

PROPERTIES OF WOOD POLYMER NANOCOMPOSITES IMPREGNATED WITH MELAMINE FORMALDEHYDE-FURFURYL ALCOHOL COPOLYMER AND NANOCCLAY

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Softwood was chemically modified by impregnation with melamine formaldehyde-furfuryl alcohol (MFFA) copolymer, dimethylol dihydroxyethylene urea (DMDHEU) and organically modified nanoclay. A decrease in the crystallinity index value was obtained, as determined by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffractometry (XRD). Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) were used for the characterization of the nanocomposites. The nanocomposites (WPNC) showed enhanced dimensional stability, chemical resistance, flame retardancy and higher mechanical properties. The UV resistance property of WPNC increased considerably as judged by the rate of weight loss, carbonyl index, lignin index, crystallinity index values, SEM and mechanical properties.

Keywords: wood, nanocomposites, characterization, nanoclay

INTRODUCTION

Wood-polymer composites (WPCs) are one of the most important trades of today's plastic industry. WPCs generally exhibit remarkable properties, such as low moisture absorption, high resistance to UV rays and insect attack etc. Wood is one of the best known natural engineering materials and perhaps it is also one of the most widely naturally available resources.¹ Over the years, wood has been treated with a variety of thermoset resins and thermoplastics for improvement of its properties.²⁻⁵

Developing water-soluble monomers will offer many advantages, and particularly environmental benefits. Water is the best solvent among all the green solvents because it is non-polluting, inexpensive and renewable.

Melamine-formaldehyde (MF) is one of the most important thermoset resins useful in decorative laminates, coatings and in the manufacture of composites. The advantages of MF resins include better hardness, mechanical properties, abrasion resistance, scratch resistance, flame retardancy and moisture resistance.^{6,7}

Impregnating wood with furfuryl alcohol, a renewable chemical obtained from sugar cane

bagasse, using heat and catalyst, has been known for decades to improve wood properties.⁸ However, the zinc chloride system, which is used as a catalyst in the process of furfurylation of wood, has a destructive effect on cellulose degradation in wood. This can affect the long-term strength properties of the modified wood. It has been found that, among the cyclic carboxylic anhydride systems, maleic anhydride is a suitable catalyst for the furfurylation process.⁹ Furfurylated wood has been found to present a number of improved properties, such as dimensional stability, weight percent gain (WPG), equilibrium moisture content, hardness, density and durability.^{10,11} However, it cannot significantly increase the thermal stability and mechanical properties, like modulus of elasticity (MOE) and static bending properties.¹² So, furfuryl alcohol was copolymerized with melamine formaldehyde resin to get overall benefits of the prepared composites.

The improvement in interfacial adhesion between the polymer and cell wall was facilitated by the use of crosslinking agents. Dimethylol dihydroxy ethylene urea (DMDHEU) can be a

useful crosslinker for the improvement of WPC properties, as it can dimensionally stabilize the wood composites. Treating the samples with DMDHEU can highly reduce degradation of cell wall during weathering, which explains why the tensile strength losses are higher for untreated wood than for the treated one.¹³

Nanotechnology is a rapidly emerging technology that creates new materials with unique properties and produces new and improved products for many applications.¹⁴ It is a challenging field to develop high-valued wood polymer nanocomposites (WPNCs).¹⁵

Wood is a porous composite that can accommodate nanounits into its structure. The addition of only a small amount of nanofiller can cause a noticeable improvement in the properties of the composites. Nanoclay modified wood will influence properties, such as surface hardness, modulus of elasticity and dimensional stability.^{15,16} Montmorillonite (MMT) is an abundantly available clay, which has rigid planar structure and is widely used to prepare intercalated nanocomposites due to its special structure. A number of studies are available on intercalation of MMT in polymers.¹⁷ Further, it has been reported in the literature that the interface between wood and MMT is fairly weak. So, MMT has to be rendered organophilic for intercalation in the polymer.^{18,19} The present work has been carried out to determine the effect of impregnation of softwood with dispersed nanoclay low molecular weight melamine formaldehyde-furfuryl alcohol (MFFA), in the presence of crosslinking agent dimethylol dihydroxy ethylene urea (DMDHEU), on various properties of the wood.

EXPERIMENTAL

Materials

Fig wood (*Ficus hispida*) was collected locally. Melamine and maleic anhydride were obtained from G.S. Chemical Testing Laboratory & Allied Industries (India). Furfuryl alcohol, glyoxal and formaldehyde were purchased from Merck (Mumbai, India). Nanoclay (clay modified by 15-35 wt% octadecylamine and 0.5-5 wt% aminopropyltriethoxy silane, Sigma-Aldrich (USA)) was used as received. All other chemicals used were of analytical grade.

Preparation of MFFA copolymer

Melamine and formaldehyde were taken in a molar ratio of 1:3 and polymerized by the bulk polymerization method at 80-85 °C by maintaining the pH at 8.5-9.0 with Na₂CO₃. Furfuryl alcohol (1 mole)

was added to the aqueous solution of methylol melamine, followed by addition of maleic anhydride as catalyst and finally polymerized for another 45 min. The viscosity (at 30 °C) of different batches of MFFA copolymer thus prepared was almost similar, as judged by the Ubbelohde viscometer.²⁰

Dispersion of nanoclay in MFFA copolymer

Nanoclay was swelled in a FA-water (1:1) mixture for 24 h with mechanical stirring. Nanoclay can swell in the FA-water mixture, which is a good solvent for the MFFA copolymer. The dispersed nanoclay was then sonicated for 30 min. Then, MFFA was slowly added to the dispersed nanoclay under stirring. This mixture was further sonicated for 15 min and kept ready for use.

Preparation of DMDHEU crosslinker

Urea was slowly added to an aqueous solution of glyoxal under nitrogen purge. The pH of the reaction mixture was then adjusted to approximately 5.5. The reaction mixture was heated to 50 °C and allowed to stir for 24 h. The temperature of the mixture was brought down to room temperature. The solution was neutralized and evaporated to near dryness by rotary evaporator to yield crude 4,5-dihydroxyethylene urea (DHEU). A portion of this DHEU was added to an aqueous formaldehyde solution and pH was adjusted to 8.2-8.5. The molar ratio of n(glyoxal), n(urea), n(formaldehyde) were taken as 1:1.10:1.95 for synthesis of DMDHEU. The reaction mixture was heated to approximately 50 °C and stirred for 24 h. It was then cooled to room temperature, neutralized and kept for subsequent use.^{21,22}

Preparation of wood polymer nanocomposites (WPNCs)

All the samples were oven dried at 105 °C to constant weight before treatment and their dimensions and weights were measured. The samples were then taken to an impregnation chamber. Loads were applied over each sample to prevent them from floating during addition of the impregnating mixture. Vacuum was applied for a specific time period for removing the air from the pores of the wood samples before addition of the prepolymeric mixture. The MFFA copolymer along with maleic anhydride or MFFA copolymer with DMDHEU, maleic anhydride or MFFA copolymer with nanoclay, DMDHEU, maleic anhydride were further introduced through a dropping funnel. The samples were then kept immersed in the impregnation chamber for 6 h after attaining atmospheric pressure. After that, the samples were taken out of the chamber and excess chemicals were wiped from the surfaces of the prepared composites. The samples were then wrapped in aluminium foil and cured at 90 °C for 24 h in an oven. This was followed by drying at 105 °C for another 24 h. To remove homopolymers, if any, formed during impregnation, the cured samples were

then Soxhlet extracted. The dimensions were remeasured by using a slide caliper, and weights were taken.²³

Measurements

Weight percent gain

Weight percent gain (WPG) after polymer loading was calculated according to the formula:

$$\text{WPG (\%)} = (W_2 - W_1)/W_1 \times 100 \quad (1)$$

where W_1 (g) is the oven dry weight of wood blocks before polymer treatment and W_2 (g) is oven dry weight of blocks after polymer treatment.

