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REVIEW PAPER

Modification of Softwood by Monomers and Nanofillers

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ABSTRACT

Technological development of wood polymer composites (WPC) is a very promising approach to overcome most of the disadvantageous properties of wood products, for example their poor mechanical strength, poor dimensional stability, susceptibility to fungal attack, weathering and the like. To find the substitute for costly items of hard wood, suitable technologies have been developed to modify softwood to meet specific end-use requirements. Various vinyl monomers and/or copolymers or thermosetting resin in combination with different types of cross linking agents, flame retarding agents have been used to improve the properties of wood. Nanotechnology is a new area of science and technology which opens up new opportunities to develop wood based products with desired properties. Now-a-days government is making strict legislations to promote green technology for the protection of environment worldwide. With the depletion of petroleum resources at alarming rate, it is high time to replace petroleum-based products by some sustainable alternative products based on vegetable biomass. The bio-based resins obtained from renewable feedstock have been widely utilized by taking the advantages of easy availability, renewable nature and low cost. The green route of modification of wood is widely encouraged. With the progress of technological development, now it is possible to avoid the hazardous influence of organic solvents by using water as solvent or diluents for modification of wood. WPC has got tremendous scope for use in diverse areas of applications.

Keywords: Nanocomposites, green technology, wood, renewable resource, environment, characterization of properties

1. INTRODUCTION

Wood is a unique and renewable resource material that has been an important substance since time immemorial of human civilization because of its easy availability unique aesthetic look and useful properties[1]. It can be reaped sustainably at a constant rate without depleting the existing resource pool. Because of the influence of increasing human activities on the environment, awareness of the society on the environment is rapidly increasing, thus environmental considerations have given due attention to effect a change in the way of utilization of materials for various purposes. Thus, chemical industries are seeking to manufacture products with minimal environmental impact. Scientists have been working to improve the utilization of raw material, reduce production inefficiencies and develop more sustainable industrial practices. The widespread occurrence, stability, hardness, lightness, elasticity and as perspective potential renewable material make wood an important raw material sources[2]. Natural look and versatility make wood a class of material for various purposes of applications. It has wide range of applications to make items like paper, pulp, construction of materials and as resource material for energy generation[3].

Wood is a natural polymeric composite consisting of cellulose, hemicelluloses and phenolic polymers of lignin. The cellulose is a polymer of D-glucopyranose units linked together by β(1→4) glycosidic bonds. Hemicelluloses are heteropolysaccharides having a lower degree of polymerization (DP) than cellulose of about 100-300. Cellulose is more ordered than hemicellulose, although some hemicellulose can form crystalline units. Water present in atmospheric moisture can easily form hydrogen bonding with the free hydroxyl groups in cellulose resulting in shrinking and swelling of wood depending upon its moisture content. Lignins have the least water sorption tendency and are amorphous, highly complex, mainly aromatic, polymers of phenylpropane units[4]. Lignin is associated with hemicelluloses through covalent bond forming lignin-carbohydrate complexes but there is no evidence of their association with cellulose. Thus, the hydroxyl groups present in the cell wall of wood are the most abundant reactive and vulnerable chemical site[3].

Mechanical anisotropy arises in wood due to its highly heterogeneous structure. Among the numerous applications, the utilization of wood in particular for flooring and hard wearing wood surfaces preferably need an improvement of strength and elasticity in the direction normal to the grain. Hence strength in lateral direction is most desirable. The success of trees as

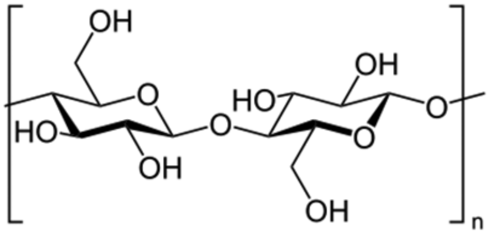

Figure 1. Chemical structure of cellulose.

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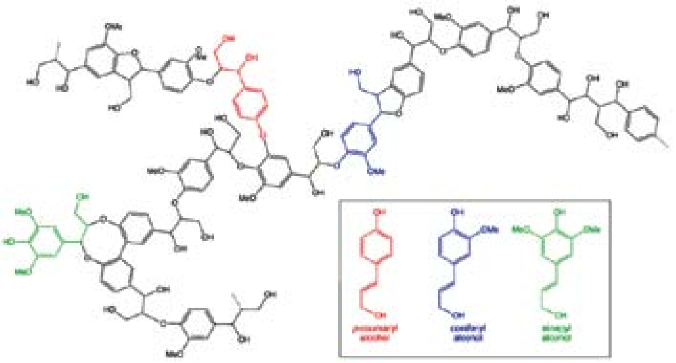

Figure 2. Chemical structure of lignin comprising about 30% of wood which determines its properties.

a dominant form of land vegetation has depended on their being able to maintain a perennating woody structure, which helps them to attain both height and longevity. This defensive strategy protects the woody cylinder against loss of integrity of both its water-conductivity and mechanical properties. Instability under changing moisture regimes is considered a major disadvantage of wood compared to other materials.

