

Effect of chemical modification with styrene and glycidyl methacrylate on the properties of pinewood

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Pinewood was impregnated with styrene and in combination with glycidyl methacrylate (GMA) as a cross-linking monomer. After the impregnation polymerization was accomplished by catalyst heat treatment. The conditions of impregnation such as monomer concentration, initiator concentration, time of impregnation and vacuum were varied to get the optimum polymer loading. Impregnation with styrene-GMA improved physical properties such as water absorption, swelling and hardness, compared to those of styrene alone. Water vapour absorption and swelling in water vapour at 90% RH also improved on treatment. FT-IR spectroscopy and scanning electron microscopy (SEM) studies of fractured wood samples showed the interaction between wood and the polymers.

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Wood is an important raw material that is cheap and easily worked. Wood is the most preferred building material because of its strong physical strength, aesthetically pleasing character and low processing cost. But it has got some disadvantages such as change in dimension with time due to environmental modulation and degradation due to insect attack that results in loss of timber value for constructional purposes. Chemical modification of wood to increase its resistance to biodegradation and “photo degradation”, to improve its dimensional stability and to decrease its flammability depends on adequate distribution of reacted chemicals in water accessible regions of the cell wall. The chemicals used for modifying wood must be capable of swelling the wood to facilitate penetration and must react with the hydroxyl groups of the cell wall under neutral or mild alkaline conditions. The chemicals should react quickly with the hydroxyl groups to yield stable chemical bonds without by products. The modified wood must retain the desired properties of the untreated wood¹⁻⁴. The wood-polymer composites (WPC) should have greater dimensional stability, compressive strength and hardness, compared with original wood^{5,6}. It was reported that wood treated with vinyl-type monomer followed by curing (radiation or catalyst) significantly improved the

moisture resistance and hardness⁷. Use of glycidyl methacrylate (GMA) with diallyl phthalate (DAP) improved the properties of rubber wood⁸. Cross-linking of material in wood provided better dimensional stability to the WPC⁹. Rubber wood treated with styrene and GMA as the cross-linking monomer improved various properties¹⁰⁻¹².

Encouraged by earlier studies¹⁰⁻¹², the present investigation has been carried out to determine the effect of impregnation of styrene in the presence of GMA as a difunctional cross-linking monomer on different properties of pinewood.

Experimental Procedure

Materials

Pinewood was collected from a local forest in Assam, India. Styrene obtained from Merck (Mumbai, India) was purified by following standard procedure¹². Glycidyl methacrylate (GMA) and 2,2'-azobis-(isobutyronitrile) (AIBN) obtained from Merck, India and were used as received. All other chemicals used were of analytical grade and used directly.

Sample preparation

The wood samples used for the study were prepared from defect free wood, cut into blocks of 2.5×1×2.5 cm (radial × tangential × longitudinal) for water uptake, hardness test and swelling in water tests.

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Impregnation procedure

All the samples were oven dried at 105°C to constant weight before treatment and the dimensions and weights were measured. The samples were then placed in an impregnation chamber followed by application of load over each sample in order to prevent them from flotation during addition of monomers. Vacuum was applied for a specific time period for removing the air from the pores of the wood before addition of monomers. Now sufficient mixture of styrene and initiator or that of styrene-GMA 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 was the minimum time to get a polymer loading, which showed maximum improvement in properties. The condition of impregnation was varied by changing different parameters like monomer concentration, initiator concentration, level of vacuum and time. 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 h in an oven. This was followed by drying at 105°C for 24 h. The cured samples were then Soxhlet extracted to remove homopolymers, if any, formed during impregnation. 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 following formula:

$$\% \text{ Wt gain (WPG)} = \{(W_t - W_o)/W_o\} \times 100$$

where W_o is the oven dry weight of untreated wood and W_t is the oven dry weight of the treated wood.

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.

Both untreated and treated wood samples were immersed in distilled water for 24 h and weight and dimensions were measured. The water uptake and the percent swelling in water was calculated based on oven dry weight and volume according to the following formulas:

$$\text{Water uptake (\%)} = \left[\frac{W_t - W_d}{W_d} \right] \times 100$$

where W_d is the oven dry weight and W_t is the weight after immersion in distilled water for 24 h

$$\% \text{ Swelling} = \left[\frac{V_{t,u} - V_o}{V_o} \right] \times 100$$

where $V_{t,u}$ 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

Oven dried 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 90%, respectively and weights were measured after 0.5, 2, 4, 8, 24, 48, 96, 120 and 168 h. It was expressed as percentage of absorbed moisture based on oven dry weight.

Samples were first dried at 105°C followed by measuring the dimensions in radial as well as tangential directions. Samples were then conditioned at 30°C and 30% RH. Finally, the samples were placed in a chamber where RH and temperature were maintained at 90% and 30°C respectively. Now, the dimensions were re-measured after 0.5, 2, 4, 8, 24, 48, 96, 120 and 168 h.