Volume increase (%)

Percentage volume increase after impregnation of wood samples was calculated by the formula:

$$\% \text{ Volume increase} = (V_2 - V_1)/V_1 \times 100 \quad (2)$$

where V_1 (cm³) is oven dry volume of the untreated wood and V_2 (cm³) is oven dry volume of the treated wood.

Hardness

The hardness of the samples was measured by using a durometer (model RR12, Hylec controls, Sydney) according to ASTM D2240 method and was expressed as shore D hardness.

FTIR study

The treated and untreated samples were ground and FTIR spectra were recorded using the KBr pellet method in a Nicolet (Madison, USA) Impact 410 Spectrophotometer.

X-ray diffraction (XRD) analysis

Crystallographic studies were done by XRD analysis using a Rigaku X-ray diffractometer (Miniflex, UK) and employing CuK α radiation ($\lambda = 0.154$ nm), at a scanning rate of 2° min⁻¹ with an angle ranging from 2° to 55°. The crystallinity index (CrI) was determined from XRD analysis using the following formula:

$$\text{CrI} = A_{\text{cryst}}/A_{\text{total}} \times 100 \quad (3)$$

where A_{cryst} is the area of the peak for 002 plane and A_{total} is the total area of the peak under the whole region.

Water uptake test

Wood samples obtained from defect-free wood were cut into blocks of 2.5 cm \times 1 cm \times 2.5 cm for water uptake and dimensional stability test. Both untreated and treated wood samples were immersed in distilled water at room temperature (30°C) and weights were taken after 0.5, 2, 6, 24, 48, 96, 120, 144 and 168 h, expressed as

$$\text{Water uptake (\%)} = (W_t - W_d)/W_d \times 100 \quad (4)$$

where W_d (g) is the oven dry weight; and W_t (g) is the weight after immersion in distilled water for a specified time period.

Water repellent effectiveness (WRE)

WRE was measured for different soaking periods. Resistance to water uptake is expressed as WRE and is calculated as:

$$\text{WRE} = (D_o - D_t)/D_o \times 100 \quad (5)$$

where D_o (g) (difference between final weight and initial weight of the sample) is the water uptake of untreated samples immersed for 0.5, 2, 6, 24, 48, 96, 120, 144 and 168 h; and D_t (g) is the water uptake of treated wood samples immersed for the same periods.

Dimensional stability test

Swelling in water

Dimensions of the oven dried samples were measured and the samples were further conditioned at room temperature (30 °C) and 30% RH. Finally, the samples were immersed in distilled water and then their dimensions were remeasured after 0.5, 2, 6, 24, 48, 96, 120, 144 and 168 h. Swelling was considered as a change in volume and expressed as the percentage of volume increase compared to oven dried samples:

$$\% \text{ Swelling} = (V_{t,u} - V_o)/V_o \times 100 \quad (6)$$

where $V_{t,u}$ (cm³) is the volume of the untreated or treated wood after water absorption; and V_o (cm³) is the volume of the untreated or treated wood before water absorption.

Antiswelling efficiency

The antiswell efficiency (ASE) index was determined to find out the dimensional stability of the treated wood specimens. The specimens were submerged in distilled water at 30 °C for different time periods after conditioning at 30% RH and 30 °C. Volumetric swelling coefficients in percentage were calculated according to Equation 6.

The percentage of ASE was calculated from the wet and oven dried volumes of treated and untreated wood specimens according to the formula below:

$$\text{ASE (\%)} = (S_c - S_t)/S_c \times 100 \quad (7)$$

where S_c (cm³) is the volumetric swelling coefficient of untreated blocks and S_t (cm³) is the volumetric swelling coefficient of the treated blocks.

Chemical resistance test

The samples were kept immersed in 4% NaOH solution and 4% acetic acid solution for 24 h. The percent swelling was calculated using the equation given below:

$$\% \text{ Swelling} = (V_{t,u} - V_o)/V_o \times 100 \quad (8)$$

where $V_{t,u}$ (cm³) is the volume of the untreated or treated wood after immersion in chemicals and V_o (cm³) is the volume of the untreated and treated wood before immersion in chemicals.

Limiting oxygen index (LOI study)

The limiting oxygen index (LOI) test was performed by using a flammability tester (S.C. Dey Co., Kolkata) according to ASTM D-2863 method. The sample was positioned upright in the sample holder of the LOI apparatus. The ratio of nitrogen and oxygen at which the sample continued to burn for at least 30 s was noted.

$$\text{LOI} = \text{Volume of O}_2 / \text{Volume of (O}_2 + \text{N}_2) \times 100 \quad (9)$$

Mechanical behavior study

The flexural strength of the samples was measured by a UTM-HOUNSEFIELD, England (model H100K-S) with a crosshead speed of 2 mm/min and by calculating the modulus of elasticity (MOE) and modulus of rupture (MOR) according to ASTM D-790 method. MOR was calculated as follows:

$$\text{MOR} = 3WL / 2bd^2 \quad (10)$$

where W is the ultimate failure load (N), L is the span between the centres of support, b is the mean width (tangential direction) of the sample and d is the mean thickness (radial direction) of the sample.

The tensile strength test was performed using a UTM-HOUNSEFIELD, England (model H100K-S) with a 10-kN load cell and a crosshead speed of 10 mm/min according to ASTM D-638 method.

Statistical analysis

Five samples of each kind were used for measuring the flexural and tensile properties and their average values are reported. All the data are expressed as means \pm SD. Results were statistically analyzed using ANOVA followed by Tukey HSD test.

Morphological studies

The morphologies of the untreated and treated wood samples were studied by using a JEOL JSM-6390LV scanning electron microscope at an accelerated voltage of 5-10 kV. The fractured surface of the samples was used for the study. These were sputtered with platinum and deposited on a brass holder.

Transmission Electron Microscopy (TEM)

The samples were embedded with epoxy resin for the preparation of (ultra)thin and polished sections. An ultramicrotome fitted with a diamond knife was used for ultrathin sectioning (approximately 100 nm thick) of the transverse film surfaces. The sections were stained with 1 wt% uranyl acetate for sufficient contrast. The sections were then mounted on grids and examined with a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 80 kV.

