

***In situ* Polymerized Wood Polymer Composite: Effect of Additives and Nanoclay on the Thermal and Mechanical Properties**

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This study concerns the preparation and characterization of wood polymer nanocomposites based on impregnation of styrene acrylonitrile co-polymer–nanoclay intercalating system in presence of glycidyl methacrylate (GMA), a cross linking agent, and vinyl trichloro silane (VTCS) as additives into Simul (*Bombex ceiba*, L.), a soft wood. The effect of nanoclay and VTCS on the properties of the resultant wood polymer nanocomposites (WPNC) has been evaluated. FTIR spectroscopy shows the interaction among wood, polymers, GMA, nanoclay and VTCS. The penetration of polymer and nanoclay into the wood cell wall is supported by SEM study. The distribution of nanoclay in the SAN polymer matrix present within the wood cell wall has been evidenced by TEM study. TGA results show an improvement in the thermostability of the resultant composites. The inclusion of VTCS enhances the self extinguishing behaviour of the WPNC as revealed by limiting oxygen index (LOI) test. Due to treatment, the resultant WPNC exhibits an improvement in all the properties like water repellancy, dimensional stability, hardness, flexural, tensile and thermal stability compared to untreated wood.

Keywords: *co-polymers, flame retardance, mechanical properties, organoclay, thermogravimetric analysis, transmission electron microscopy*

1. Introduction

Simul (*Bombex ceiba*, L.), a soft wood, is not useful for constructional purposes due to its poor dimensional stability and mechanical properties. However, these properties can be enhanced through formation of composites. Wood–polymer composites (WPC), prepared by the impregnation of vinyl monomers followed by *in situ* polymerization by either γ -radiation or catalyst heat treatment, generally exhibit enhanced strength, improved thermal properties and dimensional stability, and resistance to biodeterioration¹⁻⁴. Impregnation of woods with vinyl or acrylic monomers shows less dimensional stability in the presence of moisture⁵. Incorporation of cross linking material in wood sample provides better dimensional stability to the wood polymer composite^{6,7}.

Applications of nanotechnology to wood have been performed in recent years, for the conservation and restoration of the world's cultural heritage. Impregnation of melamine urea formaldehyde (MUF) and phenol formaldehyde (PF) prepolymer containing hydrophobic nanofillers into wood has improved significantly surface hardness, modulus of elasticity and water repellency^{8,9}.

It is well documented that the loading of clay into polymer enhances mechanical, barrier and flame retardant properties. Most authors conclude that the clay has to be used in combination with other additives in order to meet fire resistance requirements¹⁰.

Increased efforts to expand the use of wood products in institutional and commercial structures may require wood to be treated with fire retardants. Flame retardancy is generally

imparted to woods by impregnating phosphate, silica, boron type compounds into wood¹¹. The composites impregnated with bis (2-chloroethyl) vinyl phosphonate have shown maximum improvement in thermal stability. It has been reported that the improvement in fire retardancy of wood has been obtained on treatment with thio-urea–formaldehyde resin and orthophosphoric acid¹².

Although the use of halogenated compounds as flame retardant agents are gradually diminishing due to environmental problems yet these are still in use owing to various advantages like low cost, miscibility and low reduction in physical/mechanical properties of the flame retardant system. The advantage of using reactive flame retardant monomer compared to other flame retardant additives is that they can be used at relatively lower concentration. Since they are incorporated in the polymer structure, they can improve the compatibility with the polymer as well as reduce the migration of flame retardant agent to the surface.

The addition of a relatively low amount of silicon-based compounds (silicones, silicas, organosilanes, silsequioxanes and silicates) to polymers has been reported to substantially improve their flame retardancy¹³. Silane monomers are generally preferred over polysiloxane compounds for impregnation of wood. It can easily penetrate into the cell wall of wood, polymerize *in situ* and thus reduces the leaching during outdoor use. Wood treated with monomeric alkoxy silane shows improved cell wall bulking, dimensional stability, moisture uptake and durability compared to wood treated with oligomeric alkoxy silane¹⁴. Organically modified

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montmorillonite (OMT) and silica modified with 3-amino propyl trimethoxysilane enhance the flame retardant property when incorporated in ABS nanocomposites due to the synergistic effect between OMT and modified silica¹⁵.

The present paper is a continuation of the work originated by Devi and Maji¹⁶. The impregnation of vinyl trichlorosilane as an additive along with nanoclay and SAN polymer into wood and its effect on various properties like mechanical, flame retardancy, thermal stability, water absorption, dimensional stability (ASE), hardness have been investigated.

2. Experimental

2.1. Material

Simul wood (*Bombex ceiba L.*) was collected from local area Tezpur, India. Styrene obtained from E. Merck (Mumbai, India), was purified by following standard procedure. Acrylonitrile, Glycidyl methacrylate (GMA) and 2, 2'-azo bis isobutyronitrile (AIBN) obtained from Merck (Germany) were used as received. Organically modified nanoclay (Nanomer, surface modified by 15-35 wt% octadecylamine and 0.5-5 wt% amino propyl triethoxy silane) and vinyl trichloro silane were purchased from Sigma-Aldrich (USA) and Alfa Aesar, India respectively. All other chemicals used were of analytical grade.

2.2. Sample preparation

The simul wood samples used for the study were prepared from defect free wood, cut into blocks of 2.5 cm × 1 cm × 2.5 cm for dimensional stability, water uptake and hardness tests.

