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ORIGINAL PAPER

Studies on properties of softwood (*Ficus hispida*)/ PMMA nanocomposites reinforced with polymerizable surfactant-modified nanoclay

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Abstract Soft wood (*Ficus hispida*) was chemically modified by impregnation of methyl methacrylate monomer, glycidyl methacrylate (GMA), a cross-linking agent, and montmorillonite (MMT) using catalyst heat treatment. MMT was modified by using a polymerizable surfactant 2-acryloloxy ethyl trimethyl ammonium chloride (ATAC) and a mixture of surfactants ATAC and cetyl trimethyl ammonium bromide (CTAB) in a molar ratio of (1:1). A comparative study on different properties of the prepared wood polymer nanocomposite (WPNC) based on impregnation of intercalating mixture containing MMA/GMA/clay modified by both the surfactants (ATAC and CTAB) and MMA/GMA/clay modified by only surfactant ATAC were done. FTIR, XRD, and TGA studies were employed for the characterization of clay and WPNC. WPNC prepared by using combined surfactant-modified clay along with MMA/GMA exhibited improved dimensional stability, chemical resistance, thermal stability, mechanical properties, and lower water uptake than that of WPNC prepared by using single surfactant-modified clay and MMA/GMA system.

Keywords Soft wood · MMA prepolymer · Organo-MMT · Preparation · Characterization

Introduction

Wood is a cellular polymeric composite material abundantly available in nature. It is used, not only as a fuel but also as a versatile material for domestic purposes like shed and other structures, furniture, tools, vehicles, and decorative objects because of its accessibility. Though it has aesthetic appearance and is used widely in engineering applications, it has certain disadvantages like susceptible to shrinking, swelling, attack by fungi, insects, etc.

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In general, soft woods are used for fuel purposes due to their lack of strength and dimensional stability. Chemical modification of wood will make them value-added material. Over the years, researchers have tried to improve the properties of wood chemically by impregnation method with water soluble, thermosetting resins like phenol, urea, and melamine formaldehyde resin [1–3] or with vinyl polymer followed by in situ polymerization [4]. Chemical modification of wood with vinyl monomers has shown less dimensional stability. Addition of glycidyl methacrylate (GMA) as a cross-linker will enhance its properties significantly [5, 6]. Beside impregnation, researchers have also used other techniques to develop wood polymer composite (WPC). Ashori [7] has developed WPC by using thermoset as well as thermoplastic polymer as matrix and plant fiber as a reinforcement filler.

In addition to vinyl monomer, cross-linker, nanosized filler, or reinforcement will make a remarkable improvement in thermal, physical, and mechanical properties of wood. Montmorillonite (MMT) is commonly used as nanofiller because of its low cost, natural abundance, and environmentally benign behavior. Wood polymer nanocomposite (WPNC) has been prepared by impregnating water soluble phenol formaldehyde resin and Ca-MMT as nanofiller by intercalation compounding [8, 9]. A significant improvement in properties has been found when aspen wood is impregnated with melamine formaldehyde–urea resin and MMT [10]. It has also been reported that inclusion of nanoclay as reinforcement filler improves the mechanical properties and water resistance of medium density fiberboard [11]. Kiani et al. [12] has studied the effects of two fillers form pulp fiber and wood flour on thermal stability and water absorption of PVC composites.

Since clay is inorganic in nature, homogenous dispersion of clay in the hydrophobic oligomer is not possible. Therefore, clay is to be modified organically with alkyl ammonium surfactant so that the surface of clay becomes organophilic and can be further intercalated or delaminated in presence of polymer and successfully introduced into wood [13, 14].

In this study, a mixture of two surfactant 2-acryloyloxy ethyl trimethyl ammonium chloride (ATAC) and cetyl trimethyl ammonium bromide (CTAB) was employed to modify clay. CTAB is expected to increase the interlayer distance of clay layer through its long chain alkyl groups while the acrylic group of ATAC can able to copolymerize with MMA [15, 16]. Therefore, the use of mixed surfactants (ATAC + CTAB) is expected to exhibit better properties compared to that of single surfactant, ATAC. The present work aims at comparing the various properties between WPNC prepared by using MMA/GMA/ATAC-modified nanoclay and MMA/GMA/combined (ATAC + CTAB) surfactant-modified nanoclay.

Methods

Materials

Fig wood (*Ficus hispida*) was collected locally. Methyl methacrylate purchased from Merck (Germany), was purified by standard procedure. 2,2′-azobisisobutyronitrile (AIBN) was purchased from Ranbaxy Fine Chemicals Ltd. (New Delhi, India). GMA was purchased from Merck (Mumbai, India). MMT K10 and ATAC were purchased from Sigma-Aldrich (USA). CTAB was obtained from CDH (New Delhi). All other chemicals were of analytical grade.

Sample preparation

The wood samples were made into blocks of 2.5 × 1 × 2.5 cm^3 (radial × tangential × longitudinal) for dimensional stability, water uptake and chemical resistance tests, 10 × 0.5 × 2 cm^3 (radial × tangential × longitudinal) for tensile strength, and 1 × 1 × 10 cm^3 (radial × tangential × longitudinal) for bending strength measurements.

Modification of MMT

Clay was modified organically by ion exchange reaction [17]. MMT (K10) having CEC 119 mEq 100 g^{-1} was dispersed in deionised water for 24 h by using mechanical stirrer. It was then subjected to sonication for 30 min. The mixture of surfactants CTAB and ATAC (1:1 mol mol^{-1}) was prepared in deionised water separately and added slowly to the dispersed clay. The resultant mixture was stirred for another 24 h. The white precipitate obtained was filtered, washed with (1:9) hot ethanol–water followed by washing with water several times. Finally, it was dried in vacuum oven at 45 °C for 24 h and grinded into powder. Another set of organophilic clay was prepared in the similar way by using ATAC alone.

