

Preparation and Characterization of Wood/Styrene-Acrylonitrile Copolymer/MMT Nanocomposite

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ABSTRACT: Wood polymer nanocomposite (WPNC) was prepared by impregnating Simul (*Salmalia malabarica*) wood with styrene-acrylonitrile copolymer (SAN), glycidyl methacrylate (GMA), and a reactive polymerizable surfactant modified montmorillonite (MMT). The physical and mechanical properties of WPNC were investigated by using XRD, tensile tester, SEM, and FTIR. The polymer loading, dimensional stability, water uptake, mechanical property,

and thermal stability were found to improve due to inclusion of MMT. SEM micrographs showed the presence of polymer and MMT into cell wall and cell lumen. FTIR analysis confirmed the presence of MMT and SAN in WPNC. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2099–2109, 2011

Key words: simul; montmorillonite; styrene-acrylonitrile copolymer; preparation; characterization

INTRODUCTION

Wood, a renewable resource and naturally occurring composite material of biological origin, possesses unique structural characteristics that render it desirable for a broad variety of end uses. However it swells when it absorbs water and shrinks when dried. It is also susceptible to insect and fungal attack.

Woods can be classified as soft wood and hard wood. Softwoods, which are poor in strength and dimensional stability, find their uses mostly in fuel purposes. Their area of application as in making furniture, construction materials, etc., can be expanded through proper treatment such as chemical modification. The chemical modification of wood has been the subject matter of research for many decades.^{1–3} Impregnation under vacuum or pressure is the most promising among the various modification methods. Impregnating wood with polymerizable monomer formulation and then polymerizing it in place produces a wood polymer composite (WPC). WPC could be more useful for different applications and have a longer life because it is less susceptible to moisture induced swelling, shrinking, and biodeterioration and has a harder surface. Numerous reports are available in the literature for modification of wood by impregnation of polymer. The composites

prepared by wood, acrylic, or vinylic type monomers show better dimensional stability in the presence of moisture because of the confinement of more monomer in cell lumen compared with cell wall. The dimensional stability can be improved further if a monomer can enter and bulk the cell wall. Wood of different types impregnated with a polymer mixture containing a macro-monomer and styrene had improved water repellency, compression, and bending strength.⁴

Vinyl monomers and various impregnation compounds such as phenol, urea, melamine formaldehyde resin, polyethylene glycol, and isocyanate resins, etc., have been used for wood treatment. Gao and Li⁵ reported the chemical modification of poplar wood with foaming polyurethane resins leading to the improvement of dimensional stability and mechanical properties of the wood. To improve various physical and chemical properties of wood polymer composite, impregnated mixture should react with the cell wall of the wood. The use of glycidyl methacrylate with diallyl phthalate for obtaining dimensionally stable wood composite was reported in the literature.⁶ Glycidyl methacrylate could also be used as a coupling agent between solid rubber wood and styrene as suggested by Devi and Maji.⁷

For decades, many scientists around the world have made use of inorganic compounds to improve the properties of wood. Montmorillonite is one such compound which is widely used. It is cheap, abundantly available, and environmentally friendly. Moreover, it can enhance the properties such as

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dimensional stability, flame retardancy, surface hardness, barrier resistance, etc.

Nanocomposite technology with layered silicate nanoclays as *in situ* reinforcement has been extensively investigated in recent years.^{8–11} Nanomodified wood polymer composites could be a promising new approach to obtain the effective products with better physical, thermal, and mechanical properties. Various nanounits such as nanoparticles, nanotubes, nanolayers could be accommodated into wood for improvement of strength, moisture resistance, dimensional stability, etc.¹² Cai et al.¹³ prepared wood plastic nanocomposite by impregnation of melamine urea formaldehyde resin and different alluminosilicate nanofillers into solid aspen wood. They reported that impregnation of hydrophobic nanofillers dispersed in MUF prepolymer into wood improved significantly surface hardness, modulus of elasticity, and water repellency. Zhao et al.¹⁴ prepared wood/MMT nanocomposite by using phenol formaldehyde (PF) resin and found an improvement in various properties.

Styrene acrylonitrile (SAN) copolymer played an important role in many industries. Specimens treated with SAN polymer performed better weatherability than those of MMA treated wood composite.¹⁵ Clay based composite using SAN as polymer matrix improved mechanical strength and fire retardancy.^{16,17}

Most of the reports addressed the use of water soluble resin as an intermediate for making wood/montmorillonite (MMT) nanocomposite. The wood polymer nano-composites (WPNC) based on impregnation of water insoluble monomer or prepolymer and nanoclay has not been reported so far. There is enough scope to do further work in this area.

With all these ends in view, the present work has been undertaken. The present study is aimed at to prepare a styrene acrylonitrile copolymer (SAN) of low molecular weight followed by dispersion of cationic surfactant modified MMT in it. Wood is impregnated with modified MMT dispersed copolymer and polymerized under catalyst heat treatment in the presence of a crosslinker, glycidyl methacrylate. The study is also aimed at to see the effect of MMT on various physical, mechanical, and thermal properties of WPNC.

EXPERIMENTAL

Materials

Simul wood (*Salmaalial malabarica*) was collected locally. Styrene obtained from E.Merck (Mumbai, India) was purified by following standard procedure described elsewhere.¹⁸ Acrylonitrile was purchased from RANKEM (New Delhi, India). Glycidyl meth-

acrylate (GMA) and 2,2'-azo-bis-isobutyronitrile (AIBN) obtained from Merck (Mumbai, India) were used as received. 2-Acryloyloxy ethyl trimethyl ammonium chloride and montmorillonite K10 (CEC of 119 mEq/100 g) were purchased from Sigma-Aldrich (USA). All other chemicals used were of analytical grade and used directly.

