yellow colored liquid when pure, but it turns into yellowish brown color on long-standing. Furfuryl alcohol has been used in the formation of wood polymer composite for a long time (Baysal et al. 2004; Lande et al. 2010). It can be impregnated into the cells of wood owing to its low molecular weight. After impregnation, it is polymerized inside the wood cell wall and binded with the wood through radiation, catalysts, heat, or other reactants. The use of vegetable biomass as a substitute of petroleum-based chemicals is one of the sustainable solutions for an eco-friendly environment. Monomers such as furfuryl alcohol are particularly derived from hemicellulose. It is synthesized industrially through the catalytic reduction of furfural that in turn is derived from corncob and sugarcane bagasse. During the process of impregnation, furfuryl alcohol is generally transformed into furanic resin prepolymers. Modification of wood through furfurylation represents an exquisite eco-friendly method. The difficulty of using zinc chloride as catalyst in the process of furfurylation is that it can cause degradation of cellulose and hence affect the long-term strength properties of the resultant wood polymer composites. Generally, cyclic carboxylic system is found to be better than the zinc chloride system in the furfurylation process. Among the cyclic carboxylic system, maleic anhydride is the most appropriate one for furfurylation (Schneider 1995). With the increase in the weight percent gain, the water repellence of the wood polymer composites impregnated with bio-derived furfuryl alcohol has increased (Lande et al. 2004b). The degradation of furfurylated wood does not release any volatile organic compounds and therefore it is considered as an environmentally suitable product (Lande et al. 2004a).

3.2 Starch

Starch is one of the most fascinating and potential sources for biodegradable polymers among the wide class of sustainable polymers due to its low cost,

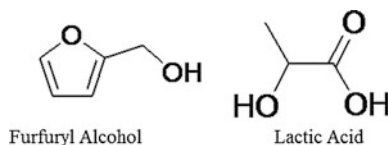


Fig. 2 Structure of furfuryl alcohol and lactic acid

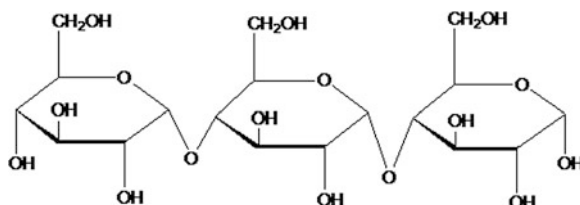
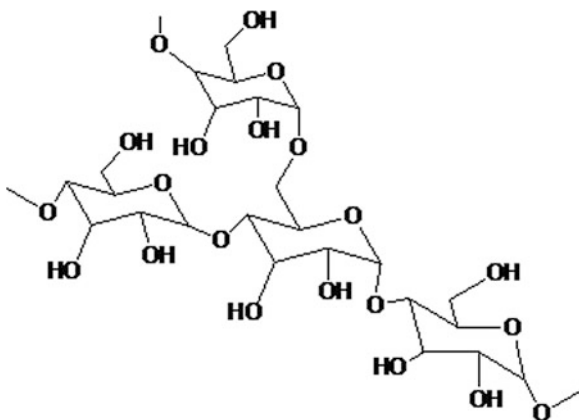


Fig. 3 Structure of amylose which contain 20–30 % structure of starch

Fig. 4 Structure of amylopectin which contains 70–80 % structure



biodegradability, easy availability, and simplicity in the method of its chemical modifications (Mathew and Dufresne 2002; Mohanty et al. 2000). Pure starch is a white, scentless, and tasteless powder that is insoluble in cold water or alcohol but becomes soluble in water when heated under shearing condition. It is the main polysaccharide which is produced by most of the green plants and composed of a large number of glucose units attached through glycosidic bonds. The linear and helical amylose and the branched amylopectin are the two main constituent polysaccharides of starch. The amount of amylose in starch varies from 20 to 30 % (Fig. 3) and that of amylopectin (Fig. 4) ranges from 70 to 80 % by weight depending on the plant. Amylopectin is a much larger molecule than amylose. Starch is a semicrystalline granule due to the presence of amylopectin and the granules vary in size depending upon its source of production. The starch granules obtained from rice (about 2 μm) is much smaller in size than the granules obtained from potato (up to 100 μm).

Plasticized starch has been gaining substantial attention and is used as a substitute for synthetic polymers where long-term durability is not required and degradation is a benefit (Tábi and Kovács 2007). Plasticized starch is also called ‘thermoplastic starch.’ It is obtained by disintegration of starch in water followed by plasticization with water and plasticizer (e.g., glycerol) using thermomechanical energy in a constant extrusion process. However, plasticized starch-based

composites possess many drawbacks like water sensitivity, poor mechanical properties, etc., in comparison with conventional synthetic thermoplastics-based composites (Cao et al. 2008a, b; Santayanon and Wootthikanokkhan 2003). Moreover, the properties of plasticized starch attain stability after several weeks. These plasticized starch are coupled with other compounds to remove the disadvantages associated with their properties. These drawbacks can be overcome by means of different physical or chemical means, including the chemical modification, (Cao et al. 2005) graft copolymerization, (Suda et al. 2002) blending with other synthetic polymers (Cao et al. 2008a, b), and incorporating fillers such as clay (Chen and Evans 2005) and nanocrystalline cellulose.

3.3 *Poly(lactic Acid)*

Poly(lactic acid) (PLA) is one of the most common and interesting biodegradable polymers that belongs to the class of aliphatic polyesters usually made from α -hydroxyacids. PLA (Fig. 2) is derived from agricultural resources such as corn, sugarcane, etc., to produce articles that are employed in the biocompatible medical device market and industrial packaging field. The fermentation of corn dextrose yields lactic acid as a by-product which is the main source for production of PLA (Vink et al. 2003). PLA is notable for its extremely biodegradable and biocompatible behavior. PLA is able to substitute petrochemical-based polymers and therefore it has acquired substantial industrial cognizance for its utility in commodity resins. It is a high-strength thermoplastic polymer which has superior mechanical properties over pure polypropylene (PP). The tensile strength and modulus of neat PLA is found to be 62 MPa and 2.7 GPa, respectively, whereas neat PP has tensile strength and modulus of 36 MPa and 1.2 GPa, respectively (Huda et al. 2005). The glass-transition temperature (T_g) and the melting temperature (T_m) of PLA are 54 and 172 °C, respectively, so it is capable of processing in blow molding, injection molding, and film forming to produce film, molded parts, and fibers (Hartmann 1998; Oksman et al. 2003). However, PLA is considered brittle for many marketable applications, though it has mechanical properties appropriate for industrialized plastic appliances (Oksman et al. 2003). The problem of brittleness and poor process capability of stiff polymers can be solved by incorporation of other materials into it. The high-molecular-weight poly(lactic acid) has similar properties with that of polystyrene and it is a rigid, colorless, lustrous, thermoplastic polymer. Poly(lactic acid) is used for single-use packaging applications because it has a rational shelf life and, when properly discarded, it will hydrolyze to natural, nontoxic products. Thus, the problem of disposal of the large amount of plastic packaging can be solved by using PLA industrially. The biodegradable green composites based on wood and PLA present attractive properties of the composites and lesser cost than competitive materials. Wood polymer composites treated with PLA have satisfactory mechanical properties comparable to that of conventional thermoplastic-based wood polymer composites (Huda et al. 2006).