For tensile strength measurement, the samples were prepared according to ASTM D 638. The samples were cut into 10 cm × 0.5 cm × 2 cm using standard method.

For bending strength measurement, the blocks were cut into dimension of 1 cm × 1 cm × 10 cm (radial × tangential × longitudinal) according to ASTM D 790 method.

2.3. Preparation of Styrene acrylonitrile co-polymer

The styrene acrylonitrile co-polymer was prepared by taking monomer of styrene and acrylonitrile in the molar ratio of 2:3, as suggested by Liu et al.¹⁷. The polymerization

was done by bulk polymerization technique in presence of 0.05 phr of AIBN in an oil bath at 70-80 °C for approximately 30 minutes. After the polymerization was over, the reaction was immediately stopped. The mixture, referred to as SAN prepolymer, was poured into a closed flask and cool down at ambient temperature. The flow out time (at 30 °C) for different prepared batches was almost similar as judged by Ubbelohde Viscometer.

2.4. Preparation of Wood/SAN/MMT/VTCS nanocomposites

In the preparation of wood polymer nanocomposites based on impregnation of polymer /nanoclay all the preliminary steps were followed as reported earlier². Here the dispersion of SAN prepolymer-organically modified nanoclay with GMA, VTCS 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 hours after attaining atmospheric pressure. This is the minimum time to get maximum polymer loading. After impregnation, samples were taken out of the chamber and excess chemicals were wiped from wood surfaces, the samples were then wrapped in aluminium foil and cured at 90 °C for 24 hours in an oven. This was followed by drying at 105 °C for another 24 hours. The cured samples were then Soxhlet extracted using chloroform to remove homo polymers, if any, formed during polymerization. Finally the samples were dried and the dimensions were measured by using slide caliper and weights were taken. The compositions are summarized in the Table 1.

2.5. Weight percent gain

Weight percent gain (WPG) after polymer loading was calculated according to formula as reported in our previous study².

2.6. Volume increase (%) after impregnation

Percentage volume increase after curing of wood samples after polymer loading was calculated according to formula as reported in our previous study².

Table 1. Composition of untreated and treated wood.

Sample code*	SAN	THF(weight %,v/v)	GMA(weight %,v/v)	Nanoclay(weight %,w/v)	VTCS(weight %,v/v)
W	—	—	—	—	—
S	100	20	—	—	—
S/G5	100	20	5	—	—
S/G5/N1	100	20	5	1.0	—
S/G5/N1/V0.5	100	20	5	1.0	0.5
S/G5/N1/V1	100	20	5	1.0	1.0
S/G5/N1/V2	100	20	5	1.0	2.0
S/G5/V2	100	20	5	—	2.0

*Untreated wood (W); styrene acrylonitrile copolymer (SAN); tetrahydrofuran(THF); glycidyl methacrylate(GMA), nanoclay, vinyl trichloro silane were designated as W, S, T, G, N and V respectively.

2.7. Hardness

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

2.8. FTIR study

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

2.9. X-ray diffraction (XRD) study

In order to assess the morphological properties of WPC, XRD analysis was applied. A Rigaku X-ray diffractometer (Miniflex, UK) was used where CuK α radiation ($\lambda=0.154$ nm) was employed at a scanning rate of 1°/min from 2° to 30° of 2 θ .

2.10. Morphological study

2.10.1. Scanning electron microscopy (SEM) study

The interfacial bonding between the cell wall polymer, nanoclay and cross linker was examined using a scanning electron microscope (JEOL JSM-6390 LV) at an accelerated voltage of 5-15 KV. Fractured surface of some of the selected wood samples coated with platinum were used for the study.

2.10.2. Transmission electron microscopy (TEM) study

For the preparation of (ultra) thin as well polished section, the samples were embedded with epoxy resin according to the method of Spurr¹⁸. Ultra-thin sections (approx. 100 nm thick) of the transverse film surfaces were sectioned using an ultramicrotome fitted with a diamond knife. The sections were stained with 1% (w/v) uranyl acetate for sufficient contrast. After staining, the sections were mounted on grids and examined with a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 80 kV.

2.11. Mechanical properties

The flexural strength of the samples was measured by UTM- HOUNSEFIELD (model H100-S), England with a cross head speed of 2 mm/min and by calculating the modulus of elasticity (MOE) and modulus of rupture (MOR) according to ASTM D790 method.

MOR was calculated as follows:

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

where W is the ultimate failure load, L is the span between 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 was performed by using UTM-HOUNSEFIELD (model H100-S), England with a 5-KN load cell and crosshead speed of 10 mm/min according to ASTM D638.

2.12. Thermogravimetric analysis

Thermal properties of the untreated and treated wood samples were measured by using a thermogravimetric

analyzer (model TA 50, Shimadzu) at a heating rate of 10 °C/min up to 600 °C under N₂ atmosphere.

2.13. Limiting oxygen index test

Limiting oxygen index (LOI) is defined as the minimum concentration of oxygen, expressed as percent volume, in a flowing mixture of oxygen and nitrogen that will support flaming combustion of a material initially at room temperature. It was performed according to ASTM D2863-77 and calculated as per formula given in our previous communication¹⁹.

2.14. Water uptake test

To determine the water uptake, the Water Absorption Test of the raw wood and WPC specimens was carried out according to ASTM D 570-99, 2002²⁰.

2.15. Water vapor exclusion test

Water vapor exclusion test was done by following the method as reported in the literature²¹.