Sample preparation

The Simul wood samples used for the study were prepared from clear defect-free wood, cut into blocks of $2.5 \times 1 \times 2.5 \text{ cm}^3$ (radial \times tangential \times longitudinal) for dimensional stability, water uptake test, and chemical resistance tests.

For tensile strength measurement the samples were prepared according to ASTM D-638. The samples were cut into $10 \times 0.5 \times 2 \text{ cm}^3$ using standard method.

For bending strength measurement, the blocks were cut into dimension of $1 \times 1 \times 10 \text{ cm}^3$ (radial \times tangential \times longitudinal).

Preparation of organo-MMT

An organophilic clay was prepared by the ion exchange reaction¹⁹ and shown in Figure 1; 0.10 g of montmorillonite (K10) with CEC of 119 mEq/100 g was oven dried at 105–110°C for two days. Then it was dispersed in 100 mL of deionized water and kept for swelling for 24 h at stirring condition. The dispersion was sonicated under ultrasonic processor for further 1 h. Approximately 0.025 mol of 2-acryloyloxy ethyl trimethyl ammonium chloride (ATAC) (in presence of 3,000 ppm hydroquinone) was slowly added to it and stirred for 15 min at room temperature. The suspension was refluxed with vigorous stirring for 6 h. The exchanged clay was filtered in suction and washed with water followed by washing with hot 1 : 9 ethanol–water mixture for removal of untreated surfactant and finally washed with distilled water for several times until no bromide ion was detected with 0.1N AgNO₃ solution.²⁰ The resulting product was vacuum dried at 45°C and crushed into powder using a mortar and a pestle. The organophilic MMT was denoted as ATAC-MMT.

Preparation of styrene acrylonitrile copolymer

To prepare styrene coacrylonitrile prepolymer, a mixture of monomers, styrene, and acrylonitrile in the molar ratio of 2 : 3 was taken and polymerized by bulk polymerization in the presence of 0.05 phr of AIBN for approximately 1 h 45 min in an oil bath at 70–80°C. After the polymerization was over, the reaction was immediately stopped. The mixture

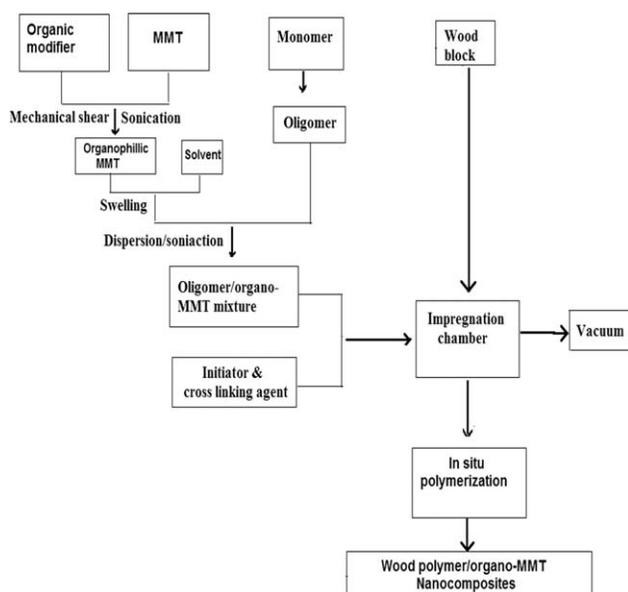


Figure 1 Flow chart diagram of WPNC preparation.

referred to as SAN prepolymer, was poured into a closed flask and placed at ambient temperature to cool down. The flow out time (at 30°C) for different prepared batches was almost similar as judged by Ubbelohde viscometer. The modified MMT was dispersed in SAN prepolymer in the presence of minimum amount of solvent (THF) and sonicated for 45 min. This mixture was taken as impregnation solution for our study.

Preparation of wood/SAN/MMT nanocomposite

Wood samples were preliminary dried in an oven at 105°C until constant weight before treatment and dimensions and weight were measured. The samples were then placed in an impregnation chamber followed by application of load over each sample to prevent them from floatation during addition of oligomers as demonstrated in Figure 2. Vacuum was applied for a specific time period for removing the air from the pores of the wood samples before addition of prepolymeric mixture. After that, vacuum was released. Now the dispersion of SAN prepolymer-ATAC modified MMT with GMA, and initiator, or dispersion of SAN prepolymer, with GMA and initiator, or that of SAN prepolymer and initiator was added from a dropping funnel to completely immerse the wood samples. The samples were then kept in the chamber at room temperature for another 4 h after attaining atmospheric pressure. This is the minimum time to get maximum polymer loading, which showed maximum improvement in properties. After impregnation, samples were taken out of the chamber and excess chemical was wiped from wood surfaces, the samples were then wrapped in aluminum foil and cured at 90°C for 24 h

in an oven. This was followed by drying at 105°C for another 24 h. The cured samples were then Soxhlet extracted using chloroform to remove homopolymers, if any, formed during polymerization. Finally the samples were dried and the dimensions were measured by using slide caliper and weights were taken.

Measurements

X-ray diffraction (XRD) studies

The XRD studies were done by Rigaku X-ray diffractometer (Miniflex, UK) using Cu-K α radiation ($\lambda = 0.154$ nm) at a scanning rate of 2° to 30° of 2 θ .