UV resistance test

The degradation study of the WPC samples was done in a UV chamber (Model: S.L.W., voltage: 230

V; Advanced Research Co., India) using a mercury arc lamp system that produces a collimated and highly uniform UV flux in the 200-400 nm range at room temperature (30 °C) and 30% RH. The exposure period was varied from 0 to 60 days. The weight loss was measured and is expressed as follows:

$$\% \text{ Weight loss} = (W_t - W_0) / W_0 \times 100 \quad (11)$$

where W_t (g) is the specimen weight at time 't' and W_0 (g) is the specimen weight before exposure. UV degradation was studied by FTIR analysis. The intensity of the carbonyl (C=O) stretching peaks at 1715 cm^{-1} in cellulose of untreated wood was measured. The net peak heights were determined by subtracting the height of the baseline directly from the total peak height. The same baseline was taken for each peak before and after exposure to UV.²⁴ The carbonyl index was calculated by using the following equation:

$$\text{Carbonyl index} = I_{1715} / I_{2924} (100) \quad (12)$$

where I represents the intensity of the peak. The peak intensities were normalized by using the -CH stretching peak of alkane at 2927 cm^{-1} . This peak was chosen as reference due to its least change during irradiation. The lignin index (LI) of the wood was calculated for all the untreated and treated wood samples. It is the ratio of the height of the lignin-characteristic band at 1510 cm^{-1} to that of the band at 2927 cm^{-1} . The band corresponding to C-H stretching of cellulose appeared at 2927 cm^{-1} , which is very stable to oxidation and remains constant throughout the UV exposure.

$$\text{LI} = I_{1510} / I_{2927} (100) \quad (13)$$

The possibility of change in cellulose crystallinity due to UV irradiation is determined by the crystallinity index (CrI). It is defined as the ratio of the areas of the bands at 1437 and 2927 cm^{-1} . The band appearing at 1437 cm^{-1} is assigned to cellulose.²⁵

$$\text{CrI} = A_{1437} / A_{2927} \quad (14)$$

Surface morphology of the UV degraded specimen was characterized by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Various parameters, such as vacuum, time of impregnation, monomer concentration, initiator concentration, amount of crosslinking agent and nanoclays, were varied to get optimum properties. The conditions for which maximum improvement of properties was obtained were the following: 500 mm Hg vacuum, 6 h time of impregnation, 5:1 (MFFA:FA-water) prepolymer concentration, 1% (w/w) maleic anhydride, 3 ml DMDHEU, 1-3 phr nanoclay.

Effect of nanoclay concentration on polymer loading (WPG %), volume increase and hardness

It was observed from Table 1 that properties, such as weight percent gain, volume increase, and hardness, improved compared to the untreated samples. The treatment with MFFA copolymer would fill the empty cell lumen, pits and parenchyma present in the wood. The hydroxyl and methylol groups present in the prepolymer would interact with the hydroxyl groups of wood. DMDHEU is a multifunctional monomer and can interact with both wood and prepolymer through hydroxyl groups. This would lead to an enhancement in the deposition of polymer. Xie *et al.* prepared wood polypropylene composites using glutaraldehyde (GA) and DMDHEU as crosslinkers, and reported that both GA and DMDHEU could crosslink with the cell wall of wood as well as with the polymer.²⁶ Further improvement in properties was observed upon treatment with nanoclay. With an increase in the

amount of nanoclay, a remarkable improvement in properties was noticed. This was due to the restriction in mobility of the polymer chains between the silicate layers. Devi and Maji reported an improvement in the weight percent gain, as well as in hardness, with an increase in the amount of nanoclay.²⁷

FTIR study

Figure 1 presents the FTIR spectra of nanoclay, MFFA and DMDHEU. Curve a represents the absorbance spectrum of nanoclay where peaks appeared at 3466 cm^{-1} for $-\text{OH}$ stretching, 2929 and 2854 cm^{-1} for $-\text{CH}$ stretching of modified hydrocarbon, 1620 cm^{-1} for $-\text{OH}$ bending, $1032\text{--}459\text{ cm}^{-1}$ for oxide bands of metals like Si, Al, Mg, *etc.* The peaks at 3404 , 2926 , 2851 , 1566 and 1510 , 1186 and 811 cm^{-1} were assigned to $-\text{OH}$ stretching, aliphatic $-\text{CH}$ asymmetric stretching, $-\text{CH}$ symmetric stretching, furan ring vibration, C-N stretching and out of plane trisubstitution of triazine ring respectively for MFFA (curve b).²⁸

Table 1
Effect of variation of nanoclay on polymer loading (WPG %), volume increase and hardness

Samples	Weight gain, %	Volume increase, %	Hardness (Shore D)
Untreated	-	-	46 (± 1.07)
Samples treated with MFFA/FA-water/DMDHEU/nanoclay			
100/20/0/0	23.63 (± 0.48)	2.11 (± 0.37)	57 (± 1.08)
100/20/3/0	25.86 (± 1.02)	2.15 (± 0.54)	60 (± 0.82)
100/20/3/1.0	32.88 (± 0.96)	2.69 (± 0.78)	66 (± 0.65)
100/20/3/2.0	38.75 (± 1.03)	2.98 (± 1.07)	72 (± 0.88)
100/20/3/3.0	42.56 (± 1.12)	3.31 (± 0.97)	74 (± 0.38)

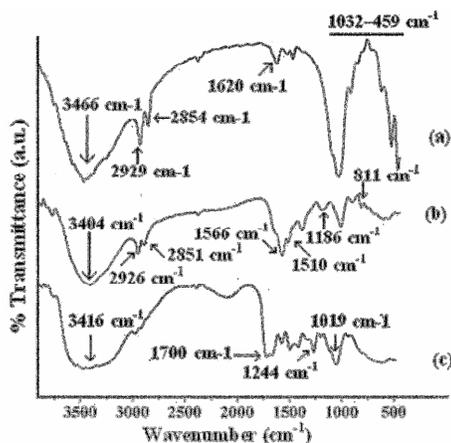


Figure 1: FTIR spectra of (a) nanoclay; (b) MFFA; (c) DMDHEU

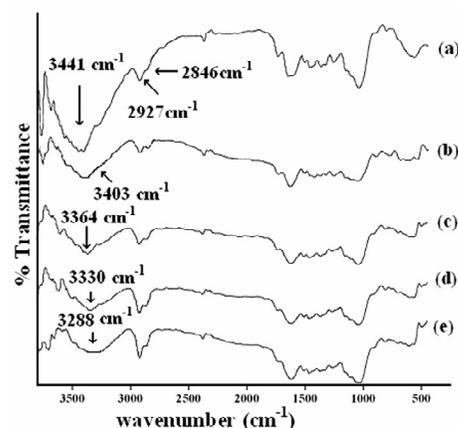


Figure 2: FTIR spectra of (a) untreated wood and wood treated with (b) MFFA/DMDHEU; (c) MFFA/DMDHEU/nanoclay (1 phr); (d) MFFA/DMDHEU/nanoclay (2 phr); (e) MFFA/DMDHEU/nanoclay (3 phr)

The spectrum of DMDHEU (curve c) shows peaks at 3416 cm^{-1} , 1700 cm^{-1} , 1244 cm^{-1} and 1019 cm^{-1} , which could be assigned to -OH stretching, C=O stretching, -CHOH stretching, -CH₂OH stretching, respectively.²⁹

Figure 2 represents the FTIR spectra of (a) untreated and treated samples with (b) MFFA/DMDHEU, (c) MFFA/DMDHEU/nanoclay (1 phr), (d) MFFA/DMDHEU/nanoclay (2 phr), (e) MFFA/DMDHEU/nanoclay (3 phr). The absorbance for the untreated wood samples appeared at 3441 cm^{-1} (-OH stretching), 2927 cm^{-1} and 2846 cm^{-1} (-CH₂ asymmetric stretching), 1736 cm^{-1} (C=O stretching), 1643 cm^{-1} (-OH bending), 1256 cm^{-1} and 1045 cm^{-1} (C-O stretching) and $1002\text{-}643\text{ cm}^{-1}$ (out-of-plane C-H bending vibration). In the curves b-e, there was a shifting and a decrease in the intensity of the hydroxyl peak, which was due to the interaction of wood, MFFA, DMDHEU and nanoclay. The peak shifted from 3441 cm^{-1} (curve a) to 3403 cm^{-1} (curve b), 3364 cm^{-1} (curve c), 3330 cm^{-1} (curve d), 3288 cm^{-1} (curve e). Furthermore, the peak intensity at 2927 cm^{-1} and 2846 cm^{-1} for -CH stretching was more pronounced in the nanoclay treated composites, compared to that in the untreated wood. The presence of the characteristic peak of MFFA and nanoclay in the wood/MFFA/DMDHEU/nanoclay composite indicated successful impregnation of MFFA and clay into wood.