Preparation of methyl methacrylate prepolymer

A prepolymer of methylmethacrylate was prepared by bulk technique at 45–50 °C in an oil bath in presence of 0.05 phr AIBN for approximately 45 min. It was then poured to a closed flask and placed at ambient temperature to cool down. The viscosity (at 30 °C) of different prepared batches of MMA prepolymer was measured and found almost similar as judged by Ubbelohde viscometer. The clay modified by ATAC/CTAB (1:1) (designated as clay I) was dispersed in solvent (THF) and added to the prepolymer. It was then sonicated for about 15 min. Similarly clay modified by ATAC (designated as clay II) was dispersed in THF, added to prepolymer and sonicated for 15 min. These mixtures were used as impregnation solution for subsequent studies.

Preparation of WPC

Wood samples were dried in an oven at 105 °C until constant weights and dimensions were obtained. The samples were then placed in an impregnation chamber. Load was applied over each sample to prevent the samples from floatation during addition of the impregnation mixture. Vacuum was applied for a specified time period for removing the air from the pores of the wood before addition of prepolymer mixture.

Now the mixture of MMA prepolymer, GMA, AIBN along with clay 1 or mixture of MMA prepolymer, GMA, AIBN along with clay 2 or MMA prepolymer with GMA and AIBN, or that of MMA prepolymer with AIBN alone was added from a dropping funnel to completely immerse the wood samples. The samples were then kept in the chamber at room temperature (30 °C) for another 4 h after attaining atmospheric pressure. This is minimum time to get maximum polymer loading. Different parameters like monomer concentration, time of impregnation, initiator concentration, GMA concentration, modified MMT concentration were changed during impregnation condition. The samples were then taken out of the impregnation chamber and the excess chemicals were wiped out from the surface. Now they were cured in an oven at 90 °C for 24 h by wrapping in aluminum foil. This was followed by drying at 105 °C in an oven for 24 h. The samples were subjected to solvent extraction using benzene as solvent for 24 h to remove the homopolymers. Finally, the samples were dried and dimension was measured using a slide caliper and weights were taken.

Measurements

Weight percent gain

WPG after polymer loading was calculated according to the formula

$$\mathrm{WPG}\ (\%) = (W_2 - W_1)/W_1 \times 100$$

where W_1 was oven dry weight of wood blocks before polymer treatment and W_2 was oven dry weight of blocks after polymer treatment.

Volume increase (%)

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

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

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

Water uptake 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 and expressed as

$$\text{Water uptake}\ (\%) = (W_\mathrm{t} - W_\mathrm{d})/W_\mathrm{d} \times 100$$

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

Hardness

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

Water vapor exclusion test

Oven-dried wood samples were conditioned at 30 °C and 30% relative humidity (RH) and weighed. Samples were then placed in a chamber where temperature and RH were maintained at 30 °C and 65%, respectively. Weights were remeasured after different time period 0.5, 2, 6, 24, 48, 96, 120, 144, and 168 h. It was expressed as a percentage of moisture absorbed based on oven dry weight.

Water repellent effectiveness (WRE)

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

$$\mathrm{WRE} = (D_\mathrm{t} - D_\mathrm{o})/D_\mathrm{o} \times 100$$

where D_o is the water uptake of untreated samples immersed for 0.5, 2,6, 24, 48, 96, 120, 144, and 168 h and D_t is the water uptake of treated wood samples immersed for the same periods.

Dimensional stability test

Swelling in water vapor

Samples were first dried at 105 °C and dimensions were measured. Samples were then placed in chamber where temperature and RH were maintained at 30 °C and 65%, respectively. The dimensions were remeasured after 0.5, 2, 6, 24, 48, 96, 120, 144, and 168 h.

Swelling in water

Dimensions of the oven-dried samples were measured and conditioned at room temperature (30 °C) and 30% RH. The samples were then immersed in distilled water and then 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,

$$\%\ \mathrm{Swelling} = (V_{\mathrm{t,u}} - V_\mathrm{o})/V_\mathrm{o} \times 100$$

where $V_{\mathrm{t,u}}$ is the volume of the untreated or treated wood after water absorption and V_o is the volume of the untreated or treated wood before water absorption.

The antiswell efficiency (ASE) index was determined to evaluate dimensional stability of 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 the formula:

$$S(\%) = (V_2 - V_1)/V_1 \times 100$$

where V_2 is the volume of the water saturated blocks and V_1 is the volume of the oven-dried blocks. The values were obtained by measuring longitudinal, tangential, and radial dimensions of the oven dried and water saturated blocks using slide caliper.

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

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

where S_c is the volumetric swelling coefficient of untreated blocks and S_t 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 by using the equation as given below:

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

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

X-ray diffraction (XRD) studies

The crystallographic studies were done by XRD analysis using Rigaku X-ray diffractometer (Miniflax, UK) and employing CuK$_\alpha$ radiation ($\lambda = 0.154$ nm), at a scanning rate of 1° min^{-1} with an angle ranging from 2° to 40°.

Fourier transform infrared spectroscopy study (FTIR)

The treated and untreated samples were grinded and FTIR spectra were recorded by using KBr pellet in a Nicolet (Madison, USA) FTIR Impact 410 spectrophotometer.

Morphological studies

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

Mechanical behavior study

The flexural properties of the samples were measured by UTM-HOUNSFIELD, England (model H100K–S) with a cross-head speed of 2 mm min^{-1} and by calculating the modulus of elasticity and modulus of rupture (MOR) according to ASTM D-790 method.

MOR was calculated as follows:

$$\text{MOR} = 3WL/2bd^2$$

where W is the ultimate failure load (N), L is the span between centers 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 properties were measured by using by UTM-HOUNSFIELD, England (model H100K–S) with a 10-kN load cell and cross-head speed of 10 mm min^{-1} according to ASTM D-638 method.