3.4 *Soy flour*

Soy flour is a mixture of soy protein and its related carbohydrate and is accessible in the form of by-product from the soybean industry. Proteins are widely available in nature in different forms from plants such as corn, soy, wheat gluten, etc., and from animals such as collagen, gelatine, etc. Biopolymers useful for various applications are derived from these proteins (Sakurada et al. 1962). Soy protein is a reactive, globular protein and is soluble in water in contrast to that of synthetic polymers which are nonreactive, planar or helical structured, and insoluble in water (Lavoine et al. 2012a, b; Siro and Plackett 2010). It has several advantages over the petroleum-based synthetic polymers and is one of the most inexpensive biopolymers. The various advantages include the purification procedure for soy protein which is an eco-friendly sustainable process. The raw material is relatively less costly and easily available because soybean is an annual crop and available worldwide. Soy proteins can be employed as resins because they can form viscous and ductile polymers. It has been reported that biocomposites based on soy flour utilized for various structural applications such as automotive parts, housing, and truck showed comparable properties to that of structural woods. Thus, these bio-based composites are appropriate for structural applications (Wool et al. 2002). For such purposes, the resin is cured at high temperature. The curing of the resin is possible at room temperature through vacuum-assisted resin transfer molding method thereby diminishing the cost and hence ecological risks.

3.5 *Polyhydroxyalkanoates*

Polyhydroxyalkanoate (PHA) is another important eco-friendly biopolymer that is synthesized by a wide variety of microorganisms as carbon and energy storage under nutrient-limiting conditions in the existence of excess carbon source (Khanna and Srivastava 2007). The polyhydroxyalkanoates family includes an extensive range of materials, from rigid and brittle to flexible and elastomeric materials (Misra et al. 2006). The processability of PHB is one of its main problems as it is of high stiff and brittle nature. The processing of PHB, under different conditions of temperature and rotor speeds in an internal mixer, will render its crystallinity to increase. Therefore, to improve the processing ability of this highly crystalline but brittle polymer, plasticizers like PVA and stearic acid are employed, as like with starch. The biodegradability and biocompatibility (with living cells) are the main characteristics of this class of polymer. Polyhydroxyalkanoate has been successfully applied to manufacture nonwoven fibrous materials, films, in biomedical and pharmaceutical applications, including drug delivery systems, implant materials, transplantology, tissue engineering, and nontoxic surgical sutures (Valappil et al. 2006).

3.6 Epoxidised Vegetable Oil

Vegetable oil is one of the most inexpensive and inexhaustible natural resource obtainable in huge quantities. It has its inherent biodegradability as well as low toxicity and the reactive sites in the oil are the double bonds present in these vegetable oils. They can be functionalized by epoxidation and the epoxidized vegetable oils show outstanding properties as it is an inexpensive, renewable materials suitable for various industrial applications. Vegetable oils are lipids derived from plants and are widely extracted from oil seeds (e.g., linseed, sunflower, hemp), although some oils may be derived from other plant sources such as pulp (e.g., avocado, palm, and olive). Chemically, the constituent of vegetable oil is triglyceride molecules consisting of a glycerol molecule bonded to three fatty acid chains. Figures 5 and 6 show the structure of a triglyceride molecule and oleic acid, linoleic acid as well as linolenic acid, respectively. A fatty acid is a carboxylic acid bonded to a long unbranched aliphatic carbon chain. The length of the majority of common fatty acids found in vegetable oils usually varies between 14 and 22 carbons atoms.

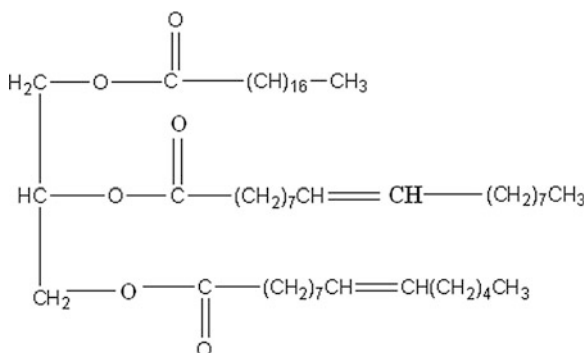


Fig. 5 Structure of a typical triglyceride molecule

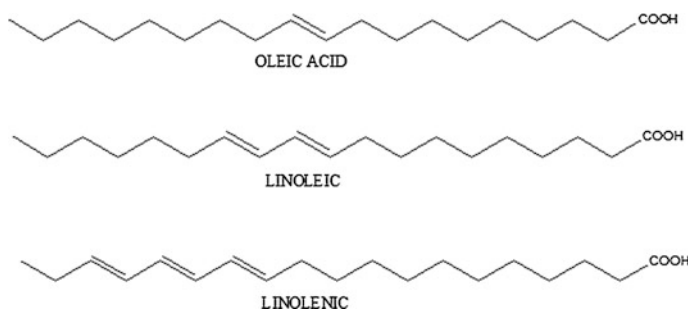


Fig. 6 Structure of oleic, linoleic, and lilonic acid

The presence of the C=C in unsaturated fatty acids is employed as the reaction sites in the formation of cross-linking. The networked structure can be achieved by a functional reaction of the C=C to enable use in high-molecular-weight products. The properties of the epoxidized resin-based composites are reliant on the extent of cross-linking reaction with the materials. The higher the cross-link density, the better is the mechanical and thermal properties.

4 Modification of Natural Polymers: Grafting

There are considerable choices to produce pioneering polymeric materials by using polymers derived from natural sources. Manufacturing products based on renewable resources that have least environmental impact and reduced reliance on fossil fuels are the motivating forces from environmental as well as economic panorama. It is necessary to improve the properties of a polymer to meet the requirements for its end-use applications. There are various ways to alter the properties of polymers, viz., grafting, blending, and curing (Bhattacharya and Misra 2004). Different techniques have been used for graft copolymerization of various monomers on polymeric backbones which include grafting by coupling chemistries, free radical polymerisation, controlled radical polymerisation, etc. (Roy et al. 2009; Tizzotti et al. 2010; Malmstrom and Carlmark 2012). ‘Grafting’ is a technique in which monomers become bonded covalently (modified) onto the polymer chain. An active site is formed at a point on the polymer chain other than its end. Graft polymerization occurs on exposure of this active site to a monomer. New hybrid products with controlled properties are formed on grafting specific synthetic polymer chains to different renewable polymers including starch, nanocrystalline cellulose, polysaccharides, cellulose, and chitosan. The naturally available polymers are least water resistant and do not possess mechanical properties of sufficient magnitude for structural applications. Therefore, synthetic polymers grafted biocomposites offer a new means to achieve innovative products with controlled properties and structure. Grafting is considered an important method to modify chemical as well as physical properties of the polymers. Novel renewable-based products have been designed through ring-opening polymerization, controlled (or living) radical polymerization, and thiol-ene or click chemistry presenting interestingly new opportunities. Generally, graft copolymers are produced through radical polymerization. In most of the cases, chain transfer reactions proceed through the removal of hydrogen atoms. Natural polymer graft copolymers have been increasingly significant due to their prospective utilization in industrial application. Thus, grafting is an influential technique for implanting considerable modification on the properties of natural polymers by using various vinyl and other monomers (Athawale and Rath 1997).