XRD study

Figure 3 shows the XRD diffractograms of (a) nanoclays, (b) MFFA/DMDHEU/nanoclay polymer composite, (c) wood, (d) wood/MFFA/DMDHEU/nanoclay (1 phr), (e) wood/MFFA/DMDHEU/nanoclay (2 phr), (f) wood/MFFA/DMDHEU/nanoclay (3 phr), respectively. The organically modified nanoclay (curve a) shows a sharp peak at $2\theta = 4.3^\circ$. The gallery distance was calculated using Bragg's equation and found to be 2.05 nm. For the MFFA/DMDHEU/nanoclay composite (curve b), the sharp peak of the organically modified clay disappeared and a broad peak due to MFFA copolymer appeared at 22.51° .³⁰ This suggested that either the full expansion of interlayers of nanoclay occurred, which was not possible to detect, or the nanoclay layers became delaminated or no crystal diffraction peak appeared.³¹ Untreated wood shows a wide diffraction peak at 22.96° due to the (002) crystal plane of cellulose. Other small peaks that appeared at 37.68° and 15.02° were assigned

to the crystallographic (040) plane of cellulose and the amorphous region of cellulose, respectively. WPNC containing modified nanoclay showed a decrease in the intensity of the peak at 22.96° . A reduction in intensity, as well as a shift of the peak corresponding to (002) crystal plane of cellulose (curves d-f) to lower angles was observed in the composites. Further, the peaks that appeared at 37.68° and 15.02° became dull.³²

Therefore, it could be concluded that crystallinity in wood decreased and some delaminated nanoclay was introduced into the amorphous region of wood cellulose.

Crystallinity determination from FTIR and XRD

Table 2 shows the crystallinity index values of untreated and treated wood samples. Among the different functions used for analysis of the diffraction peaks, fitting the curves with the Voigt functions resulted in the best fit.³³

The treated wood samples with 3 phr nanoclay showed the least value of cellulose crystallinity index, while the highest value was shown by the untreated wood. The structures of crystallites of wood cellulose became nebulous, as chemical grafting reaction occurred in wood. MFFA, DMDHEU and nanoclay broke the intermolecular and intramolecular hydrogen bonds of cellulose as they participated in the bond formation with the wood cellulose, thereby lowering the rigidity of wood cellulose.³⁴ The chemical grafting reaction occurred in the amorphous region of wood cellulose since the distribution of polymer chains in the crystallite region of cellulose was difficult.³⁵ Some hydrogen bonds were ruptured and the cellulose chains were opened up as the polymer chains reacted on the surface of the crystallites. With the progress of the reaction, more amorphous cellulose was produced. Both FTIR and XRD were employed to determine the crystallinity index values and the results found were in good agreement with each other. Thus, the treated wood samples showed lower values of the crystallinity index than the untreated wood samples.

Water uptake study

The water uptake capacities of untreated and treated wood samples are shown in Figure 4(A). Untreated wood samples had the highest water absorption capacity (curve a). When the wood samples were impregnated with MFFA copolymer, their water absorption capacity decreased (curve b).

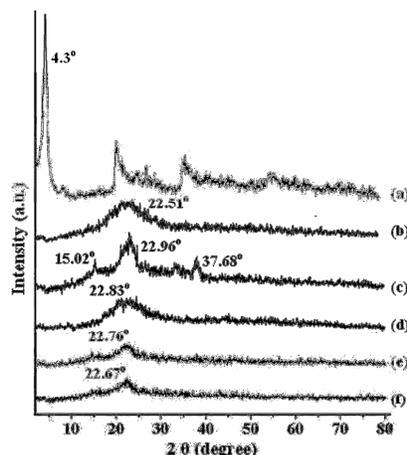


Figure 3: X-ray diffraction spectra of (a) nanoclay; (b) MFFA/DMDHEU/nanoclay polymer composite; (c) untreated wood; (d) MFFA/DMDHEU/nanoclay (1 phr) treated; (e) MFFA/DMDHEU/nanoclay (2 phr) treated; (f) MFFA/DMDHEU/nanoclay (3 phr) treated wood samples

Table 2

Crystallinity index values of the cellulose matrix of untreated and treated wood samples calculated by the area method before and after UV exposure

Samples	Untreated wood	MFFA/DMDHEU treated	MFFA/DMDHEU/nanoclay (1phr) treated	MFFA/DMDHEU/nanoclay (2phr) treated	MFFA/DMDHEU/nanoclay (3phr) treated	
Before irradiation						
XRD results	62.23	54.35	48.87	46.67	43.45	
FTIR results	62.97	53.45	48.37	45.97	43.88	
After irradiation						
FTIR results	10 days	59.33	51.78	46.87	45.11	42.99
	20 days	57.75	49.12	45.93	44.64	42.34
	30 days	55.43	47.48	45.04	43.85	41.86
	40 days	51.21	46.84	44.32	43.03	41.47
	50 days	47.24	46.01	43.72	42.67	41.10
	60 days	44.86	45.46	42.89	42.14	40.56

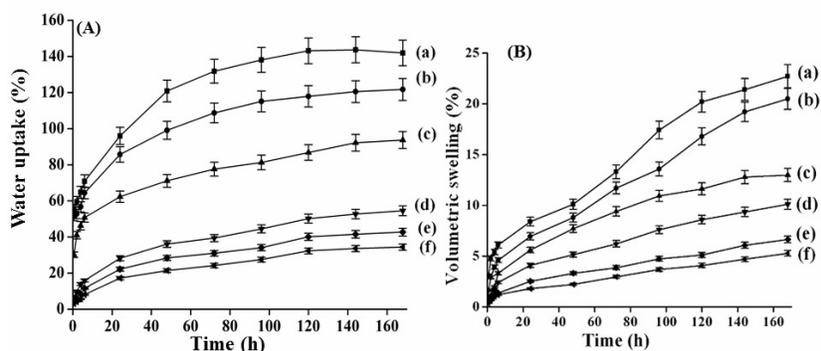


Figure 4(A): Water absorption test results of wood (a) untreated and treated with; (b) MFFA prepolymer; (c) MFFA/DMDHEU; (d) MFFA/DMDHEU/nanoclay (1.0 phr); (e) MFFA/DMDHEU/nanoclay (2.0 phr); (f) MFFA/DMDHEU/nanoclay (3.0 phr). (B): Volumetric swelling results in water at 30 °C of wood samples (a) untreated, and treated with (b) MFFA prepolymer; (c) MFFA/DMDHEU; (d) MFFA/DMDHEU/nanoclay (1.0 phr); (e) MFFA/DMDHEU/nanoclay (2.0 phr); (f) MFFA/DMDHEU/nanoclay (3.0 phr)

The empty spaces of wood were occupied by the water repellent copolymer MFFA. The water absorption capacity of wood decreased on addition of DMDHEU with MFFA (curve c). The presence of four hydroxyl groups in DMDHEU was responsible for the lower water uptake capacity. The hydroxyl groups could form a crosslinked structure with the wood and the polymer through their hydroxyl groups, resulting in a decrease in water absorption capacity.³⁶ The addition of nanoclay would further decrease its water uptake capacity. The higher the amount of nanoclay, the lower was the water uptake capacity of the wood samples (curves d-f). The clay layers acted as a barrier for the diffusion of water molecules and provided a convoluted path for water transportation through the composite.¹⁵ The water uptake of the samples decreased with an increase in the time of immersion for the untreated wood.