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

The treated and untreated samples were grounded and FT-IR spectra were recorded using KBr pellet in a Nicolet Impact 410 spectrophotometer.

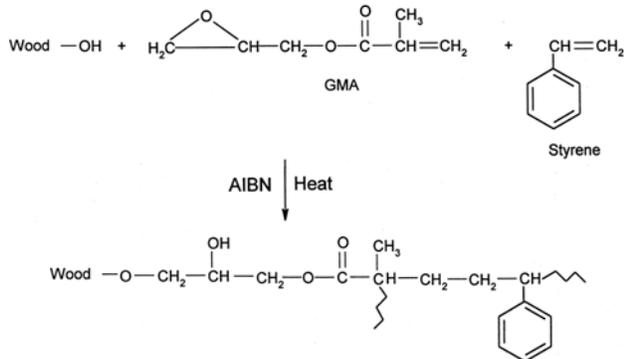
The compatibility between wood and polymers was monitored using a scanning electron microscope (model JEOL, JSM-5200) at an accelerating voltage of 15 kV. The electron microscopy photographs were taken from the fracture surfaces of the wood samples.

Results and Discussion

A series of experiments were carried out under varied conditions of vacuum, time, initiator concentration and different monomer concentrations to optimize the conditions at which polymer loading caused maximum level of swelling of wood material.

Scheme 1 shows the probable reaction among hydroxyl group of wood, epoxy group of GMA and double bond of styrene.

Table 1 shows the results of variation of initiator concentration on polymer loading (WPG) using styrene-GMA system. On increasing AIBN concentration polymer loading was found to be increased initially and then decreased. Similar observation was also reported in the literature^{15,16} during impregnation of MMA in basswood samples using AIBN catalyst. The maximum polymer loading of 31% was found



Scheme 1— Reaction between wood, styrene and GMA

Table 1—Effect of variation of initiator (AIBN) concentration on polymer loading (WPG) (%) of pinewood: [AIBN: 0.2-5% (by weight), Styrene: GMA= 100:20, time: 4 h, temperature: 30± 1°C, vacuum: 5" Hg]

Initiator Concentration (%)*	0.2	0.5	2	5
WPG (%)	18.25	22.1	31.0	25.8
Volume increase after curing (%)	0.1	0.17	1.21	0.6
Water uptake (%)	26.9	20.8	15.5	21.3
Swelling in water (%)	10.5	10.0	7.6	9.9
Hardness	51.3	44.4	52.7	46.3

*All the values reported were taken from average of five samples.

with 2% AIBN catalyst concentration (by weight) which showed maximum improvement in properties with more increase in the volume after curing.

Pinewood samples showed negligible change in volume on impregnation with styrene. But significant change in volume (%) of wood samples was noticed when GMA was introduced (Table 2). The higher the percentage of GMA, the higher was the % volume change. The results indicated that GMA was able to penetrate into the cell wall more readily as compared to styrene due to its advantageous molecular size⁸. The observation was further supported by swelling in water tests. Again samples impregnated with styrene-GMA system swelled less in water, compared to styrene treated and untreated wood samples. Improvement in hardness values was also observed with increase in the percentage of GMA. These results indicated that styrene only bulked the cell wall and did not interact fully with wood. The interaction of GMA with wood and styrene through its epoxy group and terminal double bond might be responsible for lowering in swelling. Similar observations were also noticed in the case of styrene-GMA treated rubber wood^{11,12}. Improvement in dimensional stability of wood samples due to cross-linking was also reported in literature^{9,12}.

It was found that the effect of variation of vacuum (1"-15") on impregnation, with increasing vacuum polymer loading increased first, then decreased (Table 3). Maximum improvement in the properties was obtained at 5" Hg with 30% polymer loading. It could be said that 30% polymer loading caused maximum swelling of wood samples. Beyond that the polymer might fill the wood lumens instead of cell wall resulting in no further swelling of wood.

Table 2—Effect of variation of monomer concentration on polymer loading WPG (%) and other properties:

[Styrene: GMA= 100:0 to 100:100, AIBN: 2% (by weight), time: 4 h, temperature: 30±1°C, vacuum: 5" Hg]

Samples particulars*	WPG (%)	Volume increase after curing (%)	Water uptake (%)	Swelling in water (%)	Hardness (Shore D)	
Untreated	-	-	38.7	10.0	45.4	
Treated						
Styrene	GMA					
100	0	24.9	0.1	17.5	8.2	50.0
100	20	30.9	1.2	17.0	7.6	51.3
100	50	30.3	7.3	16.1	6.3	53.0
100	100	20.6	11.5	18.1	5.2	54.5

*All the values reported were taken from average of five samples.