5 Cross-linking Agents

Cross-linking involves formation of three-dimensional arrangement of associated molecules by physicochemical bond formation linking molecular chains. Cross-linking agents are used to treat two semi-compatible or incompatible materials to get the best benefits of their properties and are used in small quantities. They are usually bifunctional compounds where one functionality is bonded with one component (say polymer) and other functionality with another (say wood) (Yanga et al. 2007). The polymers remain in the form of a three-dimensional network structure inside the wood structure or within the composite and hence assist in interaction between the polymers and wood. The resultant wood polymer composites will show improved mechanical properties dimensional stability, weather resistance, etc. Wood polymer composite developed by treatment with biopolymers have many disadvantages associated with their properties. The biopolymers have minimum water resistance capacity, lacking in terms of their mechanical properties, chemical resistance, etc. Addition of small amount of cross-linker enhances the properties of the composites as they form network structure inside the composites thereby stiffening the composites. The cross-linked structure of the composites improved the tortuous pathway for transmission of water as well as chemicals and as a consequence swelling decreased. Hence water resistance and chemical resistance of the composites can be achieved through the use of cross-linking agents. Various cross-linking agents such as *n*-methylol compounds which include dimethyloldihydroxy-ethyleneurea (DMDHEU), *n*-methylol acrylamide (NMA), 2-hydroxyethyl methacrylate (HEMA) are essential multifunctional cross-linking agents that improve the resistance of wood to weathering. DMDHEU can cross-link with wood cell wall and dimensionally stabilize the composites. A remarkable improvement in water resistance and mechanical properties has been found on treatment of WPC with DMDHEU (Hazarika and Maji 2012). NMA can also provide water resistance and enhance strength properties of the resultant composites (Hazarika and Maji 2013a, b).

6 Flame Retardants

Resistance to fire is one of the most desirable properties of the WPC. The fire resistant properties are essential particularly for application in furniture industry and residential construction (windows, roof tiles, decking). The study in the area of flame resistance of WPC is very important with regard to its safety provisions (Sain et al. 2004). The volatile substances evolved from wood during heating react with oxygen vigorously. The hydrocarbons contained in wood ignite indirectly during combustion. Thus wood is vulnerable to burning and ignition.

There has been an untiring attempt to improve flame retardancy of wood to increase its service. Additives that are incorporated into WPC to enhance its flame resistance are called flame-retarding agents. The objective of these flame-retarding

agents is to slow down the propagation of fire or circumvent the source of a fire. The main perception of flame retardancy in the condensed phase lies in the development of a protecting barrier (Jimenez et al. 2006). Thus the underlying material is shielded from heat transfer through barrier formation (Weil et al. 1999). Flame retardants are either applied to pretreated wood or blended with the impregnating monomers prior to impregnation into wood. The use of halogenated flame retardant like organic brominated compounds can enhance the flame retardancy of WPC. However, these flame retardants yield carbon dioxide and smoke because of their ineffective combustion. The other commonly used flame retardants are various silicates, organoantimony compounds, borates compounds, and organophosphorus (Watanabe et al. 2009; Li and He 2004; Baysal 2002). Most of them while ignition release noxious gases and fumes that are extremely detrimental to health and thus contaminate the environment. The service life of the product may deteriorate due to leaching of the flame retarding agents to the surface of the product. The leaching problem of the flame retardants can be receded by using polymeric flame retarding agent because they are of high molecular weight and hence enhance the service life of the product. The utilization of polymeric flame retardant derived from natural resources is advantageous from ecological viewpoint. The gum obtained from the plant *Moringa olifera* is used as flame retardant. The flammability and biodegradability of starch-based biodegradable film modified with gum derived from *Moringa olifera* has been found to improve. (Jana et al. 2000). Wood polymer composites treated with the gum polymer showed a considerable improvement in flame retardancy (Hazarika and Maji 2013a, b; Hazarika and Maji 2014a, b, c, d). The gum polymer prohibited combustion because of its phosphorus content (Ghosh and Maiti 1998). The mechanism of fire control is supposed to be liberation of oxides of phosphorus during the process of ignition which displaces the oxygen present on the surface of the material, thus prohibiting combustion.

7 Different Nano Reinforcing Agents

The progress in the field of polymer nanocomposites (polymer composites with nano-sized reinforcement), appears as a multidisciplinary research activity. Different industries have been benefitted through the wide application of polymers nanocomposite (Sengupta et al. 2007; Hambir et al. 2002). Wood polymer nanocomposites are prepared through the interesting technique of nanotechnology. Enhanced properties of bio-based wood polymer nanocomposites can be achieved when nanofillers are incorporated along with the polymer and cross-linker. The nanoparticles should have one of its dimensions lower than 100 nm and the nano-sized reinforcement elements are dispersed in the polymer matrix during the formation of the nanocomposites. This nanoreinforcement offers nanocomposites with exceptional and excellent properties that are not found in conventional wood polymer composites. The various nanoparticles include nanoclay, metal oxide nanoparticles, carbon nanotubes.

7.1 *Montmorillonite*

It typically belongs to 2:1 phyllosilicates and their structure of the crystal lattice is composed of two-dimensional layers in which a middle octahedral sheet of alumina or magnesia is merged to two exterior silica tetrahedron by the tip in order that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets. The lateral dimension may differ from 300 Å to several microns, whereas the layer width is about 1 nm. The interlayer space of clay can be extended under precise experimental conditions, and the polymer chains can enter within these gallery layers of clay. The thermal and mechanical properties of clay treated wood/PLA nanocomposites were found to improve significantly (Meng et al. 2011a, b). Besides, addition of clay also improves biodegradability, dynamic mechanical properties, water resistance, chemical resistance of the nanocomposites (Hazarika et al. 2014; Hazarika and Maji 2012).

7.2 *Metal Oxide Nanoparticles*

The metal oxide nanoparticles can display exclusive chemical and physical properties because of their small size and a high density of boundary surface sites. Nanoparticle should have a little surface free energy so as to exhibit mechanical stability (Fernández-García and Rodríguez 2007). The metal oxide nanoparticles used as nanofillers in wood polymer nanocomposites include ZnO, TiO₂, SiO₂, etc., ZnO nanoparticles are generally used as photostabilizer. In addition to its UV-stabilizing effect, nano ZnO can also enhance thermal stability of polymer nanocomposites. In polymer nanocomposite, SiO₂ nanopowder is also one of the extensively used nanofiller. SiO₂ improves the mechanical as well as thermal properties of the nanocomposite. TiO₂ has been well documented as the most outstanding photocatalyst for the decomposition of many organic pollutants in water and air (Hoffmann et al. 1995). The UV resistance along with other physical properties of the wood polymer nanocomposites improves substantially on treatment with TiO₂ (Hazarika and Maji 2013a, b).