2.16. Dimensional stability test

2.16.1. Swelling in water vapor

Samples were first dried at 105 °C and dimensions were measured. Samples were then conditioned at 30 °C and 65% RH. Finally, the samples were placed in a chamber where RH and temperature were maintained at 65% and 30 °C, respectively. The dimensions were remeasured after (0.5-168 hours).

2.16.2. 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. Swelling was considered as a change in volume and calculated according to the procedure²².

2.16.3. Anti-swelling efficiency

The anti-swell efficiency (ASE) index was determined to evaluate dimensional stability of treated wood specimens and calculated according to the procedure described in the literature²¹.

2.17. Statistical analysis

All the data for mechanical tests are expressed as means \pm SD. Results were statistically analysed using one way ANOVA (R software) followed by Tukey HSD test. Mean comparison of the results before and after UV exposure were analysed by t-test.

3. Results and Discussion

The conditions of impregnation to get the highest level of polymer loading were optimized by varying vacuum, monomer concentration, initiator concentration, and time of impregnation respectively. The conditions for highest polymer loading, which showed maximum improvement in properties, were as per the following.

Vacuum = 508 mm of Hg, SAN: THF = 5:1, GMA =5 mL, nanoclay = 1.0% (w/v), AIBN= 0.75% (w/w) and VTCS = 0.5-2.0% (v/v).

3.1. Effect of variation of VTCS concentration on polymer loading (WPG, %) and other properties

Effect of variation of VTCS concentration on WPG (%) and other properties are shown in Table 2. Polymer loading (WPG %) and volume increase (%) were found to enhance with the increase in VTCS concentration. Hardness showed a increasing trend throughout the concentration of VTCS studied. The improvement was maximum at (100:20:5:1:2) ratio of SAN: THF: GMA: nanoclay: VTCS. As expected, the addition of GMA to the SAN polymer increased the hardness²³. The hardness was found to increase further when VTCS was incorporated. Improvement in hardness was due to the presence of silane group in VTCS. The treatment of radiata pine (soft wood) and black butt (hardwood) with MMA and silane improved the hardness²⁴. The increase in volume might be due to bulking of the cell wall caused by the incorporation of chemicals. Bulking reduced the cell wall's ability to shrink and swell and thus improved dimensional stability of the wood samples²¹. The deposition was further improved by the cross linker GMA and VTCS which interacted with both the polymer and wood through their double bonds and polar groups.

3.2. FTIR study

Figure 1 shows the FTIR spectra of (a) untreated, (b) VTCS, (c) S/G5 (d) S/G5/N1, (e) S/G5/V2, and (f) S/G5/N1/V2 treated wood samples. The presence of absorption bands of untreated wood (curve-a) at 3435, 1740, 1257 cm^{-1} were for -OH stretching, C=O stretching of acetylated xylem and C-O stretching of acetyl groups respectively²⁵. The absorption bands occurred at 2967, 1602, 1406, 760, 528, 431 cm^{-1} were the characteristic peaks of -CH₂ stretching vibration, -C=C stretching vibration, CH₂ deformation, Si-C stretching, SiCl₃ antisymmetric and SiCl₃ symmetric stretching respectively²⁶. S/G5 treated samples (curve-c) showed the absorption band at 3026 cm^{-1} (-CH₂ stretching), 2240 cm^{-1} (C≡N stretching). In the spectrum of S/G5/N1 (curve-d) treated sample, the characteristic peaks for nanoclay appeared at 3465 cm^{-1} (-OH stretching), 2925 cm^{-1} (C-H stretching),

1620 cm^{-1} (OH bending) and 1030-460 cm^{-1} (oxide bands of metals). S/G5/V2 (curve-e) treated sample showed all the characteristic peaks of VTCS and SAN. The appearance of characteristic peaks for nanoclay, SAN, VTCS in the spectrum of S/G5/N1/V2 treated samples (curve-f) indicated the impregnation of SAN, nanoclay and VTCS into wood²⁷. It was noteworthy that, the characteristic bands of unsaturated double bond from GMA and VTCS occurred at 1638 and 1602 cm^{-1} . With the inclusion of VTCS, the shifting of the peak of unsaturated double bond of GMA from 1638 cm^{-1} to 1615 cm^{-1} was observed (not shown in the figure) which suggested the interaction of GMA with VTCS²².

3.3. X-Ray diffraction study

Figure 2 represents the X-Ray diffractograms of (a) untreated wood, (b) nanoclay and wood samples treated with (c) S/G5/N1, (d) S/G5/N1/V1 and (e) S/G5/N1/V2. The interlayer distance for nanoclay at $2\theta=4.1^\circ$ was calculated and found to be 2.15 nm. Similarly wood sample showed a peak at $2\theta=23.05^\circ$ which was due to crystal plane (002) of cellulose. Wood samples treated with S/G5/N1 exhibited only the characteristic peak of cellulose. The peak for nanoclay was found to disappear. Therefore it could be

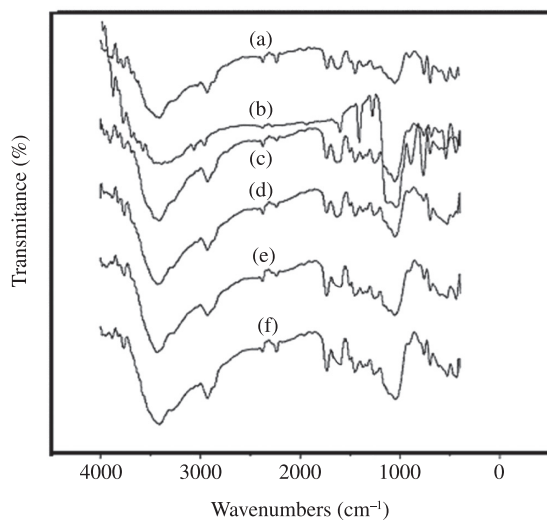


Figure 1. FTIR spectra of (a) untreated wood, (b) VTCS and wood samples treated with (c) S/G5, (d) S/G5/N1, (e) S/G5/V2 and (f) S/G5/N1/V2

Table 2. Effect of variation of VTCS on polymer loading (WPG %), volume increase and hardness.