Water-repellent effectiveness (WRE) study

Related results are shown in Table 3. The highest water repellency was exhibited by the samples treated with MFFA/DMDHEU/nanoclay (3 phr). The reason would be the same as stated earlier.

Dimensional stability test

Swelling in water

The effects of swelling in water at room temperature for both treated and untreated samples are shown in Figure 4(B). The hydrophilic nature of wood was responsible for the higher swelling of the untreated wood. The deposition of hydrophobic prepolymer on the void cell lumen of wood would decrease swelling. Further, DMDHEU could crosslink with the cell wall of wood and the polymer, resulting in enhanced dimensional stability.²⁶ The treatment of the WPC samples with modified nanoclay would decrease its swelling further. The layers of silica restricted the diffusion of water molecules through the composite. The higher the amount of nanoclay, the higher was the restriction in the diffusion of water molecules. As a result, there would be less shrinking and swelling of wood cell wall. Thus, an improvement in dimensional stability was observed.

Antiswelling efficiency

Related results are shown in Table 4. The highest antiswelling efficiency was shown by the samples treated with MFFA/DMDHEU/nanoclay

(3 phr). The reason would be similar to that stated earlier.

Chemical resistance test

The results of the swelling of the samples in 4% acetic acid and 4% NaOH solution are shown in Table 5. By impregnation of the samples with MFFA and DMDHEU, the empty pits and parenchymas of wood would be filled. So, the treated samples swelled less, compared to the untreated ones. It was observed that the incorporation of nanoclay into the samples treated with MFFA/DMDHEU decreased the swelling. A further decrease in swelling of the composite was noticed with an increase in the amount of clay. Clay layers provided a meandering path for chemicals diffusivity through the composite. In all the cases, the swelling was lower in acetic acid, compared to that in sodium hydroxide solution. This may be possibly due to the increase in interaction by sodium hydroxide with wood cellulose and clay layers.³¹

Limiting oxygen index (LOI study)

Figure 5 shows the LOI values of the untreated and treated wood samples. The treatment of the samples with MFFA copolymer would lead to higher LOI values compared to the virgin wood. The nitrogen present in MFFA released its oxides on combustion and hence displaced the oxygen present on the surface of the samples. The addition of DMDHEU would further increase the LOI values, since it was also another supplier of nitrogen.³⁷ The samples treated with MFFA/DMDHEU/nanoclay showed substantial improvement in LOI values. It was observed that with an increase in the amount of nanoclay, the LOI values of the samples also increased. The silicate layers would barricade the oxygen and heat, thereby delaying the flaming ability of the composites. Further, upon burning, the silicate layers of nanoclay produced char, which would insulate the burning material, and thus provided flame resistance to the composites.³⁸

Mechanical behavior study

Table 6 represents the tensile and flexural properties of untreated and treated wood samples. The treated samples exhibited higher tensile and flexural values than the untreated ones. MF resin is one of the stiffest polymeric resins and is known to enhance greatly the mechanical properties.⁷

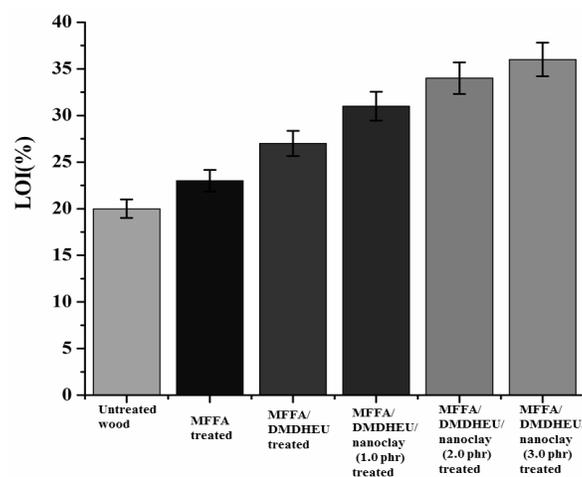


Figure 5: Limiting Oxygen Index test of untreated and treated wood samples

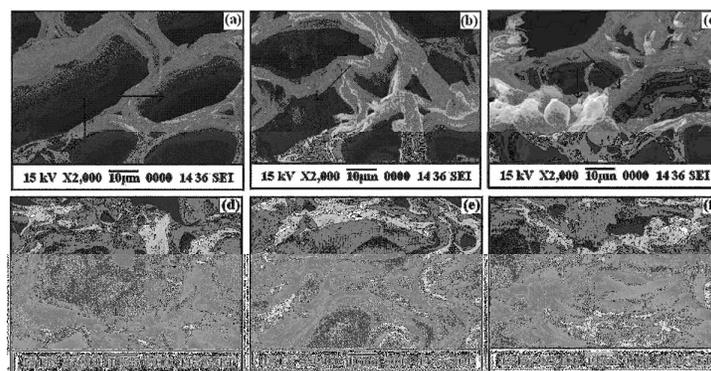


Figure 6: Scanning electron micrographs of wood samples (a) untreated and treated with (b) MFFA prepolymer; (c) MFFA/DMDHEU; (d) MFFA/DMDHEU/nanoclay (1.0 phr); (e) MFFA/DMDHEU/nanoclay (2.0 phr); (f) MFFA/DMDHEU/nanoclay (3.0 phr)

The addition of DMDHEU to MFFA copolymer would enhance the mechanical properties of the prepared composites, as DMDHEU could crosslink with the wood cell wall and with the polymer.³⁶ The values were found to increase further when modified nanoclay was added to the wood/MFFA/DMDHEU composite. There was a remarkable improvement in mechanical properties with the increase in the amount of nanoclay. The obtained higher values were due to well dispersed silicate layers, which fasten the polymer chains in their gallery and thereby restricted their mobility.³⁹

Morphological studies

Scanning electron micrographs of the fractured surfaces of the untreated and treated wood samples are shown in Figure 6. The empty cell lumens observed in the untreated wood (Fig. 6a)

were filled by the polymer, crosslinker and nanoclay (Fig. 6b-d). The presence of nanoclay could be seen in the micrograph as white spots.