Thermal study

Thermal properties of the untreated and treated wood samples were evaluated by using thermogravimetric analyzer (TGA). TGA study was carried out using a thermo gravimetric analyzer (model Metler TA 4000) at a heating rate of 20 °C min^{-1} up to 500 °C. The studies were done under nitrogen atmosphere.

Results and discussion

The maximum improvement in properties was found by varying impregnation conditions like monomer concentration, initiator concentration, vacuum, time of impregnation, amount of cross-linking agent, and modified MMT. Organophilic clay was dispersed initially in THF and finally in MMA prepolymer. The minimum ratio (v/v) of MMA and THF used for the dispersion of clay was 5:1. The final optimized conditions, at which maximum improvement of properties were observed as follows: MMA (mL): 100, THF (mL): 20, AIBN: 0.5 phr, vacuum: 508 mmHg, time of impregnation: 4 h, GMA (mL): 3, clay I: 0.5–1.5 phr, and clay II: 0.5–1.5 phr.

Effect of variation of clay on WPG %, volume increase, and hardness

Results are shown in Table 1. From Table 1, it was observed that wood treated with MMA/THF improved overall properties like weight gain (%), volume increase and hardness. This was due to deposition of polymer in the void spaces and capillaries of wood. The deposition of polymer was improved by the presence of cross-linking agent GMA which could interact with both the polymer and wood through its double bond and glycidyl group. The addition of clay further improved the properties. The improvement in properties was more in clay I treated samples compared to those of clay II treated samples. The enhancements in properties were due to restriction in the mobility of the intercalated polymer chain inside the silicate layers of clay. Further the acrylic group of ATAC in clay I could undergo copolymerization with MMA monomer while the long chain alkyl group of CTAB facilitated the expansion of clay gallery to accommodate the MMA polymer [16]. The ATAC alone in clay II might not able to expand the interlayer spacing of clay like that of clay I.

Water uptake study

Related results are shown in Fig. 1. With the increase in time of immersion, it was found that water uptake (%) increased for both treated and untreated wood samples.

Table 1 Effect of variation of clay modified with ATAC/CTAB (1:1) and only ATAC on polymer loading (WPG %), volume increase and hardness

Samples particulars	Weight % gain	Volume increase %	Hardness (Shore D)
Untreated	–	–	45 (±1.57)
Samples treated with MMA/THF/GMA/clay I/clay II			
100/20/0/0/0	23.59 (±0.83)	2.78 (±0.71)	47 (±1.14)
100/20/3/0/0	33.92 (±0.42)	2.96 (±0.31)	51 (±1.08)
100/20/3/0.5/0	37.43 (±0.57)	3.68 (±0.89)	57 (±1.21)
100/20/3/0/0.5	34.67 (±0.58)	3.13 (±1.37)	54 (±1.25)
100/20/3/1.0/0	39.56 (±1.43)	3.97 (±1.06)	58 (±1.06)
100/20/3/0/1.0	36.17 (±0.94)	3.32 (±0.63)	56 (±1.32)
100/20/3/1.5/0	40.37 (±1.02)	4.11 (±0.68)	62 (±1.12)
100/20/3/0/1.5	38.87 (±1.07)	3.73 (±1.24)	57 (±0.76)

Clay I: clay modified with ATAC/CTAB (1:1)

Clay II: clay modified with ATAC

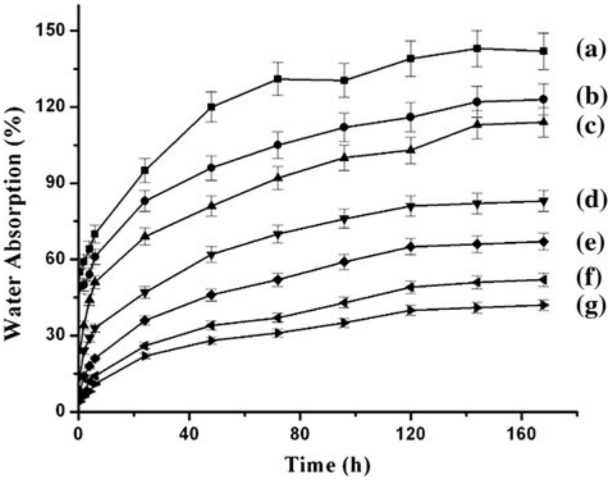

Fig. 1 Water absorption test of (*a*) untreated wood and wood treated with (*b*) MMA, (*c*) MMA/GMA, (*d*) MMA/GMA/clay I (0.5 phr), (*e*) MMA/GMA/clay I (1.0 phr), (*f*) MMA/GMA/clay II (1.5 phr), and (*g*) MMA/GMA/clay I (1.5 phr)

Untreated wood samples showed highest water absorption capacity. Samples treated with MMA showed less water uptake since the capillaries of wood were filled up by the polymer. The water uptake of the samples treated with MMA/GMA decreased further due to the cross-links formed between double bond and glycidyl group of GMA with double bond of MMA and hydroxyl group of wood, respectively [18]. Samples treated with MMA/GMA/modified MMT showed least water uptake. The layers of modified clay provided the tortuous path for water transport and hence restricted the diffusion of water molecules [10]. Wood samples treated with MMA/GMA/clay I absorbed less water compared to samples treated with MMA/GMA/

clay II. CTAB present in clay I increased the interlayer spacing of clay and enhanced the tortuous path for diffusion of water molecules.

Water vapor exclusion test

The results showing the water vapor exclusion test are presented in Fig. 2. The rate of water vapor absorption followed the order: untreated > MMA treated > MMA/GMA treated > MMA/GMA/clay II (1.5 phr) > MMA/GMA/clay I (1.5 phr). Hydrophilic nature of untreated wood was responsible for showing highest water uptake. Impregnation of wood with MMA would fill the void spaces and capillaries present in the wood. The addition of GMA would form the cross-linking between wood and polymer due to which it absorbed less water. Water diffusivity further decreased on addition of clay due to increase in tortuous path as explained earlier.