Two types of woods are available such as hard wood and soft wood. Hard woods are used for construction purposes. Soft woods are lacking in strength and mainly used for fuel purposes or often remain unutilized as a bio-waste. These soft woods can be made value added by making composites with polymers.

The sapwood of most of wood species has a low durability. Fungi may cause the biological decay in wood. The molecular structure of the cell wall components of wood can be changed on modification with suitable chemicals[5]. The conversion of hydrophilic OH-groups of wood into hydrophobic groups leads to modification to bring about improvement in properties. On such modification, the cell wall can no longer attract water molecules further, thus forming dimensionally stable material. The specific enzyme systems of degrading fungi cannot use the treated wood as a nutrient medium and no longer help in decay[6]. The modified wood is a replacement for preservative treated wood or high cost tropical hardwood species which brings new applications of wood within the reach.

Wood is a porous structure due to which it can accommodate nanounits and nanotubes. Nano science and technology has opened up a completely new way of modification of wood to obtain better properties[7]. The intercalation of nanoparticles and nanotubes along with the polymers has been widely studied[8,9]. Wood coupled with nanoparticles on a nano-scale level may significantly improve the quality of wood and can offer wood products with new functional opportunity for utilization.

2. FORMATION OF WOOD POLYMER COMPOSITES

The combination of two or more identifiable materials existing in a product to deliver desired properties is generally considered as a composite material. Nanocomposite in a broad sense, is considered as a system[10] comprising two or more constituent materials in which each constituent material not only has significantly different physical or chemical properties but they also remain distinctly separated in the system where at least one of them must remain in its nanoscopic level[10,11]. A new class of wood products has been developed with considerably improved chemical, mechanical, physical and biological properties due to the progress in the field of polymer science and technology. In many areas of industrial applications, modified wood has substituted the costly metals and alloys for large-scale applications as they generally require less maintenance, offer uniform finish and has aesthetic superiority with the overall enhancement of their characteristics[12] in general. The combination of wood with polymer is called wood polymer composite (WPC) which can be solid pieces of wood filled with polymer or polymer filled with wood fiber. The impregnation technique is one of the most advantageous approaches for modification of wood by means of vinyl monomers or desired polymers and or thermosetting resin[13-15]. All the desirable mechanical properties and water repellency can be achieved to a large extent through this technique[13]. In this technique, suitable liquid monomer or prepolymer are used to fill the cell lumens of wood under vacuum or high pressure, which is subsequently polymerized. The resulting wood-polymer composite normally retains most of the desirable characteristics of wood. Hence water or microorganisms cannot easily attack the wood matrix after modification. Such multifunctional treatment can strengthen the wood and avoids the potential disadvantages of the other modification processes. Heat flow into and out of the wood-monomer is prohibited as wood is an insulating material due to its cellular structure but once the reaction is started, the temperature of the system comprising wood, monomer, polymer composite WPC increases rapidly[16].

3. POLYMER MATRICES USED IN WOOD MODIFICATION

A permanent change in the polymeric chemical composition of wood occurs due to modification caused by the action of the chemical, biological and or physical agents generally resulting enhancement in the properties. A suitable selection of chemicals is an important criterion for the process of impregnation into wood. The modified wood should not release any toxic substances during service, should be non-toxic under service conditions and can be disposed of or can be recycled at end of service life. The diffusion and permeability of the gas or liquid are the two main dependable criteria for the impregnation process into the wood. The water and air present in the empty spaces of wood must be removed before impregnation to accomodate the treating fluid. The liquid monomer or prepolymer should be of low or medium viscosity and can be forced into wood using vacuum or pressure. The wood hardening method by this technique has been developed in mid-1960's and is being applied to both lumber and veneer wood[17].

3.1 Thermoplastic Monomers used for Impregnation into Wood

Ethylene oxide, styrene, vinyl acetate, t-butyl styrene, vinyl chloride, chlorostyrene and many of the acrylates especially methyl methacrylate, acrylonitrile etc. are some of the common vinyl monomers widely used in preparation of WPC. The monomers initially have low viscosity which enables them to enter into the pores of wood structure. But upon polymerization, the derived products remained inside the wood texture. The void spaces, capillaries and vessels in the wood structure are simply filled up by the vinyl polymers on impregnation[18] process. As the monomers are simply confined in the cell lumen instead of the cell wall, the impregnation of wood with acrylic or vinyl type monomer shows less dimensional stability[19].

3.2 Thermosetting Monomer used for Impregnation into Wood

The dimensional stability of wood can be improved considerably by the use of thermosetting resin. Water soluble thermoset resins can diffuse into the porous structure of wood, resulting in swelling and bulking of the cellwall of wood[12]. After that, the impregnated wood is heated at curing temperature of the resin. The various thermosetting resins used for impregnation into wood are phenol formaldehyde, urea formaldehyde, melamine formaldehyde and melamine-urea-formaldehyde resin[20-22,]. Bryant has studied the influence of phenolic resin impregnation on the dimensional stabilization and mechanical properties of wood[23].