Transmission Electron Microscopy (TEM)

Figure 7 presents the TEM micrographs of untreated and treated wood samples. In the untreated wood samples, radial fracture patterns perpendicular to the compound middle lamella were observed. No orientation of the cell wall components could be detected. In the case of the samples treated with MFFA/DMDHEU/nanoclay (1 phr), MFFA/DMDHEU/nanoclay (2 phr), MFFA/DMDHEU/nanoclay (3 phr) (Fig. 7 b-d), it was observed that an even dispersion of nanoclay occurred. The dispersion became more homogenous at higher percentage of loaded nanoclay, indicating successful impregnation of nanoclay into wood.

Table 3

Water repellent effectiveness (WRE, %) of WPC

Time (h)	MFFA treated	MFFA/DMDHEU treated	MFFA/DMDHEU/nanoclay (1.0 phr) treated	MFFA/DMDHEU/nanoclay (2.0 phr) treated	MFFA/DMDHEU/nanoclay (3.0 phr) treated
0.5	43.72 (± 0.65)	65.17(± 0.45)	81.22 (± 1.09)	85.13 (± 0.53)	89.11 (± 0.68)
2	41.44 (± 0.38)	55.64(± 0.55)	75.32 (± 0.75)	79.89 (± 0.75)	84.58 (± 0.76)
4	38.77 (± 0.45)	48.37(± 0.32)	73.64 (± 0.87)	76.24 (± 0.36)	80.96 (± 0.48)
6	35.63 (± 0.21)	44.25(± 0.83)	71.66 (± 0.54)	74.38 (± 1.12)	78.62 (± 0.74)
24	33.54 (± 0.67)	36.58(± 0.27)	69.36 (± 0.73)	72.13 (± 0.71)	77.51 (± 1.05)
48	30.13 (± 0.49)	30.81(± 0.74)	68.63 (± 0.95)	71.09 (± 0.46)	75.83 (± 0.94)
72	26.36 (± 0.87)	29.62(± 0.19)	68.28 (± 0.42)	70.67 (± 0.93)	74.67 (± 0.54)
96	24.52 (± 0.99)	25.46(± 0.35)	67.87 (± 0.34)	70.25 (± 0.43)	74.35 (± 0.47)
120	23.74 (± 0.42)	24.67(± 0.58)	67.41 (± 1.14)	69.78 (± 0.62)	73.76 (± 0.75)
144	22.36 (± 0.81)	24.26(± 0.61)	66.93 (± 0.88)	69.36 (± 0.82)	72.95 (± 0.41)
168	21.91 (± 0.53)	23.64(± 0.39)	66.54 (± 1.07)	68.69 (± 0.33)	72.33 (± 0.58)

Table 4

ASE (%) of treated wood samples at different time periods

Time (h)	MFFA treated	MFFA/DMDHEU treated	MFFA/DMDHEU/nanoclay (1.0 phr) treated	MFFA/DMDHEU/nanoclay (2.0 phr) treated	MFFA/DMDHEU/nanoclay (3.0 phr) treated
0.5	67.38(± 0.47)	70.72(± 0.42)	78.23 (± 0.75)	80.56 (± 0.32)	85.23 (± 0.46)
2	66.46(± 0.65)	69.34(± 0.53)	77.54 (± 0.43)	79.32 (± 0.84)	84.46 (± 0.23)
4	65.78 (± 1.10)	67.96(± 0.72)	76.72 (± 1.08)	78.64 (± 0.36)	83.82 (± 0.68)
6	65.65 (± 0.73)	67.67(± 0.38)	76.58 (± 0.27)	78.35 (± 0.54)	83.69 (± 0.77)
24	65.23 (± 0.82)	67.41(± 0.74)	76.38 (± 0.51)	78.21 (± 0.35)	83.56 (± 0.18)
48	64.54 (± 0.28)	67.28(± 0.68)	76.26 (± 0.93)	78.05 (± 0.72)	83.32 (± 0.47)
72	64.61 (± 0.49)	67.08(± 0.61)	76.11 (± 0.74)	77.67 (± 0.47)	83.21 (± 1.12)
96	64.34 (± 0.66)	66.52(± 0.87)	75.88 (± 0.65)	77.52 (± 0.27)	83.14 (± 0.09)
120	63.83 (± 0.14)	66.39(± 0.69)	75.63 (± 0.76)	77.38 (± 0.87)	82.92 (± 0.51)
144	63.68 (± 0.42)	66.26(± 0.37)	75.49 (± 0.35)	77.23 (± 0.34)	82.78 (± 0.33)
168	63.37 (± 0.63)	66.18(± 0.43)	75.32 (± 0.86)	77.14 (± 0.91)	82.63 (± 0.73)

Table 5
Chemical resistance test of untreated and treated wood samples

Medium	Time (h)	Volumetric swelling (cm ³)					
		Untreated	MFFA treated	MFFA/DMDHEU treated	MFFA/DMDHEU/nanoclay (1.0 phr) treated	MFFA/DMDHEU/nanoclay (2.0 phr) treated	MFFA/DMDHEU/nanoclay (3.0 phr) treated
NaOH solution (4%)	24	12.12 (±0.63)	7.96 (±0.68)	5.98 (±0.92)	4.06 (±1.03)	3.78 (±0.45)	3.64 (±0.96)
	168	13.34 (±0.86)	10.57(±0.73)	8.02(±0.78)	5.34 (±0.81)	4.87 (±1.01)	4.48 (±0.52)
Acetic acid (4%)	24	8.27 (±0.49)	5.76 (±0.28)	4.68(±0.54)	2.99 (±0.64)	2.76 (±0.19)	2.44 (±1.12)
	168	11.41 (±0.85)	6.59(±0.66)	5.47(±0.39)	3.88 (±0.57)	3.68 (±0.33)	3.32 (±0.67)

Table 6
Flexural and tensile properties of untreated and treated wood before and after UV degradation

Sample	Flexural properties				Tensile properties			
	Before degradation		After degradation		Before degradation		After degradation	
	Strength (MPa) (±SD)	Modulus (MPa) (±SD)						
Untreated wood	117.69 (±1.49)	5936.76 (±3.47)	100.43 (±0.86)	5017.84 (±0.58)	40.73 (±1.67)	303.76 (±7.33)	30.37 (±0.65)	223.76 (±10.12)
Wood treated with MFFA	125.55 (±1.60)	6337.57 (±2.09)	113.64 (±1.23)	5677.85 (±1.34)	43.63 (±2.18)	322.80 (±7.07)	35.78 (±1.64)	263.61 (±12.13)
MFFA/DMDHEU	128.50 (±0.80)	7237.69 (±1.71)	118.97 (±1.47)	6009.68 (±0.86)	50.62 (±3.13)	376.69 (±8.20)	43.45 (±0.73)	290.98 (±9.54)
MFFA/DMDHEU/nanoclay (1 phr)	135.53 (±1.62)	7642.52 (±1.74)	127.74 (±1.86)	6443.72 (±0.95)	58.58 (±1.70)	439.52 (±7.90)	52.43 (±0.84)	386.29 (±8.32)
MFFA/DMDHEU/nanoclay (2 phr)	138.87 (±1.55)	7831.55 (±3.25)	131.65 (1.43)	6640.95 (±1.53)	62.58 (±2.53)	465.66 (±3.23)	57.67 (±1.56)	424.90 (±11.76)
MFFA/DMDHEU/nanoclay (3 phr)	139.78 (±0.74)	7882.67 (±1.66)	133.87 (1.17)	6752.94 (±2.12)	65.61 (±4.71)	486.43 (±9.00)	61.78 (±0.75)	455.18 (±7.87)