Weight percent gain

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

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

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

Volume increase (%) after impregnation

Percentage volume increase after curing of wood samples was calculated as follows:

$$\% \text{ Volume increase} = (V_t - V_o)/V_o \times 100$$

where V_o is the oven dry volume of the untreated wood and V_t is the oven dry volume of the treated wood.

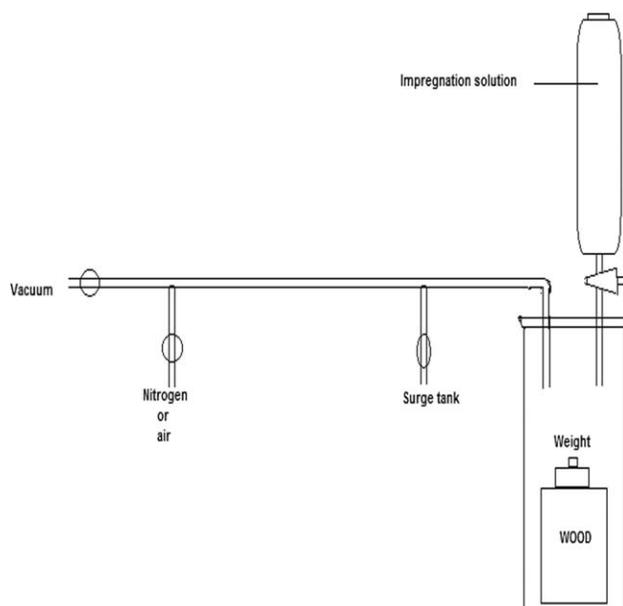


Figure 2 Set up of preparation of WPNC.

Hardness

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

Water uptake test

Both untreated and treated wood samples were immersed in distilled water at room temperature (30°C) and weight was taken after different time intervals. It is expressed as

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

where W_t is the weight after immersion in distilled water for specific time period (0.5–168 h) and W_d is the weight of the oven dry sample.

Water repellent effectiveness (WRE)

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

$$\text{WRE} = (D_0 - D_t)/D_0 \times 100$$

where D_0 is the water uptake capacity of untreated samples immersed for different time periods (0.5–168 h) and D_t is the water uptake capacity of treated wood samples immersed for the same time periods.

Dimensional stability test

Swelling in water. Dimensions of the oven-dried samples were measured and conditioned at room temperature (30°C) and 30% relative humidity. Final placement of the samples was done in distilled water and then dimensions were remeasured after different time intervals.

In this case, swelling was considered as a change in volume and expressed as the percentage of volume increase compared to oven-dried samples.

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

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

Anti swelling efficiency. The antiswell efficiency (ASE) index was determined to evaluate the 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 wood blocks and V_1 is the volume of the oven-dried wood 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 wood blocks.

Chemical resistance test

The chemical resistance tests were evaluated by immersing the samples in 4% NaOH solution and 10% acetic acid solution for 24 h. The percent of 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.

Mechanical properties

The flexural strength of the samples was measured by Zwick Tensile Tester (model Z010) 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.

The tensile strength was performed by using Zwick Tensile Tester (model Z010), Germany, with a 10-kN load cell and crosshead speed of 50 mm/min.

Thermogravimetric analysis

Thermal properties of the untreated and treated wood samples were measured by using a thermogravimetric analyzer (model TA50, Shimadzu) at a heating rate of 10°C/min up to 600°C.

Morphological study

The morphological features of untreated and treated wood samples were observed using scanning electron microscope (JEOL JSM-6390 LV) at an accelerated voltage of 5–10 KV. Fractured surface of some

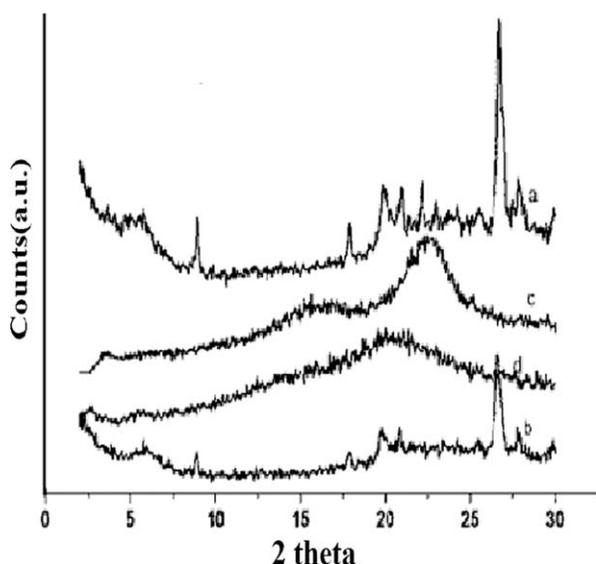


Figure 3 XRD pattern of (a) MMT (b) modified MMT (ATAC-MMT) (c) SAN-GMA-MMT treated wood composite and (d) SAN-MMT polymer composite.

of the selected wood samples coated with platinum were used for the study.

FTIR study

The treated and untreated samples were ground and FTIR spectra were recorded by using a KBr pellet in a Nicolet (model Impact 410) FTIR spectrometer.

RESULTS AND DISCUSSION

The optimum condition for impregnation at which maximum improvement in properties was obtained by varying vacuum, time of impregnation, monomer concentration, catalyst concentration, and amount of crosslinker. Modified MMT was dispersed initially in THF and finally in SAN prepolymer. The minimum ratio (v/v) of SAN and THF used for the dispersion of modified MMT was 5 : 1. The final optimized impregnating conditions were as follows: vacuum: 20 in. Hg, time of impregnation: 4 h, AIBN: 0.5%(w/v), SAN (mL):100, THF (mL): 20, GMA: 10 mL and modified MMT: 0.5–1.5%(w/v).