WRE study

Results are shown in Table 2. Maximum improvement in WRE was observed for the samples treated with MMA/GMA/clay I. The explanation was similar to that of described earlier.

Dimensional stability test

Swelling in water vapor

The results showing the effect of swelling are shown in Fig. 3. The samples treated with MMA/GMA/clay I showed least swelling in water. This was due to the

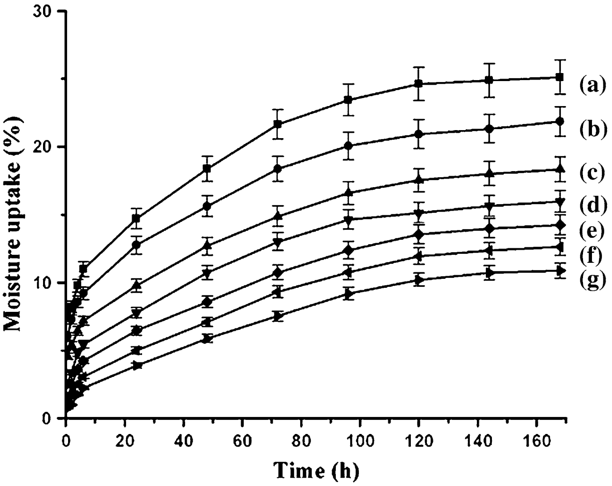

Fig. 2 Water vapor exclusion test (*a*) untreated wood and wood treated with (*b*) MMA, (*c*) MMA/GMA, (*d*) MMA/GMA/clay I (0.5 phr), (*e*) MMA/GMA/clay I (1.0 phr), (*f*) MMA/GMA/clay II (1.5 phr), and (*g*) MMA/GMA/clay I (1.5 phr)

Table 2 Water repellant effectiveness (WRE %) of WPC

Time (h)	MMA treated	MMA/GMA treated	MMA/GMA/ clay I (0.5 phr) treated	MMA/GMA/ clay I (1 phr) treated	MMA/GMA/ clay I (1.5 phr) treated	MMA/GMA/ clay II (1.5 phr) treated
0.5	47.60 (±0.5)	89.43 (±0.77)	94.37 (±0.97)	96.19 (±0.12)	97.03 (±0.32)	96.52 (±0.88)
2	44.69 (±0.76)	76.58 (±0.45)	79.26 (±1.09)	81.17 (±0.16)	90.37 (±0.03)	88.61 (±0.51)
4	42.53 (±0.47)	72.64 (±0.84)	75.44 (±0.76)	77.91 (±0.24)	86.46 (±0.43)	80.47 (±0.37)
6	38.47 (±0.86)	69.98 (±1.74)	73.51 (±0.49)	75.91 (±0.09)	78.62 (±0.12)	76.77 (±0.43)
24	37.74 (±1.38)	59.30 (±1.54)	61.73 (±0.54)	61.08 (±0.64)	69.53 (±0.37)	66.58 (±0.67)
48	33.02 (±1.63)	55.47 (±1.68)	56.07 (±0.41)	57.33 (±0.73)	62.81 (±0.15)	58.27 (±0.54)
72	29.63 (±1.52)	55.21 (±0.37)	55.68 (±0.72)	57.12 (±0.04)	61.27 (±0.56)	57.92 (±0.48)
96	26.74 (±0.74)	51.71 (± 0.47)	55.31 (±0.34)	57.11 (±0.57)	60.93 (±0.08)	57.34 (±0.72)
120	26.51 (±0.27)	49.96 (±0.29)	55.23 (±0.64)	57.04 (±0.46)	60.72 (±0.85)	57.17 (±0.57)
144	16.07 (±1.73)	49.43 (±0.74)	54.81 (±0.53)	56.94 (±0.48)	60.48 (±0.63)	58.88 (±0.04)
168	16.02 (±0.66)	49.27 (±0.52)	54.69 (±0.71)	56.83 (±0.71)	60.33 (±0.53)	58.56 (±0.58)

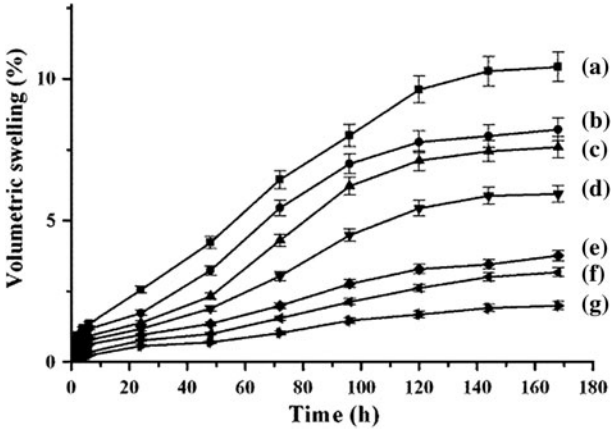

Fig. 3 Volumetric swelling in water vapor at 65% RH and 30 °C of wood samples (*a*) untreated wood and wood treated with (*b*) MMA, (*c*) MMA/GMA, (*d*) MMA/GMA/clay I (0.5 phr) treated, (*e*) MMA/GMA/clay I (1.0 phr) treated, (*f*) MMA/GMA/clay II (1.5 phr), and (*g*) MMA/GMA/clay I (1.5 phr)

increase of silicate layer spacing caused by the presence of alkyl group of CTAB along with the deposition of cross-linked MMA polymer in the void spaces of wood.

Swelling in water

The results of the effects of swelling in water at room temperature for both treated and untreated samples are shown in Fig. 4. Treated samples showed more reduction in swelling in comparison with the untreated ones. At similar clay loading, clay I treated wood samples swelled less compared to clay II treated samples. In clay I, the increase of silicate layer spacing caused by interaction of alkyl group of CTAB offered more resistance to the passage of water molecules and hence showed more reduction in swelling.