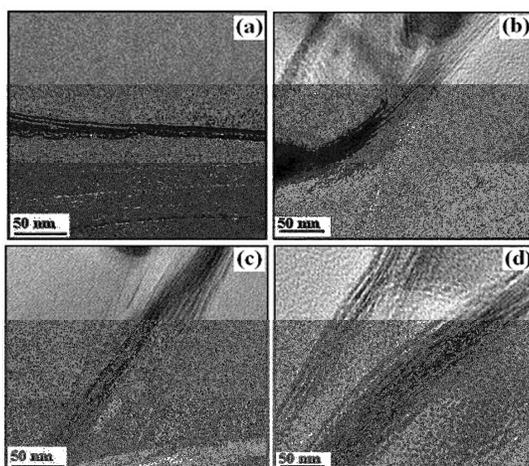


Figure 7: Transmission electron micrographs of wood samples (a) untreated wood and treated with (b) MFFA/DMDHEU/nanoclay (1.0 phr); (c) MFFA/DMDHEU/nanoclay (2.0 phr); (d) MFFA/DMDHEU/nanoclay (3.0 phr)

UV resistance

Upon exposure to UV irradiation for different time periods, both untreated and treated wood samples showed an early increase in weight due to moisture gain and later loss in weight was observed, as shown in Figure 8. The material loss induced by the degradation was lower than the early increase in weight loss. The highest weight loss was shown by the untreated wood samples. The rate of weight loss decreases with the increase in the amount of nanoclay.

The change of the carbonyl index value with time is shown in Figure 9(A). After 60 days of exposure to a UV environment, an increase in the carbonyl index value was observed for both the untreated and treated wood samples. The untreated wood samples showed the highest value of the carbonyl index, followed by the treated ones, due to higher oxidation of wood cellulose.

Chain scission in the polymer and wood was responsible for the increase in the value of the carbonyl index. The polymer chain scission lowers the density of entanglements of the polymer, decreasing the weight of the samples. Wood samples treated with MFFA/DMDHEU delayed the photodegradation process, as DMDHEU could form a crosslinked structure through its hydroxyl groups with the cellulose, thereby lowering the carbonyl index value. Further lowering of the carbonyl index values was observed upon addition of nanoclay. Nanoclay could stabilize the composites by shielding the composites from UV rays. The higher the amount of nanoclay, the lower was the carbonyl index value. Grigoriadou *et al.* reported an increase in UV stability upon addition of montmorillonite clay in HDPE.⁴⁰

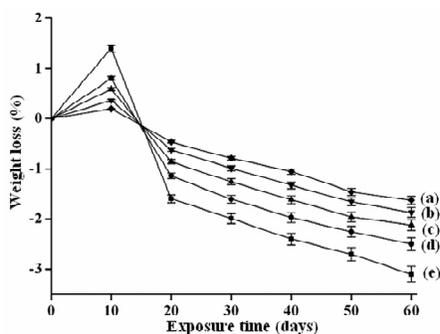


Figure 8: Weight loss versus exposure time of (a) untreated wood samples; (b) MFFA/DMDHEU treated; (c) MFFA/DMDHEU/nanoclay (1 phr) treated; (d) MFFA/DMDHEU/nanoclay (2 phr) treated; (e) MFFA/DMDHEU/nanoclay (3 phr) treated

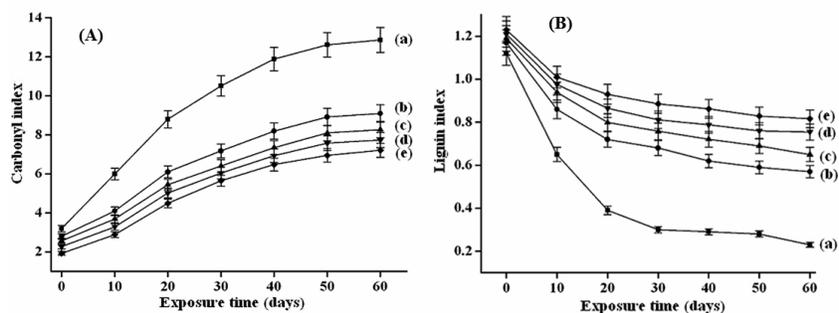


Figure 9(A): Carbonyl index values of (a) untreated wood and wood treated with (b) MFFA/DMDHEU; (c) MFFA/DMDHEU/nanoclay (1 phr); (d) MFFA/DMDHEU/nanoclay (2 phr); (e) MFFA/DMDHEU/nanoclay (3 phr); (B): Lignin index values of (a) untreated wood samples and wood treated with (b) MFFA/DMDHEU; (c) MFFA/DMDHEU/nanoclay (1 phr); (d) MFFA/DMDHEU/nanoclay (2 phr); (e) MFFA/DMDHEU/nanoclay (3 phr)

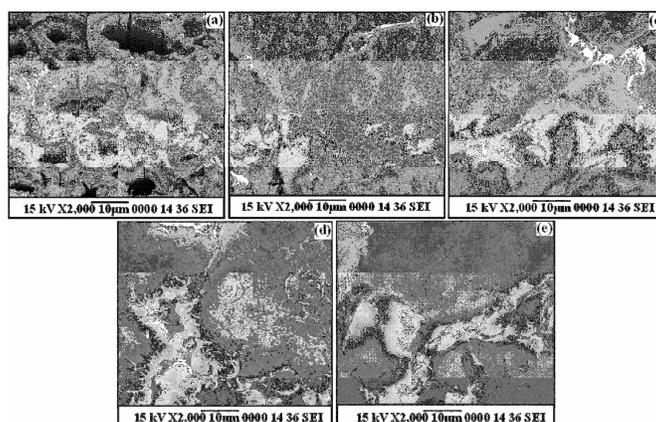


Figure 10: SEM micrographs of UV treated samples after 60 days; (a) untreated wood and wood treated with (b) MFFA/DMDHEU; (c) MFFA/DMDHEU/nanoclay (1 phr); (d) MFFA/DMDHEU/nanoclay (2 phr); (e) MFFA/DMDHEU/nanoclay (3 phr)

The lignin index values as a function of time for untreated and treated wood samples are shown in Figure 9(B). The addition of nanoclay acted as a screen for the composites as it inhibited the photodegradation of lignin from the formation of quinones, carbonyls or peroxides. The untreated wood samples showed lower lignin index values than the treated ones and the values decreased with the increase in UV exposure time. The lignin decomposed upon exposure to UV rays to form quinones and proxides. The treatment of wood with polymer and clay acted as a screen for the samples and prevented the degradation of lignin. Thus, the lignin was least affected for the treated wood and the decrease in the lignin index value is slower for the treated wood compared to the untreated one. A similar decrease in the lignin index values on exposure to UV radiation was observed for ionic liquid treated wood.⁴¹

The crystallinity index values were found to decrease for both the untreated and treated wood

samples, as shown in Table 2. The values were calculated from FTIR spectra on exposure to UV rays for different time periods. It was observed that the rate of decrease of the crystallinity index was less pronounced in the treated wood than in the untreated wood. MFFA/DMDHEU interacted with the hydroxyl group of cellulose, forming a crosslinked structure. Nanoclay prevented the photodegradation process by acting as a screen for the UV rays. Thus, the crystallinity of the composite was less affected by the UV irradiation.