XRD study

Figure 3 shows the x-ray diffraction pattern of MMT, modified MMT, and SAN-MMT polymer composite and wood/SAN-MMT polymer composite. The gallery distance for MMT (curve-a) corresponding to 2θ of 8.95° was calculated by using Bragg's equation and was found to be 0.986 nm. The diffraction peak of modified MMT (curve-b) at 2θ of 8.85° corresponded to an interlayer spacing of 0.995 nm. The increased basal spacing indicated that the clay had been exfoliated more compared to native MMT and could accommodate polymer.

The XRD patterns of SAN-clay composite is shown in curve d. It can be said that either the full expansion of the MMT gallery occurred which was not possible to detect by XRD or the MMT layers became delaminated and no crystal diffraction peak appeared.²¹ Curve c represents the XRD analysis of wood/SAN/MMT nanocomposite. The peak near 22.3° of 2θ reflected the maximum diffraction of the (002) crystal plane of cellulose. The corresponding peak for modified MMT at 2θ of 8.85° disappeared. This suggested that crystallinity in wood decreased and some exfoliated MMT nanolaminae were introduced into amorphous region of wood cellulose cell wall.

Effect of variation of clay on polymer loading (WPG %), volume increase, and hardness

Related results are shown in Table I. Polymer loading (%), volume increase (%), and hardness were found to increase when either GMA or GMA in combination with MMT were used with the SAN polymer for making WPNC. The higher the amount of clay, the higher was the improvement. The observed higher values for polymer loading, volume increase, and hardness was due to deposition of polymer and clay into the void spaces and capillaries of the wood. The GMA further increased the interaction between wood and SAN polymer. Clay also reduced the mobility of the polymer chains which was intercalated between nanoclay interlayers. Cai et al.²² reported that hardness was

TABLE I
Effect of Variation of Clay on Weight Percent Gain (WPG %), Volume Increase, and Hardness

Sample particulars	SAN:THF	GMA	Modified MMT (%)	WPG (%)	Volume increase (%)	Hardness (Shore D)
Untreated	SAN:THF(100:20)	–	–			40 (± 2.05)
Treated	SAN:THF(100:20)	–	–	20.21 (± 0.96)	3.04 (± 1.01)	42 (± 1.23)
Treated	SAN:THF(100:20)	10	–	24.21 (± 1.02)	4.07 (± 0.04)	46 (± 1.84)
Treated	SAN:THF(100:20)	10	0.50	31.03 (± 0.89)	4.38 (± 0.41)	58 (± 1.96)
Treated	SAN:THF(100:20)	10	1.00	35.77 (± 1.42)	6.29 (± 1.02)	64 (± 1.56)
Treated	SAN:THF(100:20)	10	1.50	39.47 (± 2.14)	7.09 (± 0.99)	66 (± 1.02)

Each value represents the average of three samples.

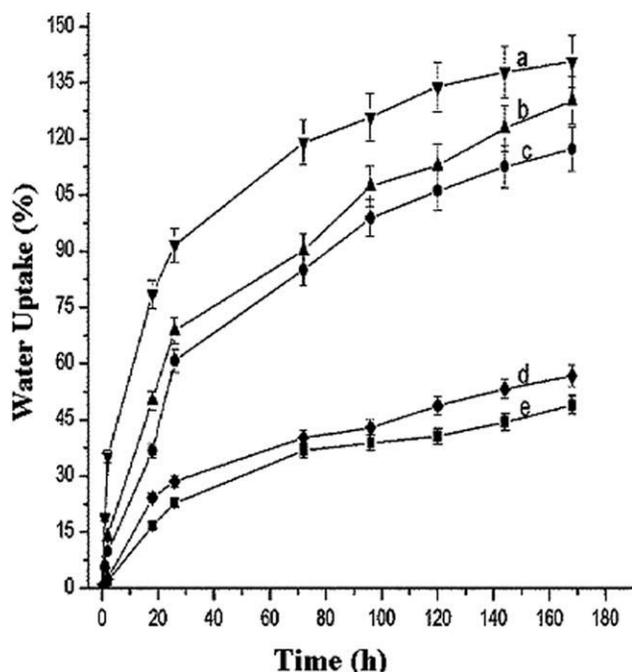


Figure 4 Water absorption of (a) untreated (b) SAN (c) SAN-GMA (d) SAN-GMA-modified MMT (0.5 phr) and (e) SAN-GMA-modified MMT (1.0 phr) treated wood samples.

improved by the addition of nanoclay into wood/melamine urea formaldehyde resin composite.

Water uptake study

The results of water uptake for treated and untreated samples are shown Figure 4. In both treated and untreated samples, water absorption increased with an increase in time of immersion. Untreated samples absorbed more water than the treated samples. Wood samples treated with SAN copolymer and modified MMT showed the least water uptake throughout the studied time period. With the increase in time, the capillaries and void spaces were getting sufficient time to become filled

up with water which resulted in an increase in the water uptake capacity. In treated samples, the void spaces decreased due to filling of the same by SAN copolymer. This showed less water absorption. The water absorption of the treated samples decreased further because of the crosslinks formed by the interaction of double bond and glycidyl group of GMA with double bond and hydroxyl group of SAN copolymer and wood, respectively. Least water absorption occurred for samples impregnated with SAN copolymer, modified MMT, and GMA. Although the MMT on treatment with cationic surfactant changed to organophilic in nature, it retained some of its hydrophilic character.²³ The surface of the modified clay had a tendency to immobilize some of the moisture. The layer of modified MMT enhanced tortuous path for water transport and thereby resulted in a decrease in water diffusivity.²⁴ Improvement in water resistance due to introduction of melamine urea formaldehyde resin and nanofiller in wood was reported in the literature.²⁵

Water repellent effectiveness (WRE) study

Table II shows the results of the WRE values for treated and untreated wood samples in water at room temperature (30°C). There was a remarkable improvement in WRE values for treated wood samples, particularly for modified MMT intercalated wood samples. In all the cases, water repellency increased initially at a faster rate and finally at a slower rate. The improvement in WRE could be explained as stated earlier.