7.3 *Carbon Nanotubes (CNT)*

CNT are cylindrical nanostructure (Fig. 7) having length starting from hundreds of nanometers to micron and even millimeters and radius in nanometer (Saito et al. 1998). The excellent mechanical and physical properties of CNTs based nanocomposites has motivated researchers in developing high-performance wood polymer nanocomposites based on carbon nanotubes (Hazarika and Maji 2014a, b, c, d). The

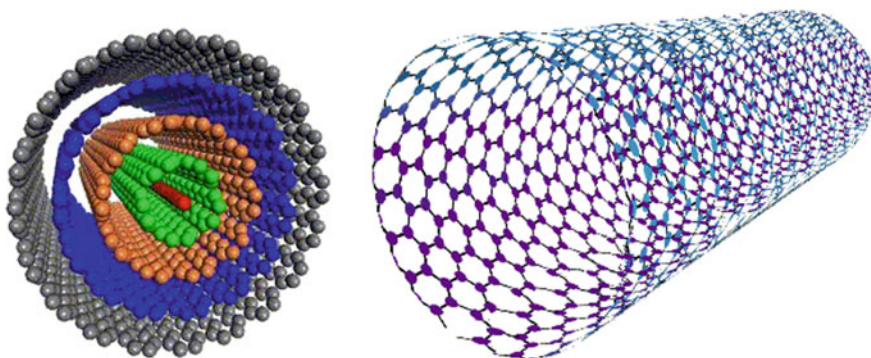


Fig. 7 Structure of CNT

various forms of CNT include, single-wall and multi-wall, networks or isolated. Starch-based MWCNT composites leads to decreased water sensitivity and improved mechanical properties (Cao et al. 2007).

7.4 Nanocellulose

Apart from the above nanoparticles, nanocellulose has been the topic of a broad range of research as reinforcing agents in nanocomposites because of their nanoscale dimension, renewability, availability, light weight, low cost, and most importantly they have minimum environmental impact and have little effect on animal/human health (Lavoine et al. 2012a, b). They offer significant properties of cellulose including its extensive ability of chemical modification, very high aspect ratio leading to the formation of versatile semicrystalline fibers which is the unique characteristic of nano materials as reinforcing agents. There is a presence of strong and complex network of hydrogen bonds which are stabilized by the ordered regions of chain packages of cellulose (Habibi et al. 2010) that resembles nanocrystalline rods. Based on their preparative methods and structure, there are two main types of nanocellulose: (i) nanocrystalline and (ii) microfibrillated cellulose.

- (i) **Nanocrystalline cellulose:** Nanocrystalline cellulose, which are extremely crystalline and rigid nanoparticles, are also called cellulose nanowhiskers or cellulose nanocrystals. This can be prepared from native fibers through acid hydrolysis. A new class of bio-based products with a broad range of applications including automotive industry, construction material, etc., have been developed by using nanocrystals as reinforcing agents. Addition of small amount of nanocrystal can increase the strength, stiffness, and resistance of the material to stress threefold its original strength. Thus incorporation of nanocrystal makes the nanocomposites an interesting high-performance material. It is also a promising green substitute for carbon nanotubes as reinforcing agents

in polymers nanocomposites and concrete. Nanocrystal reinforced nanocomposites is used in a variety of applications such as biodegradable plastic bags, textiles, wound dressings, etc.

- (ii) Microfibrillated cellulose (MFC): The constituent of MFC is nano-sized cellulose fibril having high aspect ratio. The fibrils are extracted from wood pulp through high temperature, high-pressure, and high-velocity impact which can be employed in polymer nanocomposites of high mechanical capacity (Nakagaito and Yano 2004). The strength properties of these nanocomposites are very high and the Young's modulus is found to be approximately 20 GPa. Thus, MFC-based nanocomposites that are derived from wood pulp is a promising class of substance with outstandingly high mechanical performance. The Young's modulus of the cellulose crystal is about 134 GPa, therefore MFC nanofibers are estimated to provide high stiffness to the resultant nanocomposites (Sakurada et al. 1962).

However, another type of nanocellulose is known as bacterial cellulose. Specific bacteria mainly *Gluconacetobacter* strains secrete these cellulose nanofibers extracellularly (Klemm et al. 2009; Siro and Plackett 2010). These bacterial celluloses have exceptional mechanical and physical properties due to its special fibrillar nanostructure. Its properties include high strength, high porosity, high crystallinity (up to 84–89 %, Czaja et al. 2004), and high elastic modulus (Guhados et al. 2005). Currently, bacterial cellulose is the topic of research in several fields of applications, reinforcement in nanocomposites (Juntaro et al. 2008; Nogi and Yano 2008), biomedical applications and fuel cell membranes (Evans et al. 2003).

8 Properties of Wood Polymer Nanocomposites

8.1 Dimensional Stability

The moisture content of wood depends on the atmospheric circumstance, temperature, and the relative humidity of the surrounding air. Wood is hydrophilic in nature that can soak up moisture in humid surroundings and elude it in dry surroundings. Studies reveal that thermoplastic starch-based wood composites showed lower water uptake capacity on formation of the composites (Agnantopoulou et al. 2012). After the formation of WPC, water absorption in the composites differs depending upon the content of nanoparticles and cross-linking agents. Addition of cross-linking agent forms a networked structure in the composites which hindered the diffusion of water molecules through the cross-linked structure and as a result the water absorption capacity decreases. The water molecule first saturates the porous cell wall, lumen and tubular structure of the wood fibers, and then fills up the void spaces of wood (Das et al. 2000). As the addition of nanoparticles to the composites occupies the cell wall and the lumen, the transmission of water molecules into the composites by the capillary action is prohibited. Thus the

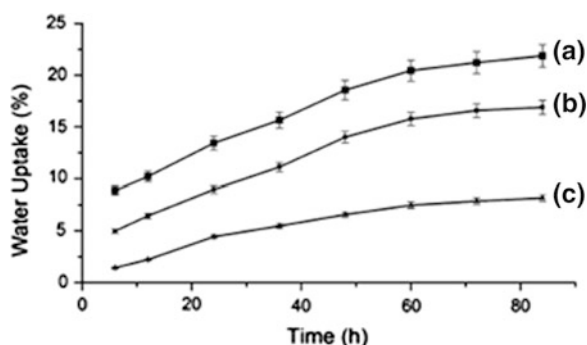


Fig. 8 Water absorption of *a* wood/MMA-g-starch/glutaraldehyde *b* wood/MMA-g-starch/*n*-methylol acrylamide *c* wood/MMA-g-starch/DMDHEU

nanoparticles fill up the voids and the lumens of the fibers of the composite and diminish the available sites for water absorption. Wood treated with starch-grafted MMA and DMDHEU has reduced water absorption capacity (Baishya and Maji 2014) as shown in Fig. 8.

8.2 Mechanical Properties

The various parameters like fiber aspect ratio, volume fraction of the fibers, its orientation, stress transfer at the interface and fiber matrix adhesion influence the properties of natural fiber reinforced composites. The mechanical properties of the composites greatly depend on the influence of various treatments of fibers, fiber content, and the use of cross-linking agents (Garcia et al. 1995; Vollenberg and Heiken 1989).