Wood impregnated with water-soluble melamine formaldehyde (MF) resin can significantly improved the surface hardness and modulus of elasticity (MOE)[24,25]. When the concentration of MF resin is increased in wood, the resistance to weathering is improved, and color changes due to UV-irradiation is also diminished[24,26].

3.3 Bio-derived Polymer used for Wood Modification

Most of the treatments adopted for preservation of wood are not only toxic for human health but also detrimental towards the environment. The rising concern for environment has led to the advancement of new polymers that are obtained from renewable resources and are easily degradable. Biological sources such as plants or vegetable oil are the main source for derivation of bio-based resin instead of petrochemicals. Renewability, declining the reliance on the limited resources of petrochemicals and low environmental impact are the major advantages of these polymers. These polymers are water soluble and hence the harmful effect of solvent can be removed by employing water as a solvent.

Several bio-based thermoset resins such as polyfurfuryl alcohol, starch, polylactic acid, polyhydroxyalkanoates and soya flour have been developed[27-29,]. Polylactic acid (PLA) is one of the most processed polymers which is produced from polycondensation of lactic acid. Lactic acid possesses carboxylic end groups which are capable of reacting with the hydroxyl groups of solid wood cell walls. Hence grafting of lactic acid oligomers and polymerization occur onto the wood structure. Wood polymer composites prepared from wood and PLA biopolymers have been regarded as an innovative biocomposite possessing remarkable physical and mechanical properties[30].

Furfuryl alcohol, is another bio-derived monomer that is produced from the hemicellulosic part of agricultural wastes, results in the formation of composites with wood having high durability, improved dimensional stability and increased hardness[31]. Furfuryl alcohol polymerizes *in situ* and permanently swells the cell walls[32]. Wood modification through furfurylation is an environmental friendly method and the degradation of the furfurylated wood by combustion do not generate any volatile organic compounds[33]. Wood impregnated with melamine formaldehyde-furfuryl alcohol (MFFA) copolymer in presence of different crosslinking agents and montmorillonite (MMT) shows a remarkable improvement in dimensional stability, chemical resistance, and mechanical properties of the composites[34].

Starch is one of the most outstanding raw materials which is produced from a great variety of crops and is a natural renewable polysaccharide. It is of lower cost as compared to other synthetic plastics and is readily available. Though starch is not a true thermoplastic, but it readily melts at high temperatures and under shear in the presence of plasticizers like glycerol, water and other polyols or polyesters behaves similar to other thermoplastic polymers[29]. The main drawbacks of starch-based materials are that they have limited long-term stability due to water absorption, poor mechanical properties and bad processability[35]. In order to minimize the disadvantages, starch is grafted with other thermoplastic polymers.

4. CROSSLINKING AGENTS

The bonding or crosslinking between the polymer chains and wood can be enhanced by the use of crosslinking agents, so that the resultant polymer remains in a 3D network inside the pores of wood. The dimensional stability, mechanical properties, chemical resistance, impact strength of WPCs can significantly be improved by the use of crosslinkers[34]. These are used in small quantities to treat two incompatible surfaces, e.g., wood and polymer[36]. They occupy a notable role in improving the compatibility, affinity, and adhesion between wood cell walls and polymers in wood cell lumen. The crosslinking agents are of different types which include organic, inorganic, and organic-inorganic groups[37]. Isocyanates, anhydrides, silanes, epoxides, β-propiolactone, and methacrylates are some of the examples of the most successful crosslinking agents that are generally used. Maleic anhydride (MAN) and glycidyl methacrylate (GMA) are some of the efficient crosslinking agents that are extensively used in traditional wood polymer composites to form bond between wood and polymers[38,39].

GMA is a bifunctional compound that has both double bond and epoxy group. The hydroxyl, amino and carbonyl groups can react with the glycidyl group of GMA[40]. The glycidyl group and terminal double bond in GMA can be exploited for the reaction with hydroxyl group of wood cellulose and for co-polymerization with vinyl or acrylic monomers respectively.

N-methylol compounds, such as dimethyloldihydroxy-ethyleneurea (DMDHEU), are an important multifunctional crosslinking agent and are mostly used in cotton fabrics industry. They are expected to enhance the resistance of wood to weathering because they can cross-link the cell wall and dimensionally stabilize the wood. The WPC has shown a significant improvement in mechanical properties and reduction in water uptake capacity[41]. N-methylol acrylamide (NMA) is a bifunctional crosslinking agent where both hydroxyl group and vinyl groups are present. NMA can serve as an effective coupling agent and improve strength and as well as water resistance of the resulting composites[42].