Dimensional stability test

Swelling in water

The effect of swelling in liquid water at room temperature for treated and untreated wood samples for different time periods is shown in Figure 5. As expected, treated samples, particularly where GMA

TABLE II
Water Repellent Effectiveness (WRE %) of Wood Polymer Composite

Time (h)	SAN-treated	SAN-GMA treated	SAN-GMA modified-MMT (0.5 phr) treated	SAN-GMA modified-MMT (1.0 phr) treated
1	66.64 (± 0.15)	71.99 (± 2.03)	93.48 (± 0.01)	96.40 (± 0.01)
2	56.39 (± 4.39)	69.93 (± 2.04)	92.73 (± 0.13)	94.69 (± 0.21)
18	35.99 (± 1.08)	53.12 (± 0.36)	69.13 (0.04)	78.60 (± 0.12)
26	24.93 (± 0.05)	33.67 (± 0.19)	68.82 (± 1.03)	75.15 (± 1.02)
72	24.02 (± 0.28)	28.60 (± 0.98)	66.20 (± 2.01)	69.09 (± 0.16)
96	15.71 (± 0.93)	21.54 (± 0.03)	65.91 (± 0.50)	68.02 (± 0.91)
120	15.48 (± 0.23)	20.73 (± 0.97)	63.58 (± 1.36)	67.82 (± 2.12)
144	10.85 (± 0.12)	18.11 (± 0.23)	61.32 (± 0.65)	65.17 (± 2.55)
168	7.45 (± 0.03)	16.50 (± 0.17)	59.31 (± 0.37)	63.23 (± 2.13)

Each value represents the average of three samples.

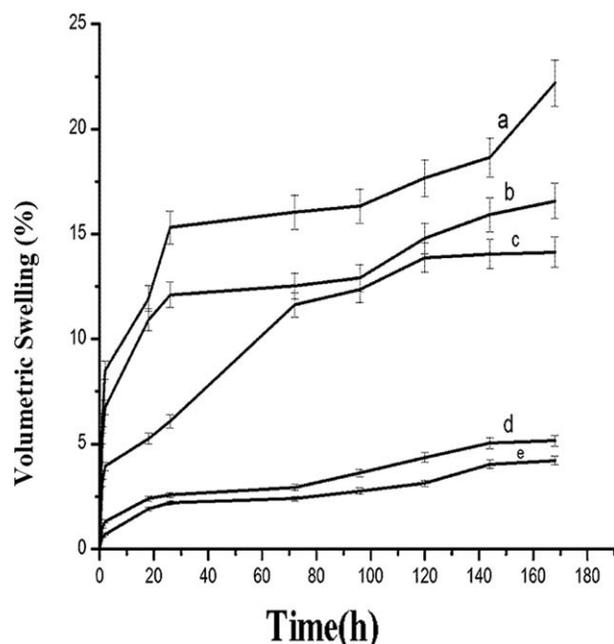


Figure 5 Volumetric swelling of (a) untreated (b) SAN (c) SAN-GMA (d) SAN-GMA-modified MMT (0.5 phr) and (e) SAN-GMA-modified MMT (1.0phr) treated wood samples.

and modified MMT were incorporated, showed more reduction in swelling.

Anti swelling efficiency

The results of antismelling efficiency of wood samples are shown in Table III. Antismelling efficiency

was found to decrease with the increase of time. The antismelling efficiency was more in the case of WPNC.

Improvement in dimensional stability of wood composites over virgin wood sample might be due to the deposition of polymer and MMT into the void spaces of wood, which prevented the cell walls from shrinking in response to moisture loss. MMT further increased the tortuous path for diffusion of water. Besides, as the polymer was less hygroscopic than wood, less water would be absorbed during humid conditions.²⁶

Chemical resistance test

Related results are shown in Table IV. It was observed that treated wood samples swelled less compared to untreated samples. The swelling was least in the case of modified MMT treated wood/SAN/GMA composite. The higher the percentage of clay, the lower was the swelling. The cell wall of the wood only thickened due to incorporation of SAN. GMA acted as a crosslinker between wood and SAN polymer and as a result swelling decreased. The inclusion of clay further increased the tortuous pathway for the diffusion of chemicals which in turn would decrease the swelling. In all the cases, the swelling was less in acetic acid compared to sodium hydroxide solution. This may be possibly due to the increase in interaction by sodium hydroxide with wood cellulose and clay layers. Increase of swelling may also be due to the formation of carboxylic acid

TABLE III
Antismelling Efficiency (%) of Treated Wood Samples at Different Time Periods