Sample particulars	WPG (%)*	Volume increase (%)*	Hardness (Shore D)*
W	—	—	35.2(±0.68)
S	24.01(±0.12)	3.08(±0.05)	42.2(±0.68)
S/G5	36.73(±0.12)	3.69(±0.18)	44.8(±0.68)
S/G5/N1	51.15(±1.25)	4.62(±0.21)	47.8(±0.68)
S/G5/N1/V0.5	54.57(±0.34)	4.91(±0.02)	50.2(±0.68)
S/G5/N1/V1.0	100.25(±0.14)	5.17(±0.06)	54.4(±0.93)
S/G5/N1/V2.0	141.03(±0.57)	5.67(±0.14)	63.8(±1.06)
S/G5/V2	43.67(±0.31)	3.89(±0.10)	46.6(±0.44)

*Each value represents the average of five samples. Standard deviation in parenthesis.

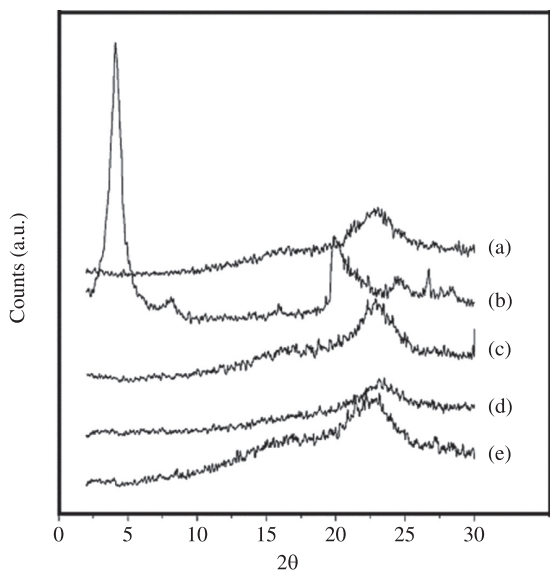


Figure 2. X-Ray diffractograms of a) untreated wood (b) nanoclay and wood samples treated with (c) S/G5/N1, (d) S/G5/N1/V1 and (e) S/G5/N1/V2

said that either the interlayer distance had expanded fully or nanoclay layers became delaminated²⁸. The addition of vinyl trichlorosilane (VTCS) to GMA/nanoclay did not alter the position of diffraction peak in wood samples. This suggested that VTCS did not affect the dispersion of nanoclay in the polymer and it had entered into the amorphous region of wood cellulose with the nanoclay.

3.4. Morphological study

3.4.1. Scanning electron microscopy study

Figure 3 shows the SEM micrographs of untreated (Figure 3a) and treated wood samples (Figure 3b-d). For untreated wood, the empty cell wall, the pit and parenchyma were seen (black arrows pointing towards cell wall and pit). In treated wood, these empty spaces were occupied by the SAN/GMA or nanoclay/GMA/SAN materials.

The adhesion between fibrous cellulose material and polymer strands enhanced due to incorporation of small amount of VTCS (black arrows pointing towards the adhesion) (Figure 3d). The increase of adhesion between fibrous cellulose material and polymer were reported by Shane et al.²⁴. The impregnated materials were either located