Scanning electron micrographs of UV degraded samples after 60 days of exposure to UV rays are shown in Figure 10. Photodegradation occurred and the surface morphology of the samples changed due to exposure to UV radiation. The untreated wood samples showed cracks on their surfaces. The samples treated with MFFA/DMDHEU underwent enhanced interfacial interaction, which

lowered the formation of cracks on the surface. The addition of nanoclay to MFFA/DMDHEU increased surface smoothness by protecting the wood from UV rays.

The changes in mechanical properties after 60 days of UV exposure are presented in Table 6. WPC treated with nanoclay showed less reduction in mechanical properties, while the highest loss was observed in the case of the untreated wood. With the increase in the amount of nanoclay, the loss of the mechanical properties was found to decrease due to the UV screening effect provided by nanoclay.

CONCLUSION

Wood polymer nanocomposites (WPNC) were prepared by vacuum impregnation of MFFA, DMDHEU and nanoclay. The WPG (%), volumetric swelling and hardness enhanced upon addition of nanoclay. The FTIR study indicated an interaction between wood, polymer and clay. XRD study confirmed that there was a decrease in the crystallinity of the WPNC. The crystallinity index values were found to decrease for the treated wood samples, as determined from FTIR and XRD. SEM study showed the existence of polymer and clay within the cell wall or lumen of wood. The uniform distribution of nanoclay in the composite was evidenced by TEM analysis. Dimensional stability, chemical resistance, flame retardant and mechanical properties were found to increase with the inclusion of nanoclay into the composite. UV resistance of the composites improved significantly, as observed from the measurement of weight loss, carbonyl index, lignin index, crystallinity index values and mechanical properties, as well as from SEM analysis.

REFERENCES

- A. K. Bledzki and J. Gassan, *Prog. Polym. Sci.*, **24**, 221 (1999).
- W. H. Lü and G. J. Zhao, *Forest. Stud. China*, **9**, 45 (2007).
- R. R. Devi, T. K. Maji and A. N. Banerjee, *J. Appl. Polym. Sci.*, **93**, 1938 (2004).
- R. N. Darie, R. Bodirlau, C. A. Teaca, J. Macyszyn, M. Kozłowski *et al.*, *Int. J. Polym. Anal. Charact.*, **18**, 315 (2013).
- J. Z. Lu, Q. Wu and H. S. McNabb Jr., *Wood Fiber Sci.*, **32**, 88 (2000).
- W. Gindl, C. Hansmann, N. Gierlinger, M. Schwanninger, B. Hinterstoisser *et al.*, *J. Appl. Polym. Sci.*, **93**, 1900 (2004).
- W. Gindl, F. Zargar-Yaghubi and R. Wimmer, *Bioresour. Technol.*, **87**, 325 (2003).
- E. Baysal, S. K. Ozaki and M. K. Yalinkilic, *Wood Sci. Technol.*, **38**, 405 (2004).
- M. H. Schneider, *Wood Sci. Technol.*, **29**, 121 (1995).
- T. M. Venas and A. Rinnan, *Chemomet. Intell. Lab.*, **92**, 125 (2008).
- S. Lande, O. Høibø and E. Larnøy, *Wood Sci. Technol.*, **44**, 105 (2010).
- B. Esteves, L. Nunes and H. Pereira, *Eur. J. Wood Prod.*, **69**, 521 (2011).
- Y. Xie, A. Krause, C. Mai, H. Militz, K. Richter *et al.*, *Polym. Degrad. Stabil.*, **89**, 189 (2005).
- P. Kiliaris and C. D. Papaspyrides, *Prog. Polym. Sci.*, **35**, 902 (2010).
- F. L. Xue and G. J. Zhao, *For. Stud. China*, **10**, 199 (2008).
- X. Cai, B. Riedl, S. Y. Zhang and H. Wan, *Composites A*, **39**, 727 (2008).
- S. S. Ray and M. Okamoto, *Prog. Polym. Sci.*, **28**, 1539 (2003).
- W. H. Lu, G. J. Zhao and Z. H. Xue, *For. Stud. China*, **8**, 35 (2006).
- M. Alexandre, P. Dubois, T. Sun, J. M. Garces and R. Jérôme, *Polymer*, **43**, 2123 (2002).
- A. Hazarika and T. K. Maji, *J. Wood Chem. Tech.*, **33**, 103 (2013).
- A. Hazarika and T. K. Maji, *Polym. Eng. Sci.*, **54**, 1019 (2014).
- A. Hazarika and T. K. Maji, *Polym. Eng. Sci.*, **53**, 1394 (2013).
- R. R. Devi and T. K. Maji, *Polym. Bull.*, **69**, 105 (2012).
- N. M. Stark and L. M. Matuana, *Polym. Degrad. Stabil.*, **86**, 1 (2004).
- C. M. Popescu, G. Singurel, M. C. Popescu, C. Vasile, D. S. Argyropoulos *et al.*, *Carbohydr. Polym.*, **77**, 851 (2009).
- Y. Xie, Z. Xiao, T. Grüneberg, H. Militz, C. A. S. Hill *et al.*, *Compos. Sci. Technol.*, **70**, 2003 (2010).
- R. R. Devi and T. K. Maji, *Wood Sci. Technol.*, **46**, 299 (2012).
- J. A. Lori, O. M. Myina, E. J. Ekanem and A. O. Lawal, *Res. J. Appl. Sci. Eng. Technol.*, **3**, 440 (2011).
- T. R. Jang, T. C. Sheu, J. J. Sheu and C. C. Chen, *Text. Res. J.*, **63**, 679 (1993).
- C. Song, T. Wang, X. Wang, J. Qiu and Y. Cao, *Sep. Purif. Technol.*, **58**, 412 (2008).
- R. R. Devi and T. K. Maji, *J. Appl. Polym. Sci.*, **122**, 2099 (2011).
- W. H. Lu and G. J. Zhao, *Front. For. China*, **3**, 121 (2008).
- M. Wada, T. Okano and J. Sugiyama, *Cellulose*, **4**, 221 (1997).
- N. E. Marcivich, M. M. Reboredo and M. I. Aranguren, *Therm. Chem. Acta*, **372**, 45 (2001).
- N. Shiraishi, T. Matsunaga, T. Yokota and Y. Hayashi, *J. Appl. Polym. Sci.*, **24**, 2347 (1979).

- ³⁶ A. Dieste, A. Krause, S. Bollmus and H. Militz, *Holz. Roh Werkst.*, **66**, 281 (2008).
- ³⁷ W. Wu and C. Y. Yang, *Polym. Degrad. Stabil.*, **85**, 623 (2004).
- ³⁸ G. Camino, G. Tartagilione, A. Frache, C. Manfredi and G. Costa, *Polym. Degrad. Stabil.*, **90**, 354 (2005).
- ³⁹ B. K. Deka and T. K. Maji, *Compos.: Part A*, **42**, 686 (2011).
- ⁴⁰ I. Grigoriadou, K. M. Paraskevopoulos, K. Chrissafis, E. Pavlidou, T. G. Stamkopoulos *et al.*, *Polym. Degrad. Stabil.*, **96**, 151 (2011).
- ⁴¹ S. Patachia, C. Croitoru and C. Friedrich, *Appl. Surf. Sci.*, **258**, 6723 (2012).