Time (h)	SAN-treated	SAN-GMA treated	SAN-GMA modified-MMT (0.5 phr) treated	SAN-GMA modified MMT (1.0 phr) treated
1	14.44 (± 0.42)	77.88 (± 0.01)	83.24 (± 0.12)	91.71 (± 2.38)
2	12.91 (± 0.12)	72.23 (± 1.02)	84.58 (± 1.05)	86.96 (± 1.26)
18	10.60 (± 2.26)	71.83 (± 0.05)	80.79 (± 2.01)	85.69 (± 1.73)
26	10.09 (± 5.97)	71.19 (± 2.03)	79.89 (± 2.32)	85.03 (± 0.66)
72	9.94 (± 4.12)	69.96 (± 0.74)	78.56 (± 2.27)	83.96 (± 2.03)
96	8.95 (± 0.99)	65.54 (± 1.55)	77.82 (± 0.62)	83.10 (± 0.04)
120	8.56 (± 2.02)	69.70 (± 0.75)	77.18 (± 2.18)	79.74 (± 0.05)
144	10.92 (± 3.96)	68.79 (± 0.06)	75.36 (± 3.12)	78.17 (± 0.03)
168	11.68 (± 0.16)	68.54 (± 0.30)	72.64 (± 2.17)	71.07 (± 5.12)

Each value represents the average of three samples

TABLE IV
Chemical Resistance of Wood Polymer Composites

Medium	Volumetric swelling (%)				
	Untreated	SAN treated	SAN-GMA treated	SAN-GMA-modified MMT (0.5 phr) treated	SAN-GMA-modified MMT (1.0 phr) treated
4% NaOH	12.540 (± 0.234)	9.870 (± 1.52)	5.539 (± 0.364)	4.537 (± 0.851)	3.075 (± 0.004)
4% Acetic acid	8.710 (± 0.411)	7.560 (± 0.96)	6.526 (± 1.056)	3.049 (± 0.006)	1.934 (± 0.707)

TABLE V
MOE and MOR Values of Untreated and Treated Wood Samples

Sample particulars	MOE (MPa)	MOR (MPa)
Untreated	3235.82 (± 442.94)	58.07 (± 4.52)
Treated with		
SAN	5750.66 (± 211.25)	78.74 (± 3.45)
SAN-GMA	5869.70 (± 542.49)	79.20 (± 5.27)
SAN-GMA-modified MMT(0.5phr)	6199.92 (± 239.39)	79.64 (± 1.23)
SAN-GMA-modified MMT (1.0 phr)	6863.9 (± 123.34)	86.86 (± 4.78)

Each value represents the average of three samples.

groups generated from the partial hydrolysis of acrylonitrile groups.

Mechanical property study

The flexural properties of virgin wood, wood treated with SAN, SAN/GMA, and SAN/GMA/modified clay are shown in Table V. The values presented in the table are the average values of three readings. Both modulus of elasticity (MOE) and modulus of rupture (MOR) were found to increase when virgin wood was treated with either SAN or SAN/GMA. This was due to the formation of bond between SAN and wood by GMA. Similar improvement in flexural properties was reported by Maji et al.²⁷ The MOE and MOR increased further with the addition of clay. The higher percentage of clay, the higher was the MOE and MOR. This might be possibly due to stiffening of the composite caused by the reduction in mobility of the polymer chains which were intercalated between the nanoclay interlayers.

The average values of the mechanical parameter obtained in tensile testes are shown in Table VI. It was observed that wood treated SAN and GMA caused an improvement in tensile strength. The tensile strength increased drastically when clay was added. This could be attributed to the combined effect of increasing interaction by GMA and reduction in the motion of the intercalated polymer chains as stated earlier. A similar trend in elongation at break (%) value was observed. This might be due to

TABLE VI
Tensile Properties of Untreated and Treated Wood Samples

Sample particulars	Tensile stress (MPa)	Elongation at break (%)
Untreated	45.90 (± 2.03)	26.03 (± 0.34)
SAN-GMA	51.23 (± 1.03)	13.34 (± 0.95)
SAN-GMA-modified MMT(1.0phr)	59.71 (± 3.25)	11.92 (± 1.17)

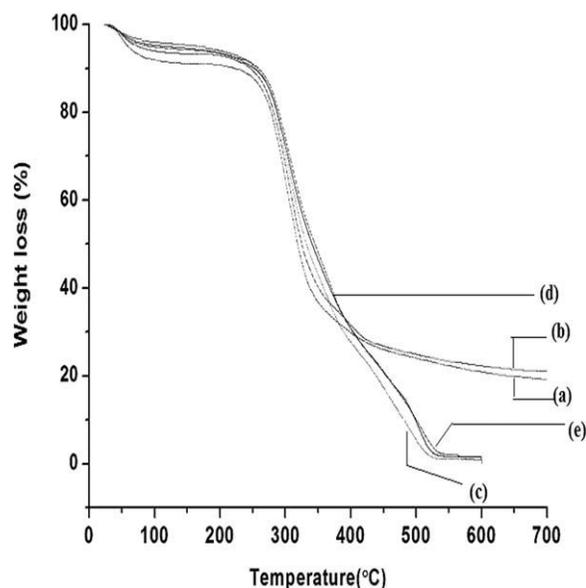


Figure 6 TGA curve of (a) untreated (b) SAN (c) SAN-GMA (d) SAN-GMA-modified MMT (0.5 phr) and (e) SAN-GMA-modified MMT (1.0 phr) treated wood samples.

the decrease in ductility caused by the reduction in mobility of the polymer chains.