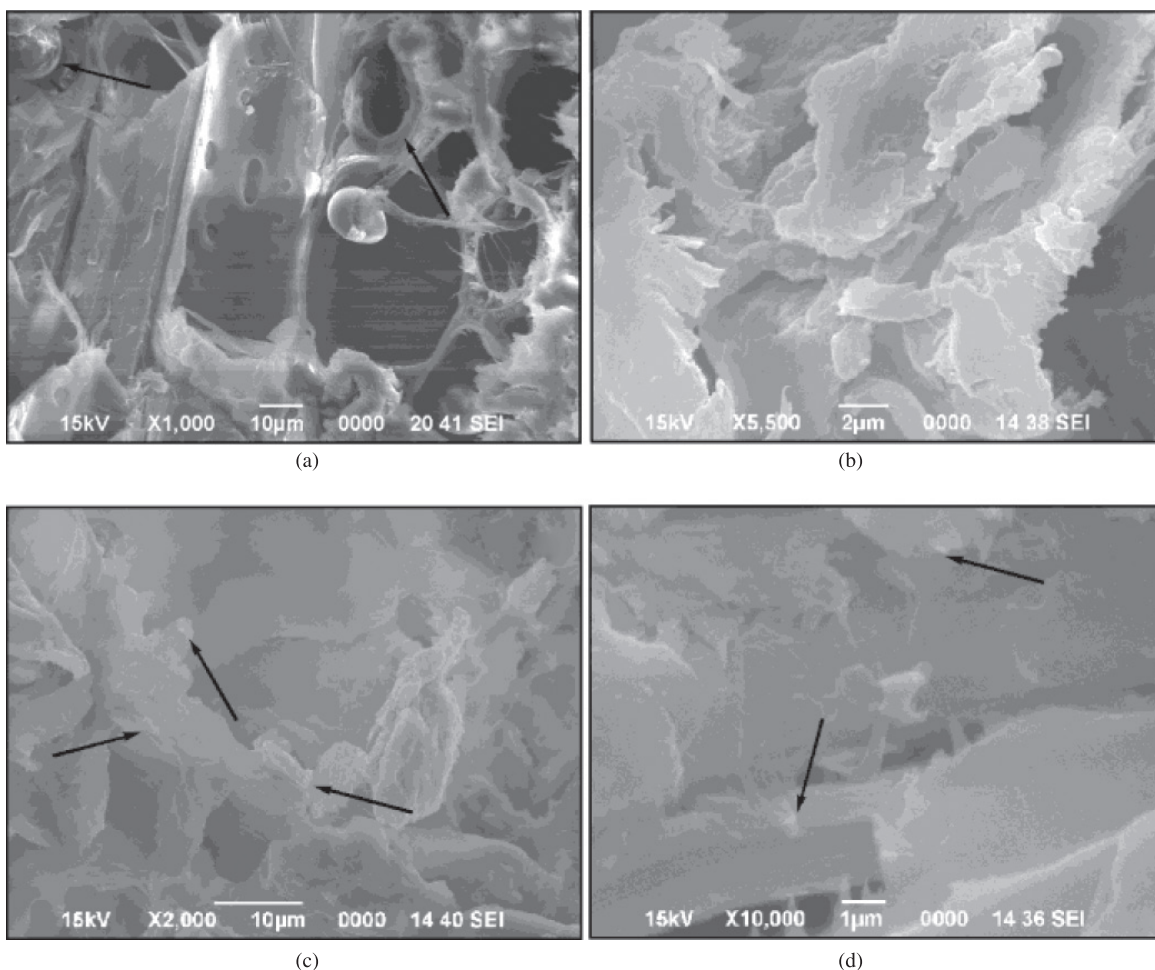


Figure 3. Scanning electron micrographs of a) untreated wood and wood samples treated with (b) S/G5, (c) S/G5/N1 and (d) S/G5/N1/V2

in the cell walls or filled in the cell lumen. The traces of nanoclay can be detected (black arrows pointed) with scanning electron microscope as shown in Figure 3 c, d. This result also suggests that the polymer formed a strong interface with wood cell walls, accounting for the pragmatic increase in mechanical strength.

3.4.2. Transmission electron microscopy study

Figure 4 represents the TEM micrographs of wood (a) untreated, and treated with (b) S/G5/N2, and (c) S/G5/N2/V2 respectively. In the case of untreated wood, the radial fracture patterns—perpendicular to the compound middle lamella was regularly arranged (Figure 4a). Moreover, no consistent orientation of the cell wall components could be

distinguished. Lamellar as well as disordered and, in few cases, moderate striations perpendicular to the compound middle lamella was observed and reported²⁹.

The dark slices for the clay silicate layers were observed in the S/G5/N1 and S/G5/N1/V2 treated wood samples (Figure 4b, c). It was evident that clays were homogeneously dispersed in the SAN polymer matrix present in the cell wall of wood. The homogeneous distribution of clay silicate layers in MUF/clay impregnated aspen wood composites was also reported by Cai et al.⁸.

3.5. Mechanical properties

Mechanical properties of WPC were evaluated by means of tensile test and flexural test (Table 3). A perceptible