The polymer and fiber properties are equally significant in enhancing the mechanical performance of the composites. The properties of fibers in a composite affect its modulus, while the matrix properties are more responsive to its tensile strength. A strong interfacial interaction, low stress concentration, and fiber orientation are some of the significant criteria to enhance the tensile strength of the composites. Tensile modulus is improved by fiber wetting in the matrix phase, high-fiber aspect ratio, and fiber orientation. The aspect ratio is one of the most vital characteristics in determining the fracture properties of the composites. An optimum interfacial adhesion is essential for good impact strength of the composites. The impact strength is also sensitive to the fiber pullout, degree of adhesion, and a mechanism to absorb energy.

The mechanical properties of wood-fiber-reinforced poly(lactic acid) composites were similar to conventional composites based on thermoplastic polypropylene. Wood-fiber-reinforced poly(lactic acid) composites had appreciably superior mechanical properties than that of the virgin resin. The use of nano reinforcing

Table 1 Mechanical properties of starch-based wood composites with different cross-linker

Sample	Flexural properties		Tensile strength (MPa)	Hardness (Shore D)
	Strength (MPa)	Modulus (MPa)		
W/MMA-g-starch/GA	30.8	2152	13.6	64.1 (± 1)
W/MMA-g-starch/N	42.7	4369	14.8	66.3(± 0.5)
W/MMA-g-starch/D	44.7	5011	15.6	72.0 (± 1)

agents in the composites improved the mechanical properties of the composites remarkably (Liu et al. 2013; Meng et al. 2011a, b). Addition of clay imposes a restriction in the mobility of the polymer chains that are entrapped in between the layers of the clay thereby stiffening of the composites.

The wood composites prepared from starch with water as a solvent and DMDHEU as cross-linker showed good mechanical properties. The results of mechanical properties are shown in Table 1 (Baishya and Maji 2014).

8.3 Chemical Resistance

The study of the chemical resistance properties of WPC is very important to improve the desirable properties of WPC for their target application and hence service life. As WPCs are mostly used for outdoor applications and they may come in regular contact to the external atmosphere or aqueous media such as acid, alkali, water and various solvents, so it is necessary to enhance their chemical resistance.

Even though there are several literatures on wood polymer composites, yet little information are available on the topic of the chemical resistance properties of these composites. The strength properties and esthetic appearance are deteriorated by chemicals. The hemicelluloses present in wood have low resistance to acid (Sjostrom 1993). Thus, wood polymer composites in which wood contains higher percentage of hemicellulose show substantially lower chemical resistance.

Wood is extremely resistant to mild chemicals and as such it provides a significant advantage over many alternative construction materials. The various alternative construction materials, like concrete and steel are prone to corrosion. WPC can effectively substitute these materials as it is resistant to acidic salt solutions, mild acids, and corrosive agents. The chemical resistance properties enhance further in case of wood polymer nanocomposites (Deka et al. 2012). The nanoparticles offer a tortuous path for diffusion of chemicals throughout the composites thereby improving its chemical resistance.

8.4 Biodegradation Properties

Generally, WPC are prepared by using synthetic thermoplastic monomers. The moisture uptake is retarded by plastic component and hence it slows down the

commencement of degradation process. These plastics are obtained from nonrenewable sources and are not biodegradable when disposed after their service life. They remain as nonbiodegradable waste and as a result they are not considered environment-friendly. Pure wood is more vulnerable to fungal attack, decay and bacterial degradation, and thus have a reduced service life. The benefits of WPC are that it can be used as an alternative to pure wood for various outdoor applications such as railing, decking, etc. They provide weather resistance and involve low maintenance. But the main disadvantage is the nondegradable plastic constituent present in the composite (Raberg and Hafren 2008). Therefore, replacement of these synthetic polymers by polymers obtained from renewable resources in WPC will remove the problem associated with their disposal at the end of their service life. Thus bio-based wood polymer composites can effectively be employed in their target applications and have a sufficient period of service life without causing any threat to the environment.

In contrast to the other constructional material such as metal, alloys and concrete, wood polymer nanocomposites are more eco-friendly due to the biodegradation nature of wood. The bacterial growth occurs in the composites because of prevailing cellulolytic as well as pectinolytic activity of bacteria. Apart from cellulose and pectin, one of the main constituents of wood is lignin which is degraded by *Bacillus* sp. (El-Hanafy et al. 2008). Addition of nanoclay into WPNC can enhance the biodegradation process of wood polymer nanocomposites (WPNC). The WPC shows enhanced biodegradability because of the presence of clay which acted as catalyst in the biodegradation process (Hazarika and Maji 2014a, b, c, d; Karak 2006).

9 Applications

WPNC products can be effectively employed in those fields of applications where WPC commodities were in use previously. WPNC has similar functions with that of solid wood but it requires lower maintenance, and has much lesser mass to strength ratio and enhanced service life. It is an exceptional composite material, experiencing worldwide high expansion rates and constituted of wood, polymer, and other additives in various proportions. WPNC can be utilized suitably for both indoor and outdoor applications. WPC are produced commercially from the mid 1960s using the radiation process. But very few bio-based wood polymer nanocomposites have been developed, with majority of their technologies remaining in the research and development stages. These eco-friendly composites endow with the designers for new substitute to meet the challenging requirements. WPNC products can be useful in electronics, constructions, automotive, etc. The bio-based WPNC may be used as an alternative to steel and fiberglass and thus can be employed as a replacement for the automotive parts which is the most important market recognized for the utilization of WPCs (Ashori 2008). These composite materials have been efficiently used in many areas of applications including furniture industry, measurement

engineering building industry, automotive industry, flooring such as solid plank flooring, laminated flooring, and fillets for parquet flooring. The main advantages of parquet flooring are its abrasion resistance and hardness which is useful in traffic commercial installations. Though it has high cost, its ease of maintenance and the long service life have justified the high price of parquet flooring over conventional flooring. They can be successfully utilized for making various sports equipment such as baseball bats, hockey sticks, golf club heads, etc., and musical instruments such as finger boards of stringed instruments, wind instruments, mouthpieces of flutes and trumpets, etc.

10 Conclusion and Future Prospect

The lower grade wood that remain unutilized and exists as a biowaste can be fabricated into valuable product by indigenous technical knowledge. Biopolymer-based wood polymer nanocomposites is of significant interest due to its renewable nature, low relative density, biodegradability, low cost, ease of processing advantages, and high specific strength. The development of WPNC by means of different polymers and nano reinforcing agents results in enhancement of properties of WPNC. A notable enhancement in properties of the nanocomposites is indicated by the laboratory study, yet a methodical study has to be performed for extensive industrial application of the product. The furfurylated wood has already been commercialized for numerous applications like roof decking, furniture, parquet flooring, ship decking, and playground equipment. The production of furfurylated wood from Lithuania is 500 m³/year and that from Norway is 5000 m³/year. These bio-based WPNC will find much more application in various areas in the near future.