5. FLAME RETARDING AGENTS

Fire resistance of wood-polymer composites can be improved by the incorporation of additives called flame retarding (FR) agents. They are often mixed with the impregnating monomers before impregnation or applied to pretreated wood. Some common examples of FR agents include alumina trihydrate ($Al(OH)_3$), boric acid (H_3BO_3), silicone dioxide (SiO_2), magnesium oxide (MgO), tributyl phosphate, alkenyl esters of phosphorus acids and borax ($Na_2B_4O_7$)[43,44]. The thermal decomposition and degradation of wood is prevented on addition of magnesium oxide and boron compounds during high-temperature processing of the composite[37]. Most of the FR agents release toxic fumes and gases on combustion. These gases are highly detrimental to health and pollute the environment. The leaching problem of FR agents from the composite materials can be reduced by the use of polymeric flame retarding agent because they have high molecular weight and thus, enhanced the service life of the polymer product. The utilization of FR polymer of renewable source is advantageous from environmental point of view. An improvement in flame retardancy and biodegradability of starch based biodegradable film modified with gum derived from *Moringa oleifera* has been reported by Jana[45], *et al.* Wood samples treated with the gum obtained from the plant can have remarkable impact on flame retardancy, thermal stability and other physical properties[46].

6. DIFFERENT NANOFILLERS USED IN THE PREPARATION OF WPC

The essence of nanotechnology is the ability to work at molecular level to create large structures with fundamentally new molecular organization. Nano technology offers an attractive technique to prepare WPC product using layered silicate clay and metal oxide nanofillers. All the desired properties of the composites may be improved simultaneously. Applications of nanotechnology to modify wood have been executed in recent years, for the conservation and restoration of the world's cultural heritage.

6.1 Montmorillonite

Montmorillonite belongs to the structural family known as the 2:1 phyllosilicates. When clay is modified organically it becomes well-suited with the organic polymers and its surface energy is lowered. Under well defined experimental conditions, the gallery layers of clay can be expanded and the polymer chains are able to penetrate within these silicate layers. The addition of nanoclay in WPC significantly influences wood properties, including mechanical, thermal, dynamic mechanical behavior, and the biodegradability[47].

6.2 ZnO Nanoparticles

ZnO is commonly used for protection against ultra-violet radiation and therefore it finds application generally in cosmetic industry. It is considered as an ideal UV blocker[48] Inorganic UV absorbers possess many advantages compared to organic absorber which includes higher thermal stability, nontoxicity, chemical stability and non-irritant nature. Similar to other nanoparticles, dispersion of ZnO nanoparticles in organic solvent and polymer matrices results in agglomeration of particles because of their high surface energy[49,50]. Laachachi and co-workers[51] have reported the increased thermal properties of PMMA by incorporation of ZnO and organo-montmorillonite. WPC treated with nanoclay and ZnO can enhance mechanical properties, thermal stability, water repellency, UV resistance properties of the composites[52].

6.3 SiO_2 Nanoparticles

SiO_2 nanopowder is one of the most extensively used nanofillers in the field of polymer composite. SiO_2 nanoparticles is widely used in industries for various purposes, such as thermal insulators, humidity sensors, pharmacy, pigments, catalysis, electronic and thin film substrates. It has attracted the attention of the researchers in recent times due to their easy preparation[53]. SiO_2 is reported to enhance the mechanical as well as thermal properties of the composite. SiO_2 nanoparticles also impart an increase in tensile and impact strength of epoxy nanocomposite[54]. Nano-SiO_2 abates its free formaldehyde emission and improves the bonding strength of UF adhesive as reported in literature[55]. Wood modified with nano-SiO_2 in combination with different polymers and crosslinkers can enhance the mechanical properties, water repellency and other properties[56].

6.4 TiO_2 Nanoparticles

TiO_2 has received wide acceptance due to some of the advantageous properties like chemical inertness, high refractive index, strong oxidizing power of the photogenerated holes, low cost and non-toxicity. Titanium dioxide (TiO_2) has been recognized as the most excellent photocatalyst for the degradation of many organic pollutants in water and air[57]. Since reactions take place on the surface of nanosized TiO_2 powder, it has a large specific surface area, and good photocatalytic activities. Wood impregnated with polymer and TiO_2 can substantially improve the UV resistance and other physical properties of the composites[46].

7. MODIFICATION OF NANOFILLERS

Surface grafting of different nanofillers is an important task to retain homogenous dispersion of these nanoparticles in the polymer matrix. The nanoparticles have high surface energy and strong van der Waals' attraction between them. Therefore there is a strong tendency to agglomerate when they are dispersed in the polymer matrix. The surface modification stabilizes the nanoparticles and prevents agglomeration. The most common method is incorporation of suitable organic groups to the surface atoms. The uniform dispersion of the nanoparticles in the polymer matrix creates a strong interfacial interaction between the polymer and the nanoparticles that promotes to a considerable enhancement of the properties of the resultant materials. The modification can be done by ammonium or phosphonium salts which increases hydrophobicity of the nanoparticles. Maji and coworkers have successfully modified the surface of SiO_2 and ZnO nanoparticles by using N-cetyl-N,N,N trimethyl ammonium bromide (CTAB) and used along with high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), and polyvinyl chloride (PVC) for the preparation of wood polymer nanocomposites[58]. The hydrophobic groups can also be grafted on the surface of the nanoparticles through the reaction between silane coupling agents[59].