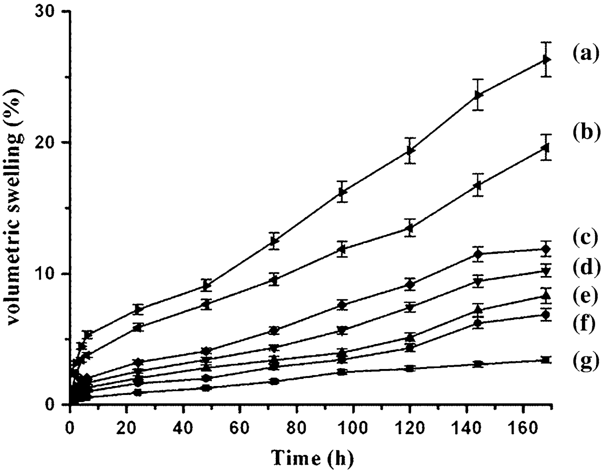

Fig. 4 Volumetric swelling in water at 30 °C of wood samples (*a*) untreated wood and wood treated with (*b*) MMA, (*c*) MMA/GMA, (*d*) MMA/GMA/clay I (0.5 phr), (*e*) MMA/GMA/clay I (1.0 phr), (*f*) MMA/GMA/clay II (1.5 phr), and (*g*) MMA/GMA/clay I (1.5 phr)

Antiswelling efficiency

The results of the ASE are shown in Table 3. ASE was highest in case of the samples treated with MMA/GMA/clay I.

The improvement of the dimensional stability was due to the combined effect of deposition of polymer inside the void spaces and capillaries of wood and the presence of clay. The clay layer acted as a barrier for the diffusion of water molecules.

Table 3 ASE (%) of treated wood samples at different time period

Time (h)	MMA treated	MMA/GMA treated	MMA/GMA/clay I (0.5 phr) treated	MMA/GMA/clay I (1 phr) treated	MMA/GMA/clay I (1.5 phr) treated	MMA/GMA/clay II (1.5 phr) treated
0.5	59.12 (±0.07)	65.65 (±0.89)	73.18 (±0.84)	78.45 (±0.56)	90.64 (±0.67)	85.39 (±0.61)
2	57.38 (±0.86)	57.41 (±0.06)	68.52 (±0.42)	72.36 (±0.36)	89.49 (±0.46)	79.31 (±0.93)
4	56.70 (±0.05)	84.71 (±0.72)	87.53 (±1.08)	88.22 (±0.71)	89.05 (±0.68)	88.43 (±1.21)
6	56.20 (±1.42)	84.27 (±0.74)	87.31 (±0.64)	87.69 (±0.29)	88.53 (±0.47)	87.91 (±0.58)
24	55.28 (±0.67)	83.06 (±0.82)	86.77 (±0.28)	87.32 (±0.52)	87.49 (±0.04)	87.48 (±0.17)
48	54.91 (±0.07)	82.14 (±1.63)	86.28 (±0.57)	86.72 (±0.47)	86.75 (±0.32)	86.87 (±0.47)
72	54.64 (±0.23)	81.97 (±1.46)	85.82 (±0.44)	86.02 (±0.63)	85.78 (±0.08)	86.13 (±0.03)
96	53.06 (±0.42)	81.15 (±1.12)	85.37 (±0.75)	85.56 (±0.52)	84.55 (±0.37)	85.73 (±0.34)
120	52.75 (±0.69)	80.89 (±1.45)	84.92 (±1.04)	85.13 (±0.84)	83.49 (±0.46)	85.25 (±0.23)
144	51.34 (±0.57)	80.36 (±0.08)	84.46 (±0.68)	84.63 (±0.12)	83.36 (±0.02)	84.83 (±1.02)
168	51.22 (±0.88)	80.14 (±0.75)	84.03 (±0.42)	84.27 (±0.96)	83.12 (±0.06)	84.62 (±0.73)

Chemical resistance test

Results are shown in Table 4. Swelling was least in the case of samples treated with MMA/GMA/clay I. With the increase in the amount of clay swelling decreased. The void spaces and capillaries of the wood were filled up by MMA. GMA enhanced the interaction through the formation of cross-linking between MMA and wood which resulted in decrease of swelling.

Clay layers further restricted the path for the diffusion of chemicals and hence swelling decreased. The interaction between sodium hydroxide, wood cellulose, and clay layers might be responsible for the observed higher swelling of samples in sodium hydroxide compared to acetic acid.

XRD studies

Figure 5 shows the XRD patterns of unmodified and organically modified MMT. The diffraction peak for unmodified MMT (curve a) appeared at $2\theta = 8.37°$. Clay I (curve b) and clay II (curve c) showed sharp peak at $2\theta = 5.97$ and 7.09, respectively. The shifting of peak to lower angle indicated that interlayer spacing of silicate layers increased. The shifting was more in the case of clay treated with combined surfactants. The alkyl group of CTAB was responsible for the expansion of the MMT gallery. The increase of MMT interlayer spacing by the use of combined surfactant CTAB and 2[(acryloyloxy) ethyl](4-benzyl-)dimethyl ammonium bromide was reported in literature [16].