The final properties of the nanocomposites are determined by interfacial interaction between the wood fibers, polymers, nanoparticles, and other additives. Research on preparation of WPCs by using techniques like gamma radiation, electron beam (EB), or radio frequency (RF) to polymerize the monomer(s) within the composite is nearly instantaneous. The inclusion of pigments into impregnation solutions like supercritical fluid, e.g., SC-CO₂ as the medium of impregnation may be studied extensively to investigate diversified value-added uses for modified wood, particularly for flooring and other value-added applications.

The performances of these bio-based nanocomposites are judged by their properties. One of the efficient ways to improve the properties of the final composites is the addition of nanoparticles. Attempt should be made to prepare bio-based WPNC by using nanomaterials obtained from lignocellulosic materials such as cellulose nanowhiskers and nanofibres to enhance their properties. The flame retardant obtained from the *Moringa oleifera* has remarked influence on the thermal stability and flame retardancy of the composites and moreover it is environment friendly. The use of vegetable oil-based resin along with natural additives including hardener may be tried to get fully biodegradable wood polymer composites.

Therefore, attempts should also be made to obtain cross-linking agents, reinforcing agents, resins from various natural sources to develop bio-based WPNC with enhanced properties or develop new technology suitable for the future ecological goals. The preparation of biodegradable polymer-based wood composites with new processing technique and improved properties related to physical, mechanical, chemical properties are some of the aspects that need a lot of consideration. However, the use of these biocomposites is restricted in many fields because of the high cost of the some of the biopolymers. Development of new manufacturing technology, raw materials from which the polymers are derived may decrease the cost of the bioresins for production of composites. Thus, investigation in the area of bio-based WPNC may lead to new perspective to meet with the global challenges and maybe utilized as substitute to conventional composites that may broaden its horizon of applications.

References

- Adeosun SO, Lawal GI, Balogun SA, Akpan EI (2012) Review of green polymer nanocomposites. *J Miner Mater Charact Eng* 11:385–416
- Agnantopoulou E, Tserki V, Marras S, Philippou J, Panayiotou C (2012) Development of biodegradable composites based on wood waste flour and thermoplastic starch. *J Appl Polym Sci* 126:E272–E280
- Ashori A (2008) Wood–plastic composites as promising green-composites for automotive industries. *Bioresour Technol* 99:4661–4667
- Athawale VD, Rath SC (1997) Synthesis and characterization of starch–poly(methacrylic acid) graft copolymers. *J Appl Polym Sci* 66:1399–1403
- Baishya P, Maji TK (2014) Studies on Effects of different crosslinkers on the properties of starch based wood composites doi:[10.1021/sc5002325](https://doi.org/10.1021/sc5002325)
- Baysal E (2002) Determination of oxygen index levels and thermal analysis of scots pine (*Pinussylvestris* L.) impregnated with melamine formaldehyde-boron combinations. *J Fire Sci* 20:373–389
- Baysal E, Ozaki SK, Yalinkilik MK (2004) Dimensional stabilization of wood treated with furfuryl alcohol catalysed by Borates. *Wood Sci Technol* 38:405–415
- Bhattacharya A, Misra BN (2004) Grafting: a versatile means to modify polymers techniques, factors and applications. *Prog Polym Sci* 29:767–814
- Cao X, Chang PR, Huneault MA (2008a) Preparation and properties of plasticized starch modified with poly caprolactone based waterborne polyurethane. *Carbohydr Polym* 71:119–125
- Cao X, Chen Y, Chang PR, Huneault MA (2007) Preparation and properties of plasticized starch/ multi walled carbon nanotubes composites. *J Appl Polym Sci* 106:1431–1437
- Cao X, Chen Y, Chang PR, Muir AD, Falk G (2008b) Starch-based nanocomposites reinforced with flax cellulose nanocrystals. *express Polym Lett* 2:502–510
- Cao X, Wang Y, Zhang L (2005) Effects of ethyl and benzyl groups on the miscibility and properties of castor oil-based polyurethane/starch derivative semi-interpenetrating polymer networks. *Macromol Biosci* 5:863–871
- Chen B, Evans JRG (2005) Thermoplastic starch-clay nanocomposites and their characteristics. *Carbohydr Polym* 61:455–463
- Czaja W, Romanovicz D, Brown RM (2004) Structural investigations of microbial cellulose produces in sattionary and agitated culture. *Cellulose* 11:403–411

- Das S, Saha AK, Choudhury PK, Basak R, Mitra BC, Todd T, Lang S, Rowel RM (2000) Effect of steam pretreatment of jute fiber on dimensional stability of jute composite. *J Appl Polym Sci* 76:1652–1661
- Deka BK, Maji TK (2011) Effect of TiO_2 and nanoclay on the properties of wood polymer nanocomposite. *Compos Part A* 42:2117–2125
- Deka BK, Maji TK (2012) Effect of nanoclay and ZnO on the physical and chemical properties of wood polymer nanocomposite. *J Appl Polym Sci* 124:2919–2929
- Deka BK, Maji TK (2013) Effect of SiO_2 and nanoclay on the properties of wood polymer nanocomposite. *Polym Bull* 70:403–417
- Deka BK, Mandal M, Maji TK (2012) Effect of nanoparticles on flammability, UV resistance, biodegradability, and chemical resistance of wood polymer nanocomposite. *Ind Eng Chem Res* 51:11881–11891
- Devi RR, Maji TK (2011) Preparation and characterization of wood/styrene-acrylonitrile copolymer/mmt nanocomposite. *J Appl Polym Sci* 122:2099–2109
- El-Hanafy AA, Elsalam HA, Hafez EE, Borg EL (2008) Molecular characterization of two native Egyptian ligninolytic bacterial strains. *J Appl Sci Res* 4:1291–1296
- Evans BR, O'Neill HM, Malyvanh VP, Lee I, Woodward J (2003) Palladium bacterial cellulose membranes for fuel cells. *Biosens Bioelectron* 18:917–923
- Fernández-García M, Rodríguez JA (2007) Metal oxide nanoparticles, nanomaterials: inorganic and bioinorganic perspectives doi: [10.1002/9781119951438.eibc0331](https://doi.org/10.1002/9781119951438.eibc0331). (Encyclopedia of Inorganic and Bioinorganic Chemistry)
- García ZF, Martínez E, Castillo AA, Castano VM (1995) Numerical analysis of the experimental mechanical properties in polyester resins reinforced with natural fibers. *J Reinf Plast Compos* 14:641–649
- Ghosh SN, Maiti S (1998) Adhesive performance, flammability evaluation and biodegradation study of plant polymer blends. *Eur Polym J* 34:849–854
- Giudice CA, Pereyra AM (2007) Fire resistance of wood impregnated with soluble alkaline silicates. *Res Lett* 2007:1–4
- Guhados G, Wan WK, Hutter JL (2005) Measurement of the elastic modulus of single cellulose fibers using atomic force microscopy. *Langmuir* 21:6642–6646
- Habibi Y, Lucia LA, Rojas OJ (2010) Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chem Rev* 110:3479–3500
- Hambir S, Bulakh N, Jog JP (2002) Polypropylene/clay nanocomposites: effect of compatibilizer on the thermal, crystallization and dynamic mechanical behavior. *Polym Eng Sci* 42:1800–1807
- Hartmann MH (1998) Biopolymers from renewable resources. In: Kaplan DL (ed) Springer, Berlin, Chapter 15, pp 367–411
- Haygreen JG, Bowyer JL (1982) Forest products and wood science: an Introduction, 1st edn. Iowa State University Press, Ames, Iowa
- Hazarika A, Maji TK (2014a) Properties of softwood polymer composites impregnated with nanoparticles and melamine formaldehyde furfuryl alcohol copolymer. *Polym Eng Sci* 54:1019–1029
- Hazarika A, Maji TK (2012) Effect of different crosslinkers on properties of melamine formaldehyde-furfuryl alcohol copolymer/montmorillonite impregnated softwood (*Ficus hispida*). *Polym Eng Sci* 53:1394–1404
- Hazarika A, Maji TK (2013a) Study on the properties of wood polymer nanocomposites based on melamine formaldehyde-furfuryl alcohol copolymer and modified clay. *J Wood Chem Technol* 33:103–124
- Hazarika A, Maji TK (2013b) Synergistic effect of nano- TiO_2 and nanoclay on the ultraviolet degradation and physical properties of wood polymer nanocomposites. *Ind Eng Chem Res* 52:13536–13546
- Hazarika A, Maji TK (2014b) Properties of softwood polymer composites impregnated with nanoparticles and melamine formaldehyde furfuryl alcohol copolymer. *Polym Eng Sci* 54:1019–1029