8. PREPARATION TECHNIQUE OF WOOD POLYMER NANOCOMPOSITES

Wood samples obtained from defect-free wood were cut and dried in an oven at 105 °C to constant weight and were then taken in an impregnation chamber. Vacuum was applied for a specific time period for removing the air from the pores of the wood samples before addition of the respective prepolymeric mixture (mixture of monomer or prepolymer, crosslinker, initiator, flame retardant, nanoparticles, etc.). The samples were kept immersed in the impregnation chamber for approximately 6 h after attaining atmospheric pressure. The samples were then wrapped in aluminium foil and cured at 90 °C for 24 h in an oven. The cured samples were Soxhlet extracted to remove homopolymers, if any, formed during impregnation. A flowchart diagram for the preparation of wood polymer nanocomposites (WPNC) is shown in Fig. 3.

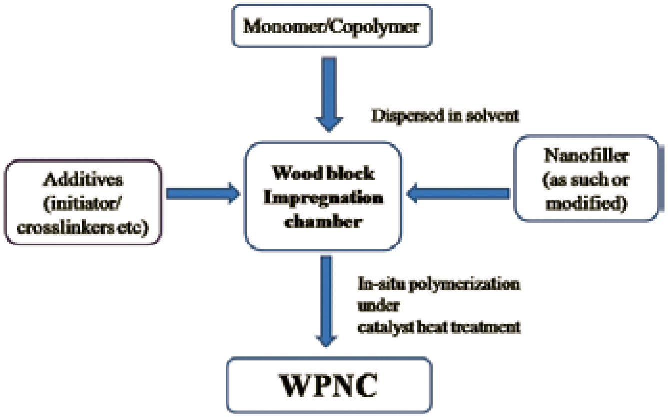

Figure 3. Flowchart diagram for preparation of WPNC.

9. CHARACTERIZATION OF WOOD POLYMER NANOCOMPOSITES

Structural characterization of wood polymer composites had been investigated by most of the researchers over the century. Devi, *et al.* prepared wood polymer nanocomposites by impregnation of intercalating mixture of styrene acrylonitrile co-polymer in combination with nanofillers like TiO_2, SiO_2 and nanoclay. The characterization of the composites was done by using Fourier Transform Infrared spectroscopy (FTIR) as well as X-Ray diffractometry (XRD). Both FTIR and XRD studies indicated an interaction between wood, polymer and different nanofillers[59]. The interaction of the hydroxyl group of wood cellulose with polymers and nanofillers was revealed from the decreased intensity of the -OH stretching peak as reported by Deka[60-62], *et al.* Fig. 4 shows the FTIR spectra of untreated wood (curve a) and wood polymer composites (curve b). A decrease in the intensity of the hydroxyl groups and shifting of the peak to lower wave number indicated the formation of the composites. Devi[14], *et al.* studied the interaction of rubber wood with styrene and glycidyl methacrylate (GMA) by FTIR technique.

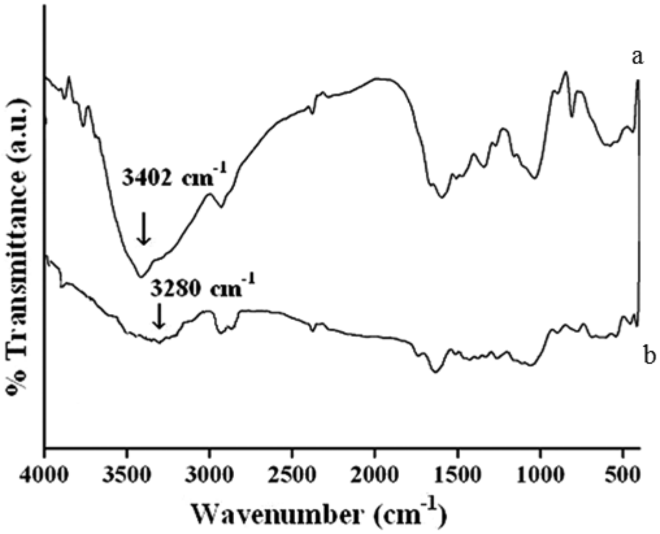

Figure 4. FTIR spectra of (a) untreated wood (b) wood treated with polymer/crosslinkers in the presence nanofillers.

A decrease in crystallinity of wood cellulose was observed on formation of wood polymer nanocomposites as revealed by XRD studies[7]. Untreated wood showed a wide diffraction peak at 22.96°, 37.68° and 15.02° due to the (002) crystal plane, 040 crystal plane and amorphous region of cellulose respectively. Maji and coworkers reported that the intensity of the crystalline peak appeared at 22.96° for MFFA/DMDHEU/ nanoclay treated wood decreased and other peaks became dull (Fig. 5). The disappearance of diffraction peak of nanoclay in the composites indicated that either the nanoclay layers had been delaminated or the XRD study was not able to detect the clay layers[63].