Figure 6 shows the XRD spectra of untreated wood and the composites. Wood powder (curve a) shows a wide diffraction peak near 22.91° of 2θ which was due to the maximum diffraction of the (002) crystal plane of cellulose. Cellulose is the principal constituent of wood. Curve b represents the XRD spectra of clay I treated PMMA composite. A broad band peaking at around $2\theta = 16.27°$, which is due to the presence of PMMA matrix present in the composite [19]. Curves c and d showed the XRD spectra of wood samples treated with PMMA/GMA/clay II and PMMA/GMA/clay I. In both the cases, the intensity of the diffraction peak of cellulose (002) crystal plane decreased. The crystalline peak of cellulose was also found to shift to 22.8 for clay II and 22.5 for clay I from 22.9°. Furthermore, the characteristic peak for modified MMT at 5.97° disappeared. It could be said that either the full expansion of clay galleries occurred which was not possible to detect by XRD or the MMT layers became delaminated and no crystal peak appeared [9]. The XRD results suggested that crystallinity in wood composite decreased and some silicate nanolamina were penetrated into the amorphous region of cellulose wood cell wall. Similar observation was reported by Devi and Maji [20].

FTIR study

Figure 7 represents the FTIR spectra of unmodified MMT and MMT modified with combined surfactant (CTAB + ATAC) and ATAC alone. Unmodified MMT (curve a) showed bands at 3,431 cm^{-1} (–OH stretching), 1,636 cm^{-1} (–OH bending), 1,052–532 cm^{-1} (oxide bands of Al, Mg, Si, etc.). In CTAB/ATAC (curve b)

Table 4 Chemical resistance test of the WPC samples

Medium	Duration (h)	Volumetric swelling						
		Untreated	MMA	MMA/GMA	MMA/GMA/clay I (0.5 phr)	MMA/GMA/clay I (1 phr)	MMA/GMA/clay I (1.5 phr)	MMA/GMA/clay II (1.5 phr)
NaOH solution (4%)	24	12.33 (±0.33)	7.46 (±0.48)	7.43 (±0.87)	6.31 (±0.03)	5.84 (±0.53)	4.65 (±0.04)	5.38 (±0.06)
	168	14.76 (±0.46)	9.69 (±0.01)	9.58 (±0.52)	7.88 (±0.64)	7.01 (±0.41)	5.89 (±0.32)	6.91 (±0.37)
Acetic acid (4%)	24	7.63 (±0.75)	4.89 (±0.04)	4.87 (±1.01)	4.33 (±0.08)	3.91 (±0.11)	2.12 (±0.47)	3.67 (±0.43)
	168	10.11 (±0.83)	5.88 (±1.13)	5.36 (±1.07)	5.19 (±0.33)	5.03 (±0.09)	3.18 (±0.76)	4.73 (±0.53)

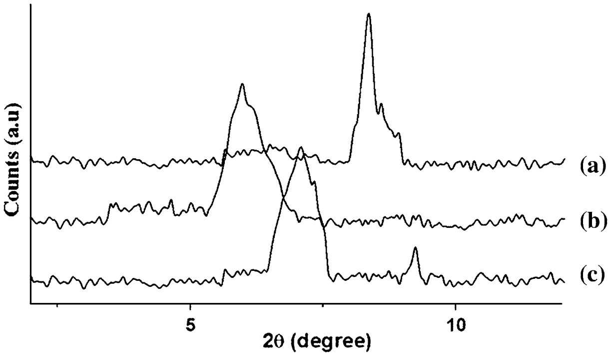

Fig. 5 XRD micrographs of (*a*) unmodified clay and clay modified by (*b*) ATAC/CTAB (1:1), and (*c*) ATAC

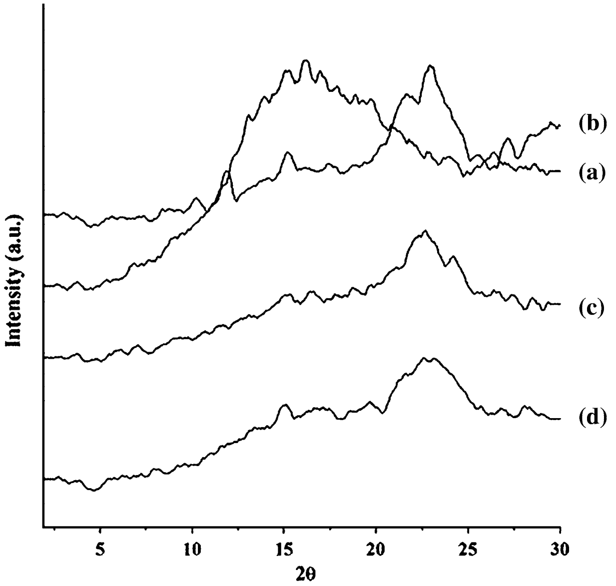

Fig. 6 XRD micrographs of (*a*) untreated wood, (*b*) MMA/GMA/clay I composite, and wood treated with (*c*) MMA/GMA/clay II, and (*d*) MMA/GMA/clay I

modified MMT, two new peaks appeared at 2,927 and 2,853 cm^{-1} were due to $-CH_2$ asymmetric stretching. Another peak appeared at 1,477 cm^{-1} was due to $-CH_2$ plane scissoring vibration of modifying hydrocarbon of the surfactant [20]. Similar peaks were also observed in the spectrum of MMT modified with ATAC (curve c).

Figure 8 shows the FTIR spectra of untreated and treated wood samples. Pure wood (curve a) showed absorption bands at 3,432 cm^{-1} (–OH stretching), 2,926 cm^{-1}, and 2,853 cm^{-1} ($-CH_2$ asymmetric stretching), 1,739 cm^{-1} (C=O stretching), 1,663 for (–OH bending), 1,251 and 1,020 cm^{-1} (C–O stretching) and 1,000–645 cm^{-1} (out of plane C–H bending vibration). Wood/PMMA (curve b)