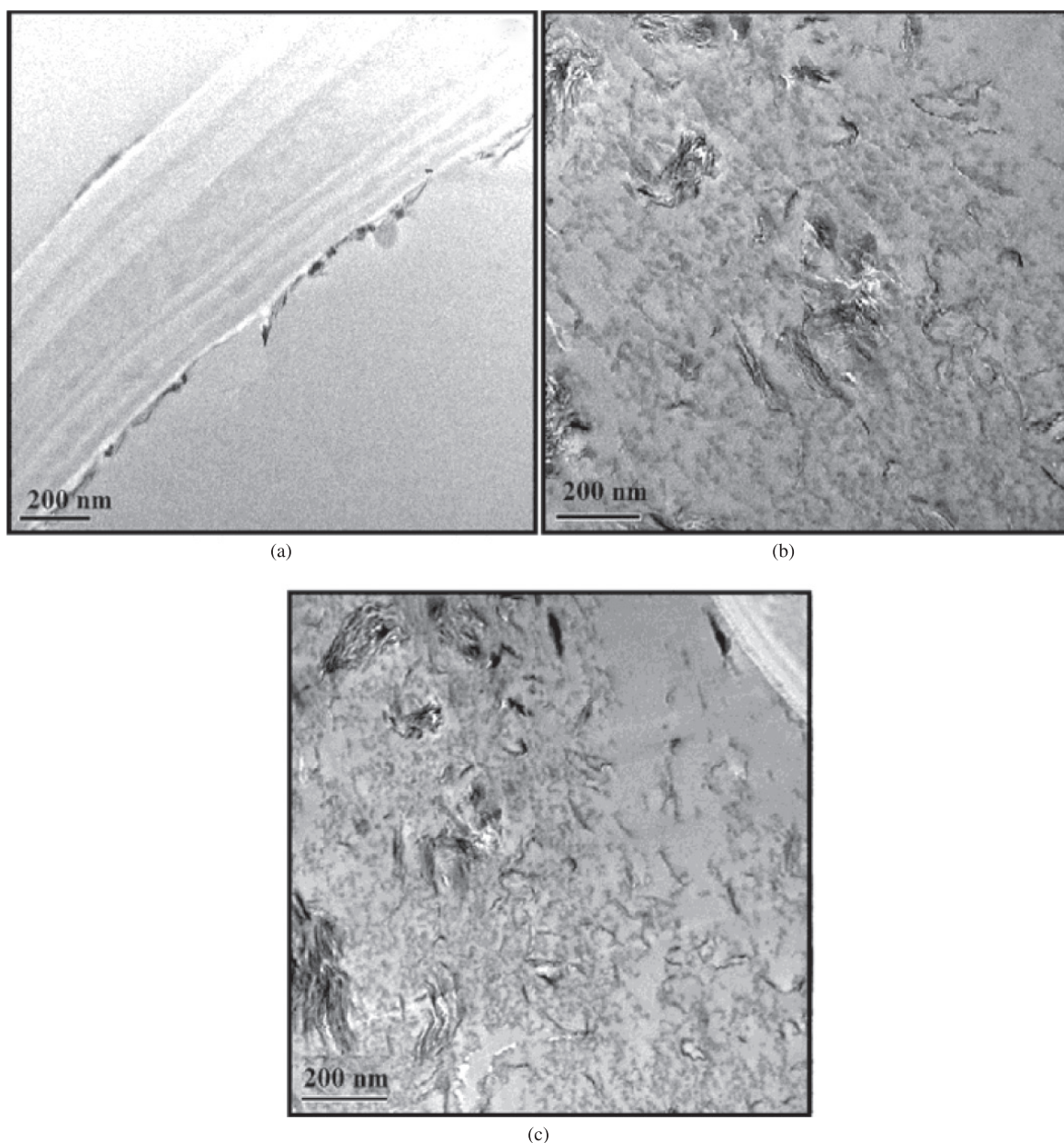


Figure 4. TEM micrographs of a) untreated wood, and wood samples treated with (b)S/G5/N1, and (c) S/G5/N1/V2

increase in tensile strength and flexural properties were observed in the WPC prepared by the inclusion of nanoclay and VTCS. It was observed that wood treated with SAN and GMA caused an improvement in tensile strength and flexural properties. Both the tensile strength and flexural strength increased drastically when clay was added. This could be attributed to the combined effect of increasing interaction between wood and SAN by GMA and stiffening of composites due to reduction in mobility of the intercalated polymer chains. The tensile as well as flexural properties were found to improve on addition of vinyl trichloro silane and nanoclay with SAN/GMA. The improvement in properties might be due to the formation of cross links between wood and SAN by both GMA and VTCS. Silane coupling agent improved the mechanical properties of bamboo fibre filled natural rubber composites³⁰.

3.6. Thermogravimetric analysis

Table 4 showed the initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m) and residual weight (%) (RW) for untreated and polymer treated wood samples with or without nanoclay and vinyl trichloro silane. In all the cases, there was no significant difference in T_i values except in clay and VTCS treated wood polymer composite (WPC). The T_m values of clay and VTCS treated samples were more compared to those of other treated

samples. RW (%) values of wood polymer composites treated with VTCS/clay were found less compared to that of untreated wood.

Table 4 shows the temperature of decomposition (T_D) values at different weight losses for different samples. T_D values of polymer treated wood samples were observed higher than those of virgin wood samples. T_D values increased due to incorporation of GMA.

T_D values increased further on inclusion of nanoclay. The higher T_D values might be due to the formation of cross linked structure by GMA. The cross linking reduced the rate of degradation of degradable components like CO, CO₂ etc. formed during decomposition. Similar findings were reported by Devi and Maji³¹. The presence of silicate layer acted as a barrier and hindered the diffusion of volatile decomposition products³². The degree of cross linking increased further due to the addition of VTCS and hence decreased the rate of elimination of volatile decomposed products. Limiting Oxygen Index (LOI) study

The LOI values are summarized in the Table 3. The LOI test assumed that inherently less flammable materials required greater oxygen concentrations to produce the heat necessary for the continued production of flammable volatiles and flame propagation. Wood treated with SAN/GMA/nanoclay-VTCS system exhibited maximum flame retardancy as evident from higher LOI value. The higher

Table 3. Tensile and flexural properties of treated and untreated wood samples.

Sample particulars	Tensile properties*		Flexural properties*		LOI (%)*
	Tensile modulus (MPa)	Tensile strength (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)	
Untreated W	847(±4.6) ^a	27.96(±0.7) ^a	6327(±24.5) ^a	22.91(±1.09) ^a	11.1(±0.05)
Treated with					
S	902(±2.9) ^b	34.41(±1.3) ^b	6512(±42.5) ^b	40.74(±0.40) ^b	16.0(±0.03)
S/G5	911(±2.7) ^c	38.63(±0.7) ^c	7060(±38.8) ^c	50.05(±1.31) ^c	18.6(±0.10)
S/G5/N1	944(±2.5) ^d	44.98(±1.8) ^d	8328(±81.1) ^d	58.25(±0.36) ^d	25.99(±0.04)
S/G5/N1/V0.5	970(±1.3) ^e	47.07(±0.3) ^e	8580(±53.0) ^e	61.14(±0.21) ^e	26.34(±.24)
S/G5/N1/V1.0	975(±3.5) ^f	48.00(±1.2) ^e	8657(±25.4) ^e	62.14(±0.39) ^e	27.5(±0.24)
S/G5/N1/V2.0	1177(±5.8) ^g	51.54(±0.7) ^f	8755(±33.7) ^e	63.24(±0.30) ^e	30.2(±0.05)
S/G5/V2.0	901(±3.7) ^b	38.35(±0.8) ^b	7093(±43.13) ^c	45.75(±0.30) ^g	25.1(±0.06)

*Each value represents the average value of five samples. The same letters are not significantly different at $p = 5\%$. Comparisons were done within each formulation.