The fine structures of wood polymer composites were investigated by scanning electron microscopy (SEM) as shown in Fig. 6. The void spaces of wood (Fig. 6(a) were filled up on impregnation with polymers (Fig. 6(b). The addition of crosslinkers enhanced the deposition of polymers into the empty pits and capillaries (Fig. 6(c). The presence of nanofillers in the composites could be detected in the form of some white patches as shown in the micrograph (Fig. 6(d). A SEM study of fig wood impregnated with PMMA, GMA and MMT inferred that the presence of GMA as crosslinking agent increased the deposition of polymer into the void spaces of wood. Further the presence of MMT could be detected as some white patches in the micrograph[64]. Wood polymer nanocomposite (WPNC) was prepared by impregnation of styrene-acrylonitrile copolymer (SAN), vinyl trichlorosilane (VTCS) modified ZnO nanoparticles and glycidyl methacrylate (GMA) as a crosslinking agent into cellular structure of wood. SEM study showed the presence of polymer, nano ZnO in empty cell wall and capillaries of wood[65].

The presence of nanofillers in the composites could be

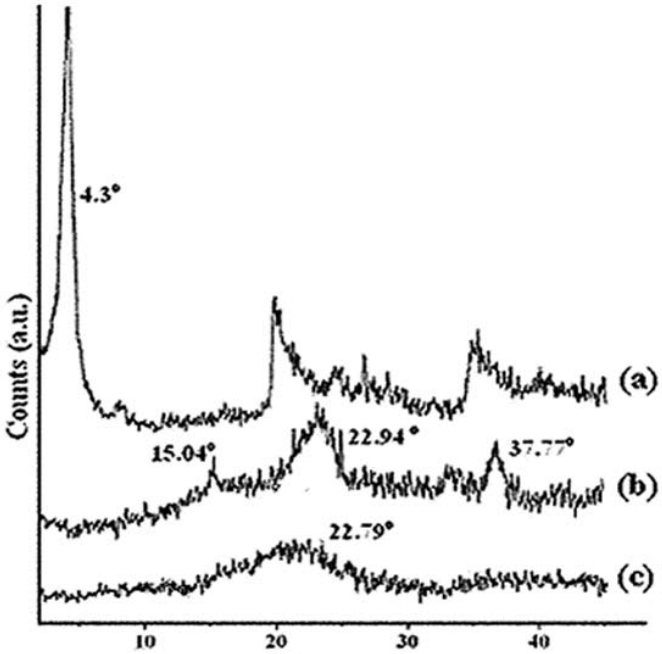

Figure 5. XRD micrograph of (a) nanoclay (b) untreated wood (c) wood treated with MFFA/DMDHEU/nanoclay.

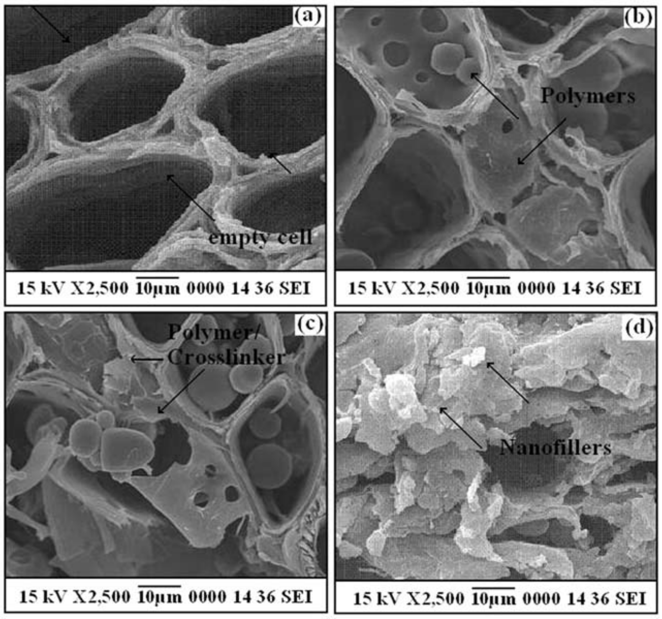

Figure 6. Scanning electron micrograph of (a) untreated wood samples and wood treated with (b) PMMA (c) PMMA/GMA (d) PMMA/GMA/MMT.

investigated by transmission electron microscopy (TEM). The presence of clay and metal oxide nanoparticles could be seen in the form of some dark slices and dark spots in the micrograph as shown in Fig. 7.

Uniform distribution of ZnO nanoparticles was observed in the micrograph when WPNC was prepared by impregnation of styrene-acrylonitrile copolymer (SAN), vinyl trichlorosilane (VTCS) modified ZnO nanoparticles and glycidyl methacrylate (GMA)[65].