- Hazarika A, Maji TK (2014c) Strain sensing behavior and dynamic mechanical properties of carbon nanotubes/nanoclay reinforced wood polymer nanocomposite. *Chem Eng J* 247:33–41
- Hazarika A, Maji TK (2014d) Thermal decomposition kinetics, flammability, and mechanical property study of wood polymer nanocomposite. *J Therm Anal Calorim* 115:1679–1691
- Hazarika A, Mandal M, Maji TK (2014) Dynamic mechanical analysis, biodegradability and thermal stability of wood polymer nanocomposites. *Compos Part B* 60:568–576
- Hetzer M, Kee D (2008) Wood/polymer/nanoclay composites, environmentally friendly sustainable technology: a review. *Chem Eng Res Des* 86:1083–1093
- Hill CAS, Abdul KHPS, Hale MD (1998) A study of the potential of acetylation to improve the properties of plant fibres. *Ind Crops Prod* 8:53–63
- Hoffmann MR, Martin ST, Choi WY, Bahnemann W (1995) Environmental application of semiconductor photocatalysis. *Chem Rev* 95:69–96
- Huda MS, Drzal LT, Misra M, Mohanty AK (2006) Wood-fiber-reinforced poly(lactic acid) composites: evaluation of the physicomechanical and morphological properties. *J Appl Polym Sci* 102:4856–4869
- Huda MS, Mohanty AK, Misra M, Drzal LT, Schut EJ (2005) Green composites from recycled cellulose and poly(lactic acid): physico-mechanical and morphological properties evaluation. *Mater Sci* 40:4221–4229
- Hussain F, Hojjati M, Okamoto M, Gorga RE (2006) Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. *J Compos Mater* 40:1511–1575
- Jana T, Roy BC, Maiti S (2000) Biodegradable film modification of the biodegradable film for fire retardancy. *Polym Degrad Stab* 69:79–82
- Jimenez M, Duquesne S, Bourbigot S (2006) Intumescent fire protective coating: toward a better understanding of their mechanism of action. *Thermochim Acta* 449:16–26
- John MJ, Thomas S (2008) Biofibres and biocomposites. *Carbohydr Polym* 71:343–364
- Johnson MR, Tucker N, Barnes S (2003) Impact performance of miscanthus/ novamont mater bi biocomposites. *Polym Test* 22:209–215
- Juntaro J, Pommet M, Kalinka G, Mantalaris A, Shaffer MSP, Bismarck A (2008) Creating hierarchical structures in renewable composites by attaching bacterial cellulose onto sisal fibers. *Adv Mater* 20:3122–3126
- Karak N (2006) Polymer (epoxy) clay nanocomposites. *J Polym Mater* 23:1–20
- Khanna S, Srivastava AK (2007) Production of poly (3-hydroxybutyric-co-3-hydroxyvaleric acid) having a high hydroxyvalerate content with valeric acid feeding. *J Ind Microbiol Biot* 34:457–461
- Klemm D, Schumann D, Kramer F, Hesler N, Koth D, Sultanova B (2009) Nanocellulose materials—different cellulose, different functionality. *Macromol Symp* 280:60–71
- Lande S, Høibø OA, Larnøy E (2010) Variation in treatability of Scots pine (*Pinussylvestris*) by the chemical modification agent furfuryl alcohol dissolved in water. *Wood Sci Technol* 44:105–118
- Lande S, Westin M, Schneider M (2004a) Chemistry and ecotoxicology of furfurylated wood. *Scand J For Res* 19:14–21
- Lande S, Westin M, Schneider M (2004b) Properties of furfurylated wood. *Scand J For Res* 19:22–30
- Lande S, Westin M, Schneider MH (2003) Development of modified wood products based on furan chemistry. *Mol Cryst Liq Cryst* 484:367–378
- Lavoine N, Desloges I, Dufresne A, Bras J (2012a) Microfibrillated cellulose—its barrier properties and applications in cellulosic materials: a review. *Carbohydr Polym* 90:735–764
- Lavoine N, Desloges I, Dufresne A, Bras J (2012b) Microfibrillated cellulose—its barrier properties and applications in cellulosic materials: a review. *Carbohydr Polym* 90:735–764
- Leszczynska A, Njuguna J, Pielichowski K, Banerjee JR (2007) Polymer/montmorillonitenanocomposites with improved thermal properties. Part II. Thermal stability of montmorillonite nanocomposites based on different polymeric matrixes. *Thermochim Acta* 454:1–22