Table 4. Thermal analytical data for untreated and treated wood samples.

Sample particulars	T_i (°C)	^a T_m (°C)	^b T_m (°C)	RW (%)		Temperature of decomposition (T_D) in (°C) at different weight loss (%)					
				500 (°C)	20	30	40	50	60	70	
W	250	300	—	22.0	285	306	310	325	340	440	
Treated with											
S	260	290	330	18.01	290	304	310	320	373	400	
S/G5	263	298	371	18.38	300	321	343	380	408	420	
S/G5/N1	261	—	368	18.57	304	325	378	390	410	420	
S/G5/N1/V0.5	262	305	369	18.69	312	329	367	395	413	424	
S/G5/N1/V1.0	264	310	378	20.68	320	340	375	400	417	430	
S/G5/N1/V2.0	270	320	380	21.70	321	347	388	410	418	447	
S/G5/V2.0	255	300	369	18.40	298	323	358	383	409	416	

the VTCS, the higher was the LOI value. Laoutid et al. reported that LOI value of vinyl bromide based copolymer increased with the increase in vinyl bromide content in the copolymer³³. The flame retardancy effect appeared to originate from the clay's ability to contribute to char formation. This char layer formed an insulative layer to slow down heat transfer and retarded movement of gases to feed the flame³⁴. The reduction in flammability in polymer layered silicate nano materials was due to the pyrolysis of the polymer and a collapse of the nanocomposite structure to form a silicate-carbon barrier that provided thermal protection to the underlying virgin polymer and as a result slowed the rate of volatilization of fuel¹³. The enhancement in properties might be due to the synergistic effect between clay and VTCS during combustion of wood. Giudice et al. reported that wood impregnated with silicate improved the fire resistance properties³⁵. Boonkrai et al. reported that organically modified clay and silica modified with 3-amino propyl trimethoxy silane improved the flame retardancy properties of ABS nanocomposites¹⁵.

3.7. Water uptake study

The results of water uptake for treated and untreated samples are shown in Figure 5. In both treated and untreated samples, water absorption increased with the increase in time of immersion.

Untreated samples absorbed more water than the treated samples. Wood samples treated with SAN copolymer decreased the water uptake throughout the studied time period due to the filling up the void volumes present in wood by the same. GMA treated wood showed lower water absorption because of the cross links formed by the interaction of double bond and glycidyl group of GMA with SAN copolymer and hydroxyl group of wood respectively^{2,23}.

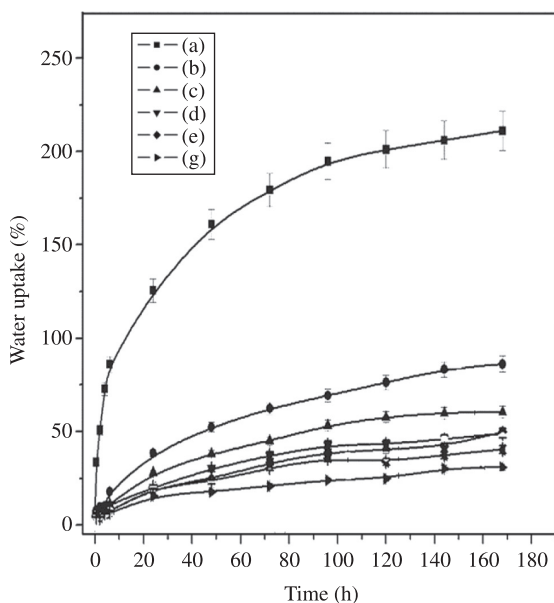


Figure 5. Water uptake % of wood samples (a) untreated and treated with (b) S, (c) S/G5, (d) S/G5/V2, (e) S/G5/N1, (f) S/G5/N1/V1 and (g) S/G5/N1/V2 at 65% RH and at 30 °C

The addition of nanoclay or silane further decreased the water uptake capacity. Nanoclay treated samples showed lower water absorption compared to silane treated samples. The silicate layers of the clay generated the tortuous pathway and increased the barrier property for diffusion of water within the composites⁸. Wood samples treated with the combination of nanoclay and silane showed least water absorption. Nanoclay provided the tortuous path whereas silane agent enhanced the crosslinking and thus reduced the available free volume for absorption of water. The more the silane, the lower was the free volume available for absorption of water. Hence nanoclay and silane treatment decreased the water uptake capacity of SAN treated wood samples.

3.8. Water vapor exclusion test

In a series of water vapor exclusion study at 65% RH and at 30 °C for various time periods, treated samples absorbed less water vapor than untreated samples. The trend and explanation for water vapor uptake of different samples were similar to those of samples taken for water uptake study as shown in Figure 5.