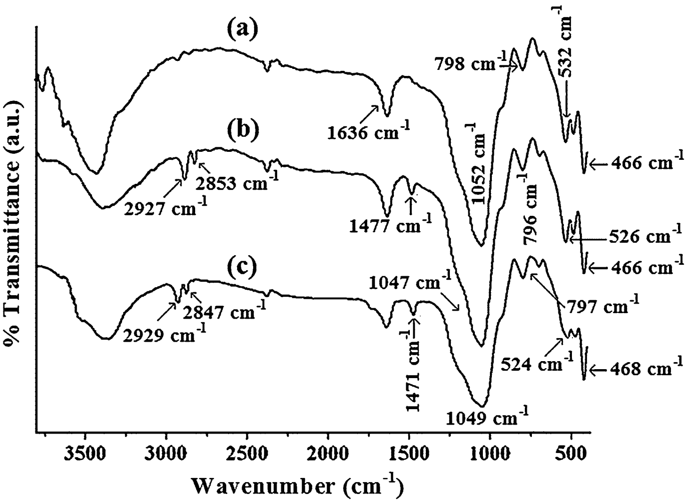

Fig. 7 FTIR spectra of (*a*) unmodified MMT, (*b*) clay I, and (*c*) clay II

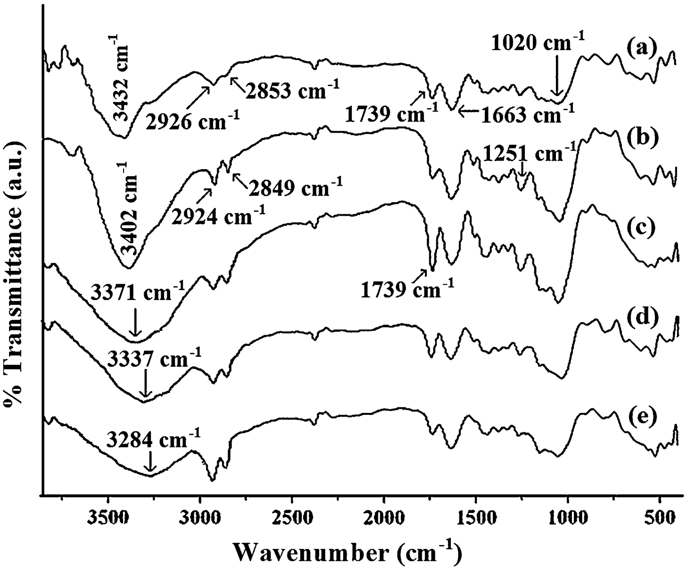

Fig. 8 FTIR spectra of (*a*) untreated wood and wood treated with (*b*) MMA, (*c*) MMA/GMA, (*d*) MMA/GMA/clay II, and (*e*) MMA/GMA/clay I

showed characteristic bands at 2,924 and 2,849 cm^{-1} for –CH$_2$ stretching, 1,251 cm^{-1} for C–O stretching of PMMA [21]. Curve c shows the spectrum for wood treated with MMA and GMA. The peak at 1,735 cm^{-1} for ester group became prominent and the intensity of bands for –OH stretching decreased as well as shifted to lower wave number. This was due to improvement in interaction between the hydroxyl group of wood and the PMMA polymer by GMA. Curve d and e represent the spectra for wood treated with MMA/GMA/clay II and MMA/GMA/clay I, respectively. It was observed that the intensities of –OH stretching was decreased and shifted to 3,371 cm^{-1} (curve c), 3,337 cm^{-1} (curve d) and 3,284 cm^{-1} (curve e) compared to 3,432 cm^{-1} (wood). The decrease in intensity and shifting of peaks to lower wave number might be due to the interaction of hydroxyl group of wood and clay with GMA and polymer. Further, it was observed that $-\text{CH}_2$ asymmetric peak intensity at 2,926 and 2,853 cm^{-1} was more pronounced in treated samples than the untreated ones indicating the interaction between wood, PMMA/GMA, and modified clay. Similar decrease and shifting in intensities of –OH stretching to lower wave number was reported by Deka and Maji [22] while studying the FTIR analysis of wood/polymer/clay nanocomposite.

Morphological studies

Figure 9 shows the SEM micrographs of fractured surfaces of unmodified and modified wood samples. The empty cell wall of wood was seen in untreated wood sample (Fig. 9a). These empty spaces were filled with the MMA polymer, MMA/GMA, MMA/GMA/clay (Fig. 9b–e). The polymeric materials were found to be present either in the cell lumen or in the cell wall. The presence of nanoclay was detected as white spot in the micrographs. (Fig. 9d, e).

Mechanical properties

Table 5 shows the value of flexural and tensile properties of untreated and treated wood samples. Both the flexural and tensile properties were found to enhance for the wood samples after the impregnation of MMA and GMA. The incorporation of GMA with MMA into untreated wood samples facilitated bond formation between

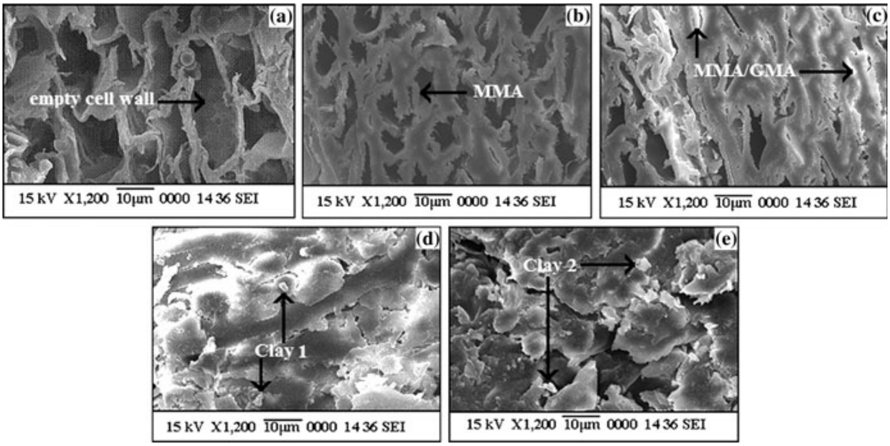

Fig. 9 Scanning electron micrographs of (**a**) untreated wood and wood treated with, (**b**) MMA, (**c**) MMA/GMA, (**d**) MMA/GMA/clay II, and (**e**) MMA/GMA/clay I