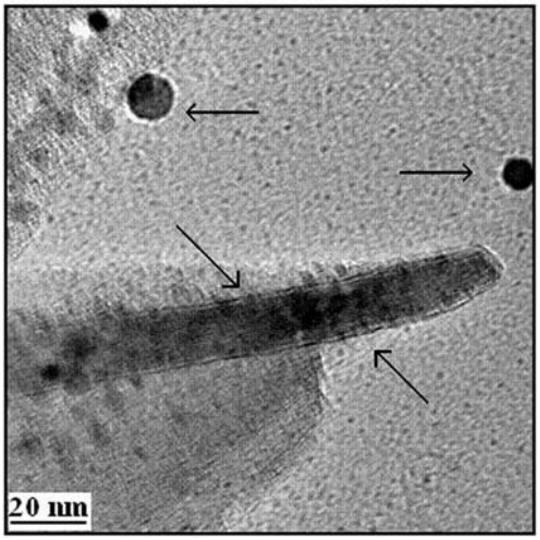

Figure 7. TEM micrograph of wood sample treated with clay and metal oxide nanoparticles.

10. PROPERTIES OF WOOD POLYMER NANOCOMPOSITES

10.1 Mechanical Properties

Different types of wood were impregnated with a polymer mixture containing a macromonomer and styrene and showed an improvement in water repellency, compression and bending strength properties[66]. Bending strength in terms of Modulus of elasticity (MOE) and Modulus of rupture (MOR) was measured for wood impregnated with styrene and GMA. Treated wood showed an improvement in properties over the untreated wood samples. Hardness and dynamic mechanical properties also improved for treated wood[67]. Wood impregnated with melamine formaldehyde-furfuryl alcohol copolymer (MFFA), n-methylol acrylamide (NMA), a crosslinking agent, and organically modified montmorillonite (MMT) exhibited lower water uptake, higher dimensional stability, enhanced chemical resistance, thermostability, flame retardancy, and better mechanical properties compared to unmodified clay treated wood samples[42]. The impact of wood treatment on the dynamic mechanical properties had also been investigated. Both storage modulus and loss modulus of treated wood samples were found to increase compared to untreated samples[67]. The increase in properties was attributed to the improvement in interaction of wood with polymer, crosslinker and nanofillers. A shifting of the tan δ peak towards higher temperature was observed for the wood polymer composites treated with nanoclay. The tan δ peak for the untreated wood was observed at 70 °C and on addition of nanoclay the peak shifted to 130 °C as shown in Fig. 8. This was due to the restriction in the mobility of the polymer chains inserted in between the gallery layers of clay. Further the intensity of the peak got reduced for the treated wood samples[47].

10.2 Dimensional Stability

Dimensional instability of wood has been a blessing and curse to wood users for thousands of years. Wood impregnated with melamine formaldehyde−furfuryl alcohol copolymer,

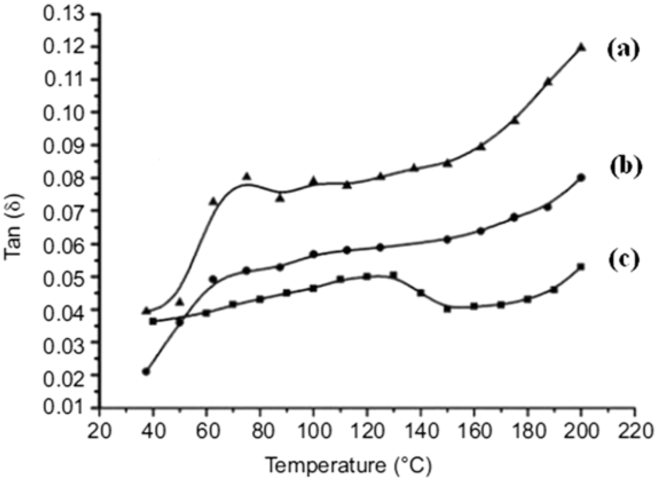

Figure 8. Tan δ values of (a) untreated wood and wood treated with (b) styrene-acrylonitrile (SAN) copolymer/GMA (c) SAN/GMA/nanoclay.

dimethylol dihydroxyethylene urea, a cross-linking agent, nanoclay, nano-TiO_2, and a renewable polymer obtained as a gum from the plant Moringa oleifera, improved significantly the dimensional stability, mechanical properties, flame retardancy, thermal stability and UV resistance properties[46]. Treatment of wood with nano SiO_2 and nanoclay along with polymers and different crosslinkers enhanced the dimensional stability and mechanical properties of the composites[68-70].

10.3 Thermal Stability and Flame Retardancy

Thermal stability and flame retardancy are one of the most covetable properties of WPNC to expand the scope of application of wood products. Rubber wood (Hevea brasiliensis) impregnated with styrene as the monomer in combination with diethyl allyl phosphate (DEAP) as flame-retardant, improved thermal stability, flame retardancy, water repellency and mechanical properties[71] etc. Flame retardancy could be achieved by the use of organohalogen, organophosphorus, organoantimony compounds, various silicates and borates compounds[72,73]. The use of polymeric flame retardant obtained from renewable resource might reduce the leaching problem and is eco-friendly. The gum obtained from the plant Moringa oleifera could be used as flame retardant that may substantially improve the flame retardancy and thermal stability of the composites. An enhancement in thermal stability and flame retardancy of the composites treated with MFFA copolymer, DMDHEU, nanoclay and plant polymer was observed as judged by increase in activation energy[63].