- Li B, He JM (2004) Investigation of mechanical property, flame retardancy and thermal degradation of LLDPE–wood-fibre composites. *Polym Degrad Stab* 83:241–246
- Li Y, Liu Z, Dong X, Fu Y, Liu Y (2013) Comparison of decay resistance of wood and wood-polymer composite prepared by in-situ polymerization of monomers. *Int Biodeter Biodegr* 84:401–406
- Liang F, Wang Y, Sun XS (1999) Green composites using cross-linked soy flour and flax yarns. *J Polym Eng* 19:383–393
- Liu R, Cao J, Luo S, Wang X (2013) Effects of two types of clay on physical and mechanical properties of poly(lactic acid)/wood flour composites at various wood flour contents. *J Appl Polym Sci* 127:2566–2573
- Malmstrom E, Carlmark A (2012) Controlled grafting of cellulose fibres—an outlook beyond paper and cardboard. *Polym Chem* 3:727–733
- Martínez-Hernández AL, Velasco-Santos C (2012) Keratin fibers from chicken feathers: structure and advances in polymer composites. Nova Publishers, New York, pp 149–211
- Martínez-Hernández AL, Velasco-Santos C, de-Icaza M, Castaño VM (2007) Dynamical-mechanical and thermal analysis of polymeric composites reinforced with keratin biofibers from chicken feathers. *Compos Part B Eng* 38:405–410
- Mathew AP, Dufresne A (2002) Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. *Biomacromolecules* 3:609–617
- Md. Islama S, Hamdana S, Talibb ZA, Ahmeda AS, Md. Rahmana R (2012) Tropical wood polymer nanocomposite (WPNC): The impact of nanoclay on dynamic mechanical thermal properties. *Compos Sci Technol* 72:1995–2001
- Meng QK, Hetzer M, De Kee D (2011a) PLA/clay/wood nanocomposites: nanoclay effects on mechanical and thermal properties. *J Compos Mater* 45:1145–1158
- Meng QK, Hetzer M, Kee DD (2011b) PLA/clay/wood nanocomposites: nanoclay effects on mechanical and thermal properties. *J Compos Mater* 45:1145–1158
- Misra SK, Valappil SP, Roy I, Boccaccini AR (2006) Polyhydroxyalkanoate (PHA)/inorganic phase composites for tissue engineering applications. *Biomacromolecules* 7:2249–2258
- Mohanty AK, Misra M, Drzal LT (2002) Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. *J Polym Environ* 10:19–26
- Mohanty AK, Misra M, Hinrichsen G (2000) Biofibres, biodegradable polymers and biocomposites: an overview. *Macromol Mater Eng* 276–277:1–24
- Nakagaito AN, Yano H (2004) The effect of morphological changes from pulp fiber towards nanoscale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites. *Appl Phys A* 78:547–552
- Nogi M, Yano H (2008) Transparent nanocomposites based on cellulose produced by bacteria offer potential innovation in the electronics device industry. *Adv Mater* 20:1849–1852
- Oksman K, Skrifvars M, Selin JF (2003) Natural fibres as reinforcement in polylactic acid (PLA) composites. *Compos Sci Technol* 63:1317–1324
- Pandey JK, Kumar AP, Misra M, Mohanty AK, Drzal LT, Singh RP (2005) Recent advances in biodegradable nanocomposites. *J Nanosci Nanotechnol* 5:497–526
- Panshin AJ, de Zeeuw C (1980) Textbook of wood technology: structure, identification, uses, and properties of the commercial woods of the United States, 4th edn. McGraw Hill Inc., New York
- Paul DR, Robeson LM (2008) Polymer nanotechnology: nanocomposites. *Polymer* 49:3187–3204
- Raberg U, Hafren J (2008) Biodegradation and appearance of plastic treated solid wood. *Int Biodeterior Biodegrad* 62:210–213
- Raj RG, Kokta BV, Maldas D, Daneault C (1989) Use of wood fibers in thermoplastics. VII the effect of coupling agents in polyethylene-wood fiber composites. *J Appl Polym Sci* 37:1089–1103
- Rowell RM, Young RA, Rowell JK (1997) Paper and composites from agro-based resources. CRC Lewis Publishers, Boca Raton FL
- Roy D, Semsarilar M, Guthrie JT, Perrier S (2009) Cellulose modification by polymer grafting: a review. *Chem Soc Rev* 38:2046–2064

- Sain M, Park HS, Suhara F, law S (2004) Flame retardant and mechanical properties of natural fibre-PP composites containing magnesium hydroxide. *Polym Degrad Stab* 83:363–364
- Saito R, Dresselhaus G, Dresselhaus MS (1998) Physical properties of carbon nanotubes. Imperial College Press, London
- Sakurada I, Nukushina Y, Ito T (1962) Experimental determination of the elastic modulus of crystalline regions in oriented polymers. *J Polym Sci* 57:651–659
- Santayanon R, Wootthikanokkhan J (2003) Modification of cassava starch by using propionic anhydride and properties of the starch-blended polyester polyurethane. *Carbohydr Polym* 51:17–24
- Schneider MH (1995) New cell wall and cell lumen wood polymer composites. *Wood Sci Technol* 29:135–158
- Scott G (2000) Green- polymers. *Polym Degrad Stab* 68:1–7
- Sengupta R, Chakraborty S, Bandyopadhyay S, Dasgupta S, Mukhopadhyay R, Auddy K, Deuri AS (2001) A short review on rubber/clay nanocomposites with emphasis on mechanical properties. *Polym Eng Sci* 47:1956
- Siro I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose* 17:459–494
- Sjostrom E (1993) Wood chemistry: fundamentals and applications, 2nd edn. Academic Press, New York
- Agustin MB, Ahmmad B, Leon ERPD, Buenaobra JL, Salazar JR, Hirose F (2013) Starch-based biocomposite films reinforced with cellulose nanocrystals from garlic stalks. *Polym Compos* 34:1325–1332
- Suda K, Kanlaya M, Manit S (2002) Synthesis and property characterization of cassava starch grafted poly[acrylamide-co-(maleic acid)] superabsorbent via- γ irradiation. *Polymer* 43:3915–3924
- Tábi T, Kovács JG (2007) Examination of injection molded thermoplastic maize starch. *Express Polym Lett* 1:804–809
- Tizzotti M, Charlot A, Fleury E, Stenzel M, Bernard J (2010) Modification of polysaccharides through controlled/living radical polymerization grafting-towards the generation of high performance hybrids. *Macromol Rapid Commun* 31:1751–1772
- Valappil SP, Misra SK, Boccaccini AR, Roy I (2006) *Expert Rev Med Devices* 3:853–868
- Vink ETH, Rabago KR, Glassner DA, Gruber PR (2003) Applications of life cycle assessment to nature works polylactide (PLA) production. *Polym Degrad Stab* 80:403–419
- Vollenberg PHT, Heiken D (1989) Particle size dependence of the Young's modulus of filled polymers: 1 Preliminary experiments. *Polymer* 30:1656–1662
- Watanabe M, Sakurai M, Maeda M (2009) Preparation of ammonium polyphosphate and its application to flame retardant. *Phosphorus Res Bull* 23:35–44
- Wegner T, Skog KE, Ince PJ, Michler CJ (2010) Uses and desirable properties of wood in the 21st Century. *J Forest* 108:165–173
- Weil ED, Levchik SV, Ravey M, Zhu W (1999) A Survey of recent progress in phosphorus-based flame retardants and some mode of action studies. *Phosphorus, sulfur, Silicon Relat Elem* 144:17–20
- Wool RP, Khot SN, Lascala JJ, Bunker SP, Lu J, Thielemans W (2002) Affordable composites and plastics from renewable resources Part II: Manufacture of composites. *Advancing sustainability through green chemistry and engineering. ACS Symp Ser* 823:205–224
- Xie F, Pollet E, Halleja PJ, Avérous L (2013) Starch-based nano-biocomposites. *Prog Polym Sci* 38:1590–1628
- Xie Y, Hill CAS, Xiao Z, Mai C, Militz H (2011) Dynamic water vapor sorption properties of wood treated with glutaraldehyde. *Wood Sci Technol* 45:49–61
- Yang KK, Wang XL, Wang YZ (2007) Progress in nanocomposite of biodegradable polymer. *J Ind Eng Chem* 13:485–500
- Yanga HS, Kimb HJ, Parkc HJ, Leed BJ, Hwang TS (2007) Effect of compatibilizing agents on rice-husk flour reinforced polypropylene composites. *Compos Struct* 77:45–55