Table 5 Flexural and tensile properties of untreated and treated wood loaded with different percentage of clay

Sample	Flexural properties		Tensile properties	
	Strength (MPa)	Modulus (MPa)	Strength (MPa)	Modulus (MPa)
Untreated wood	119.3 ± 0.24	6009 ± 0.78	40.1 ± 0.68	299.6 ± 16.12
Wood treated with PMMA	121.3 ± 0.87	6097 ± 1.15	43.6 ± 1.25	310.7 ± 14.62
PMMA/GMA	122.1 ± 1.21	6120 ± 1.12	46.5 ± 1.16	324.1 ± 16.37
PMMA/GMA/0.5 phr clay I	123.7 ± 1.18	6504 ± 0.76	50.3 ± 1.42	354.6 ± 17.87
PMMA/GMA/1.0 phr clay I	123.9 ± 1.32	8812 ± 1.16	56.2 ± 1.53	408.5 ± 18.34
PMMA/GMA/1.5 phr clay I	129.6 ± 0.94	8893 ± 1.42	74.2 ± 1.23	469.5 ± 15.38
PMMA/GMA/1.5 phr clay II	127.3 ± 1.14	8836 ± 1.19	62.1 ± 1.17	447.6 ± 16.42

wood and polymer through its glycidyl group and double bond, respectively. Devi and Maji [23] studied the impregnation of styrene–acrylonitrile copolymer into wood and observed an increase in mechanical properties due to the incorporation of GMA. The values were further increased after the incorporation of organically modified clay. The higher the amount of clay, the higher was the tensile and flexural values. The observed higher values might be due to the well dispersion of silicate layers of clay and the restriction in the mobility of the polymer chains inside the intercalated layers of clay. At similar clay loading, wood samples treated with clay I exhibited better tensile and flexural values compared to clay II treated wood samples. The long alkyl chain of CTAB could expand the gallery of MMT and thereby could accommodate more MMA polymer. The mobility of the polymer chains were more restricted in clay I treated wood composite compared to clay II treated wood composite. Hence clay I treated wood composite showed higher tensile and flexural values.

Table 6 Thermal analysis of WPNC

Sample	T_i	$T_m{}^a$	$T_m{}^b$	Temperature of decomposition (T_D) in °C at different weight loss (%)				RW% at 600 °C
				20%	40%	60%	80%	
Untreated wood	165	308	396	265	299	330	–	27.1
Wood treated with PMMA	192	316	404	273	307	339	384	8.1
PMMA/GMA	215	321	411	282	315	347	396	10.6
PMMA/GMA/clay I (0.5)	229	329	418	291	321	353	410	13.5
PMMA/GMA/clay I (1.0)	245	336	425	301	332	364	439	16.4
PMMA/GMA/clay I (1.5)	272	351	439	321	354	384	–	23.1
PMMA/GMA/clay II (1.5)	258	342	432	310	345	375	556	19.8

T_i value for initial degradation

[a] T_m value for first step, [b] T_m value for second step

Thermogravimetric analysis

Table 6 represents the initial decomposition temperature (T_{i}), maximum pyrolysis temperature (T_{m}), decomposition temperature at different weight loss (%) (T_{D}) and residual weight (RW%) for the untreated wood samples and treated wood samples. T_{i} values of treated samples were higher than untreated samples. The polymer increased the thermal resistance and the compatibilizer increased the interfacial adhesion between wood and polymer. T_{i} value increased further after the incorporation of clay. The intercalated silicate layers of clay provided a barrier to the passage of decomposed volatile products throughout the composite. Better the distribution of silicate layers, higher is the barrier effect and hence better is the property [24]. With the increase in the amount of clay (0.5–1.5 phr), the thermal stability of the wood composite increased. Wood samples treated with double surfactant (CTAB + ATAC) modified clay exhibited higher thermal stability than those of treated with single surfactant (ATAC) modified clay. This might be due to the presence of long alkyl chain of CTAB along with the acryloxy group of ATAC that increased the interaction among wood, polymer, and clay.

T_{m} values for both the stages of pyrolysis for composites were more than untreated wood samples. T_{m} values for the first stage of pyrolysis was due to the depolymerization of hemicellulose, glycosidic linkage of cellulose, and thermal decomposition of cellulose [25] while the second stage of pyrolysis was due to the degradation of PMMA [26]. The incorporation of GMA improved T_{m} values for both the stages. The values increased further after the incorporation of clay. T_{D} values of (ATAC + CTAB)-modified clay (clay I) treated WPC samples were higher than those of ATAC-modified clay (clay II) treated WPC samples.

RW values of untreated wood sample were found maximum. RW values decreased after incorporation of polymer. GMA and clay further improved the RW values.

Conclusion

Chemical modification of Fig wood (*F. hispida*) were done by the impregnation of MMA prepolymer, GMA cross-linker and clay modified with either ATAC/CTAB (1:1) or ATAC. The WPG (%), volumetric swelling, hardness, water uptake (%), WRE (%), dimensional stability, and chemical resistance of WPC were found to enhance upon incorporation of clay. Samples treated with MMA/GMA/clay I showed more improvement in properties than MMA/GMA/clay II treated samples. X-ray studies revealed that gallery distance in clay layer increased due to treatment with CTAB and ATAC. X-ray studies also showed that the crystallinity in WPNC decreased. FTIR study indicated that there was some interaction between wood, MMA, GMA, and clay. The inclusion of clay improved thermal stability and mechanical properties. SEM study showed the existence of polymer, clay within the cell wall, or lumen of wood. The improvements in properties were more in WPNC treated with ATAC/CTAB-modified clay compared to WPNC treated with ATAC-modified clay.

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