10.4 UV Resistance Properties

Discoloration, increase in surface roughness and reduction of gloss arises in wood due to loss of the aesthetic appearance of wood on exposure to UV radiation. Solar radiation, moisture, heat, atmospheric pollutants and micro-organisms are some of the factors that contribute to weathering of wood[74]. Rowell[75] found during artificial accelerated weathering test that wood treated with butylenes, methyl isocyanate or butylene oxide eroded to the same extent as untreated ones. Acetylation was reportedly reduce the weight loss of veneers during weathering compared to untreated controls. The protection, however, was restricted to cellulose[76] and lignin was hardly protected[14]. Acetylated wood exposed to accelerated weathering developed less cracks than similarly exposed untreated controls; however, greying of the surface was not reduced[78]. The UV resistance properties of wood treated with ZnO nanoparticles and polymers was reported to enhance after treatment[52,65]. Wood impregnated with MFFA copolymer, nanoclay, nano TiO_2 and plant polymer had a marked influence on the UV resistance properties and other physical properties[46]. After a period of 60 days of UV exposure, the loss in flexural strength was 15.53 per cent for untreated wood samples whereas it was 1.96 per cent for the wood samples treated with MFFA/DMDHEU/nanoclay/TiO_2 (3 phr)/plant polymer. Loss in tensile strength was found to be 23.25 per cent and 2.7 per cent for the untreated and treated wood samples. Similarly the loss in weight was also found to be higher for treated wood samples compared to untreated wood samples.

11. INDUSTRIAL APPLICATIONS

WPNC is unique composite material with the functions similar to that of timber, but they require less maintenance, and have much lower weight to strength ratio. It is composed of wood, polymer and additives in different proportions and is experiencing high growth rates globally. WPNC products can be successfully used in those areas where WPC products were already in use. WPNC products are appropriate for both indoor and outdoor utilizations. WPNC products can be applied in constructions, electronics, automotives, marine and aerospace. WPNC may replace fiberglass and steels, thus can be applied as a substitute for the automotive components which is the major market identified for the application of WPCs. Automakers are making continuous effort to enhance the recyclability of newly formed vehicles from the point of view of environmental protection. These products have already been effectively used in many areas including building industry, furniture industry, automotive industry, measurement engineering, etc. WPC has largely been used in flooring which includes top veneers of laminated flooring, solid plank flooring, and fillets for parquet flooring. As for sports equipment, patents have been issued for golf club heads, baseball bats, hockey sticks, and parts of laminated skis. WPCs are used for mouthpieces of flutes and trumpets, wind instruments, and finger boards of stringed instruments. One area with prospective application is the use of veneer laminates for furniture, such as desk writing surfaces and tabletops. A history of the commercialization of WPCs and future opportunities is covered by Schneider and Witt[15]. Some residential construction applications of WPCs, such as in windows, sidings, and roof tiles, are rapidly unveiling the market are currently being developed.

12. CONCLUSIONS AND FUTURE SCOPE

The low-quality wood which mainly remains as a bio-waste can be developed into value-added products through innovative technology. Modification of wood represents an outstanding prospect to make best use of the value from the forest resource and hence contributes to the worldwide competitiveness of the wood industry. A new dimension has been provided to the area of wood modification when the impregnation technique has been combined with nanotechnology. Thus the developed composites display some value-added properties such as abrasion resistance, surface hardness, and dimensional stability, etc.

The formation of WPC using polymers and different nanofillers results in overall improvement in properties of the nanocomposites. The laboratory study of the composites exhibits a remarkable improvement in properties of the composites. But a thorough investigation has to be done on a large scale for commercial utilization of the product. Maximum improvement in properties can be achieved by fine tuning in the ratio of clay with different nanofiller. The combined use of both vacuum and pressure will help in better penetration of polymer/nanofillers into the porous structure of wood in order to attain further improvement in properties. The inclusion of pigments into impregnation solutions like supercritical fluid e.g. SC-CO_2 as the medium of impregnation should be studied extensively to investigate diversified value added uses for modified wood, particularly for flooring and other value-added applications. As government is more concerned for assuring resource sustainability and promoting green technology, therefore, a thorough investigation of composites in terms of the biodegradability, fire resistance, pest resistance and low emission of volatile organic compound is also required. The monomer/polymers which are used for impregnation are mainly derived from petrochemical resources which are nonrenewable and moreover on degradation or decomposition most of them emit volatile organic compounds. Consequently they are harmful for the environment. Therefore bio-based resins have been gaining attraction as they are obtained from renewable resources and have least harmful effects from the stand point of environmental concern. During processing on a large scale in industrial applications, the use of water as a solvent can help to minimize all the hazardous effects of petrochemicals diluents. Research on preparation of wood polymer composites by using techniques like gamma radiation, electron beam (EB) or radio-frequency (RF) to polymerize the monomer(s) within the composite, is nearly instantaneous. This can lead to high volume output and enable other manufacturing operations to be performed immediately after EB or RF exposure.

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