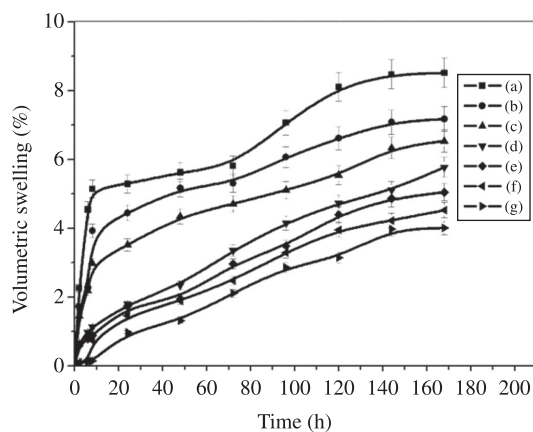


Figure 6. Volumetric swelling in water vapor for wood samples (a) untreated and treated with (b) S, (c) S/G5, (d) S/G5/V2, (e) S/G5/N1, (f) S/G5/N1/V1 and (g) S/G5/N1/V2 at 30% RH and at 30 °C

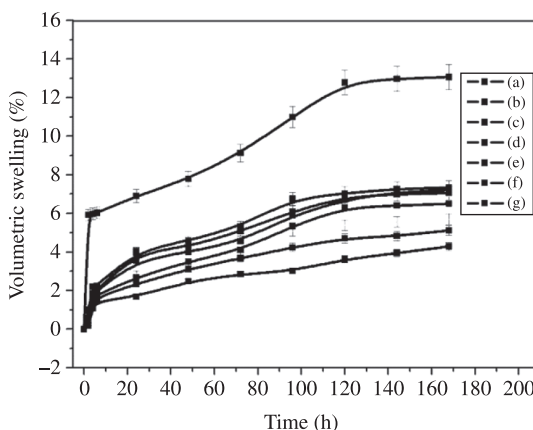


Figure 7. Volumetric swelling in water for wood samples (a) Untreated and treated with (b) S, (c) S/G5, (d) S/G5/V2, (e) S/G5/N1, (f) S/G5/N1/V1 and (g) S/G5/N1/V2 at 30% RH and at 30 °C

Table 5. Anti- swelling efficiencies of wood polymer composites.

Time(h)	S	S/G5	S/G5/V2	S/G5/N1	S/G5/N1/V1	S/G5/N1/V2
2	81.86	83.55	88.64	91.69	96.10	96.94
4	83.05	84.74	89.83	92.88	97.28	98.13
6	84.06	85.76	90.84	93.89	98.30	99.15
24	100.0	101.69	106.77	109.83	114.23	115.08
48	114.57	116.27	121.35	124.40	128.81	129.66
72	138.11	139.81	144.91	147.96	152.71	153.22
96	168.98	170.67	175.76	178.81	183.22	184.07
120	197.11	198.81	203.90	206.94	211.31	212.40
144	203.22	204.91	210.00	213.05	217.45	218.30
168	202.37	204.06	209.15	212.20	216.61	217.45

3.9. Dimensional stability test

3.9.1. Swelling in water vapour and liquid water

The results showing the effect of swelling in water vapour for untreated and treated wood samples at 65% RH and room temperature (30 °C) for different time periods were shown in Figure 6.

Similarly, Figure 7 shows the effect of swelling in liquid water at room temperature for treated and untreated wood samples. As expected, wood treated with GMA and silane showed least swelling. The explanation was similar to that of discussed earlier.

3.9.2. Anti swelling efficiency

The results of anti swelling efficiency of wood samples are shown in Table 5. Anti swelling efficiency was found to increase with the increase of time. The anti swelling 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 nanoclay into the void spaces of wood, which prevented the cell walls from shrinking in response to moisture loss. Nanoclay further increased the tortuous path for diffusion of water. Besides this, the polymer was less hygroscopic than wood, less water would be absorbed during humid conditions¹⁹.

The dimensional stability was further improved by addition of VTCS. VTCS could form crosslinks and thus reduced the shrinkage and swelling caused by the water and as a result dimensional stability would be improved. Treatment of Scots pine with a mixture of two alkoxy silanes increased the ASE was reported in the literature³⁶. GMA treatment remarkably improved the anti-swell efficiency of styrene impregnated rubber wood².

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4. Conclusions

The ultimate goal of impregnation of styrene acrylonitrile co-polymer and nanoclay into soft wood was to improve the properties of soft wood. Wood polymer nanocomposites were prepared by the treatment of styrene acrylonitrile copolymer/nanoclay-GMA intercalating mixture in presence of VTCS. FTIR study showed the incorporation of VTCS and nanoclay in the wood/SAN composite. XRD analysis indicated that VTCS did not affect the dispersion of nanoclay into the polymer. Water uptake, dimensional stability and mechanical properties were improved due to incorporation of VTCS with nanoclay. SEM study revealed the presence of nanoparticles into wood cell wall and wood lumen and improvement in adhesion between wood and polymer by incorporation of VTCS. The uniform distribution of silicate layers of nanoclay in the WPC was studied by TEM. TGA and LOI study showed that thermal stability and flame retardant properties of wood polymer nanocomposites were improved due to incorporation of small amounts of VTCS with nanoclay.

From this work, it has been shown that styrene acrylonitrile co-polymer, nanoclay, GMA and VTCS are promising materials for the improvement of the soft wood performance and so, further studies to this direction are worthwhile.

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