Thermogravimetric analysis

Figures 6 and 7 show the TG and DTG curves for untreated and polymer treated wood samples. Table VII shows the initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m), and residual weight (%) (RW) for untreated and polymer treated

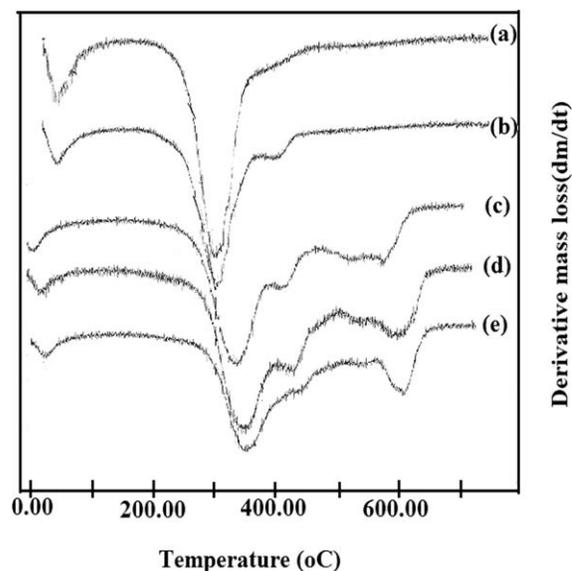


Figure 7 DTG curve of (a) untreated (b) SAN (c) SAN-GMA (d) SAN-GMA-modified MMT (0.5 phr) and (e) SAN-GMA-modified MMT (1.0 phr) treated wood samples.

TABLE VII
Thermal Analytical Data for Untreated and Treated Wood Samples

Sample particulars	T_i (°C)	$T_{m_i}^a$ (°C)	$T_{m_{ii}}^b$ (°C)	$T_{m_{iii}}^c$	RW (%) 600 (°C)
Untreated	56	300	383	–	20.0
Treated with SAN	71	305	408	–	22.0
SAN-GMA	110	308	366	497	1.3
SAN-GMA-modified MMT(0.5phr)	140	308	375	507	2.7
SAN-GMA-modified MMT(1.0 phr)	140	307	377	509	4.0

^a T_m value for first step.

^b T_m value for second step.

^c T_m value for third step

TABLE VIII
Temperature of Decomposition (T_D) at Different Weight Losses of Untreated and Treated Wood Samples

Sample particulars	Temperature of decomposition (T_D) in (°C) at different weight loss (%)							
	20	30	40	50	60	70	80	90
Untreated	277	292	305	318	335	396	–	–
SAN treated	280	297	309	322	349	408	–	–
SAN-GMA treated	286	300	313	331	358	389	438	473
SAN-GMA/modified MMT(0.5phr) treated	288	300	321	347	368	401	447	489
SAN-GMA/modified MMT(1.0 phr) treated	292	309	321	342	372	405	450	499

wood samples and T_m values of MMT treated wood samples. Both T_i and T_m values of treated samples were higher than untreated samples. T_m values of MMT treated sample were higher compared to samples without MMT. RW values of MMT treated samples were found more than samples without MMT. The higher the MMT, the higher was the residual weight.

Table VIII shows the temperature of decomposition (T_D) values at different weight losses for different samples. The T_D values of polymer treated wood samples were observed to be higher than those of virgin wood samples. These values increased further on addition of GMA or clay. The higher the amount of clay, the higher was the T_D value. The higher T_D value might be due to the combined effect of crosslinking by GMA and the presence of a silicate layer. The crosslinking reduced the rate of the degradation of degradable components in the composites. The silicate layer acted as a barrier and hindered the diffusion of volatile decomposition products.²⁸

Morphological study

SEM micrographs of untreated (black arrows pointing to pit and cell wall) and treated wood samples (black arrows pointing to SAN, SAN/GMA, and MMT) are shown in Figure 8(a–e). For untreated wood, the empty cell wall, the pit, and parenchyma were seen. In treated wood, these empty spaces were occupied by the SAN polymer, SAN/GMA, or modified MMT/GMA/SAN materials. The impregnated materials were either located in the cell walls or filled in the cell lumen.

FTIR study

Figure 9 shows the FTIR spectra of MMT, modified MMT, SAN-modified MMT composite, wood, and WPNC. The band (shown in curve a) at 3457 and 1639 cm^{-1} were due to OH stretching and OH bending

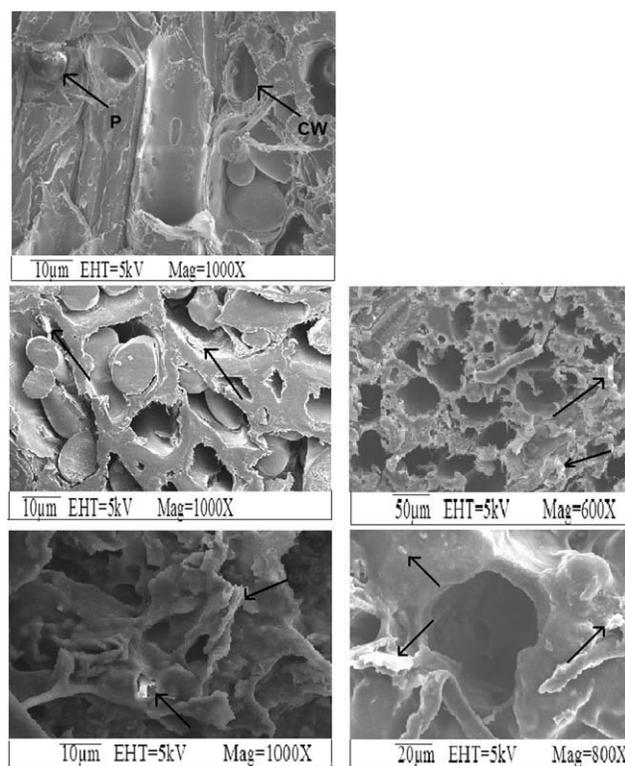


Figure 8 SEM micrograph of (a) untreated (arrows indicate P, pit; CW, cellwall) (b) SAN (c) SAN-GMA (d) SAN-GMA-modified MMT (0.5 phr) and (e) SAN-GMA-modified MMT (1.0 phr) treated wood samples.

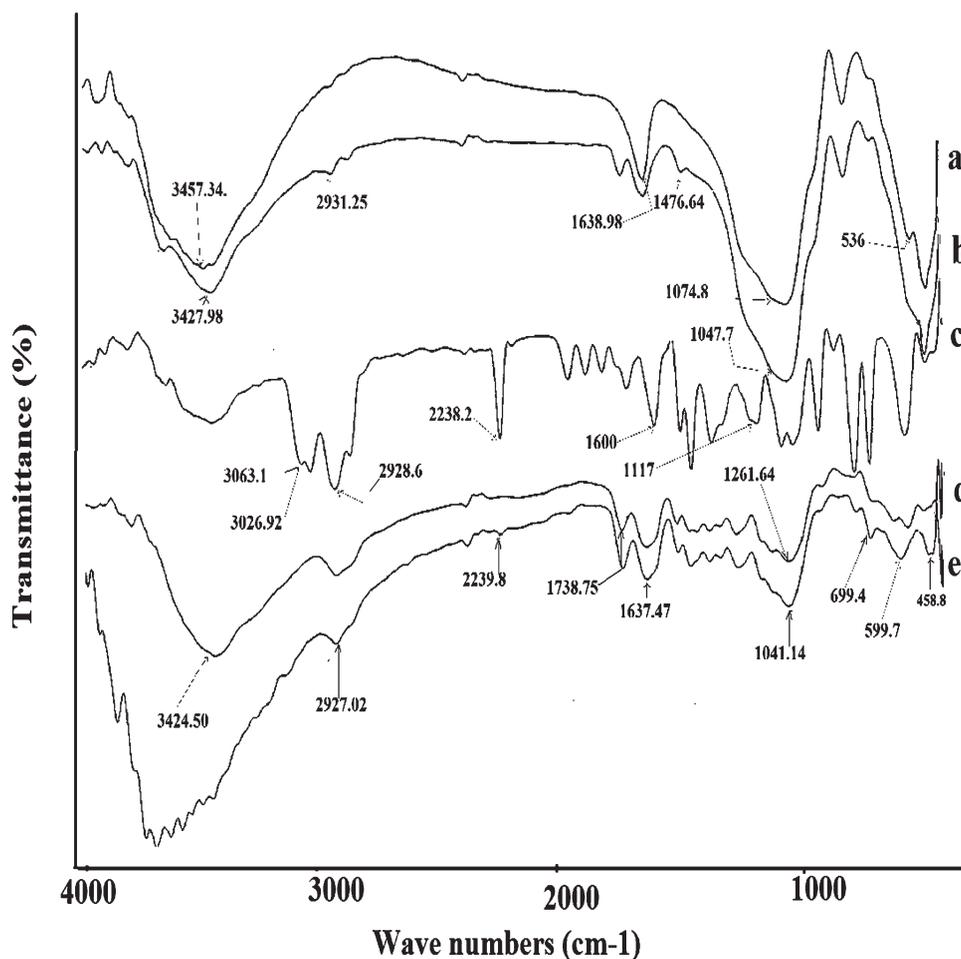


Figure 9 FTIR spectra of (a) MMT (b) modified MMT (c) SAN-MMT composite (d) untreated wood and (e) SAN-GMA-modified MMT treated wood samples.

vibration. The band at 1048 and 536 cm^{-1} were attributed to in plane Si—O—Si stretching for layer silicates and Si—O bending.²⁹ In modified MMT (curve b), the characteristic absorption band appeared at 2931 and 1476 cm^{-1} were due to $-\text{CH}_2$ asymmetric stretching, $-\text{CH}_2$ plane scissoring. In the spectrum of SAN-MMT (curve c), the new peaks at 3026, 2927, 2239, and 1117 cm^{-1} were observed along with the other peaks for modified MMT. These peaks were assigned to symmetric $-\text{CH}_2$ stretching, $\text{C}\equiv\text{N}$ stretching, aromatic ring stretching, and out of plane Si—O stretching, respectively. The wood characterized by the absorption bands (shown in curve d) appeared at 3400 cm^{-1} (OH stretching), 1738 cm^{-1} ($\text{C}=\text{O}$ stretching of acetylated xylem), and 1261 cm^{-1} ($\text{C}-\text{O}$ stretching of acetyl group).³⁰ The presence of characteristic peaks of modified MMT, SAN in WPNC indicated the impregnation of SAN and MMT into wood.

CONCLUSIONS

Wood polymer nanocomposites were prepared by using wood, SAN polymer, and modified clay. There

was no remarkable improvement in interlayer spacing of MMT due to modification with a cationic surfactant. XRD analysis indicated that some nanosilicate layer entered into the amorphous region of wood cellulose. Dimensional stability, water repellent effectiveness, hardness, and chemical resistance improved significantly due to incorporation of MMT into wood polymer composite. Water uptake for modified MMT treated wood composite also decreased. Modulus of elasticity and modulus of rigidity of WPNC improved. Thermal stability of the WPNC enhanced on addition of GMA and MMT. SEM study revealed the presence of some polymer and MMT into wood lumen or wood cell wall. FTIR study indicated that MMT was incorporated into the wood polymer composite.

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