The results showing the effect of variation of impregnation time on polymer loading are presented in Table 4. Loading was found to be increased throughout the time period studied (up to 20 h). Both water uptake and swelling in water decreased with increasing in polymer loading. Overall improvements in properties were obtained when impregnation was done for 4 h. With increasing time, the capillaries and void spaces were getting more time to become filled up with monomers, which in turn would lead to increase the loading. The decrease in space to hold the water due to impregnation by polymer might be responsible for observed lower values.

In a series of water vapour exclusion study in 90% RH and at 30°C for various time periods, treated samples absorbed less water vapour than untreated samples (Fig. 1). The absorption of water vapour followed the trend: untreated > styrene treated > styrene-GMA (5:1) treated > styrene-GMA (2:1) treated > styrene-GMA (1:1) treated samples.

The results showing the effect of swelling in water vapour at 90% RH and room temperature (30°C) up to

Table 3— Effect of variation of vacuum on loading and other properties

[Styrene:GMA= 100:50, vacuum: 1-15"Hg, AIBN: 2% (by weight), time: 4 h, temperature: 30±1°C]

Vacuum applied (Inches of Hg)*	WPG (%)	Volume increase after curing (%)	Water uptake (%)	Swelling in water (%)
1	10.0	0.1	38.5	15.6
5	30.3	7.3	16.2	7.3
10	35.7	2.9	15.6	11.6
15	29.9	0.2	25.4	12.3

*All the values reported were taken from average of five samples.

Table 4—Effect of variation of time on loading and other properties: [Styrene:GMA= 100:50, AIBN: 2%(by weight), time: 2-20 h, vacuum: 5"Hg, temperature: 30±1°C]

Time (h)*	WPG (%)	Volume increase after curing (%)	Water uptake (%)	Swelling (%) in water	Hardness
2	21.1	5.2	32.1	7.8	47.8
4	30.0	7.3	16.1	6.3	53
6	32.3	6.3	20.2	11.7	46.9
8	35.8	6.1	20.5	3.7	48.0
20	40.3	1.9	16.9	3.9	55.4

*All the values reported were taken from average of five samples.

168 h are presented in Fig. 2. As expected treated samples particularly those where GMA was incorporated showed more reduction in swelling. Similar type of observation was also reported earlier¹².

The interactions between wood, styrene and GMA were confirmed by FT-IR spectroscopy^{11,12,16,17}. The FT-IR spectra of treated and untreated wood samples are presented in Fig. 3 (I-V). From the FT-IR spectra it was found that the peak at 1736 cm⁻¹, which was due to carbonyl stretching vibration, became more pronounced on treatment with styrene-GMA. The position of the peak at 3395.02 cm⁻¹ (O-H stretching) for untreated wood remained almost unchanged by the incorporation of styrene, but shifted to higher wave number on incorporation of GMA with styrene. The intensity of C-O stretching vibration (1058.41 cm⁻¹)

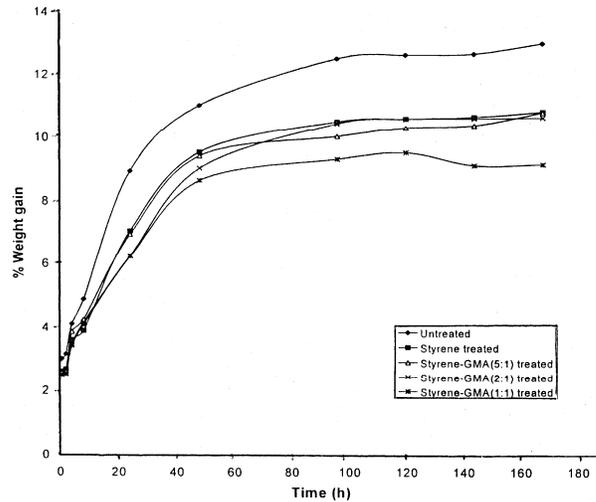


Fig. 1—Weight gain of WPC in water vapour at 90%RH and 30°C

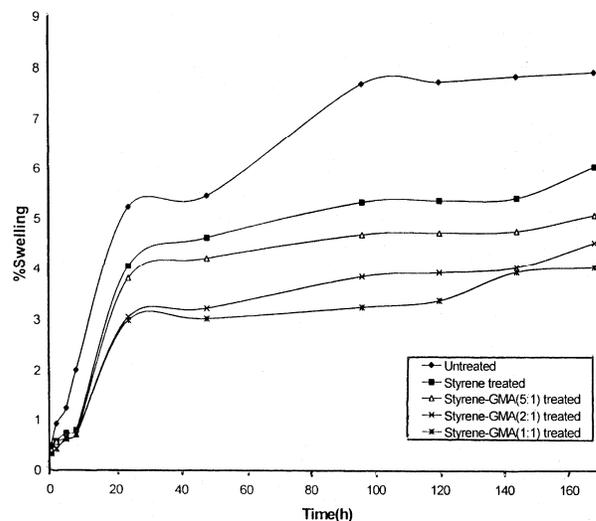


Fig. 2—Swelling of WPC conditioned at 90%RH and at 30°C

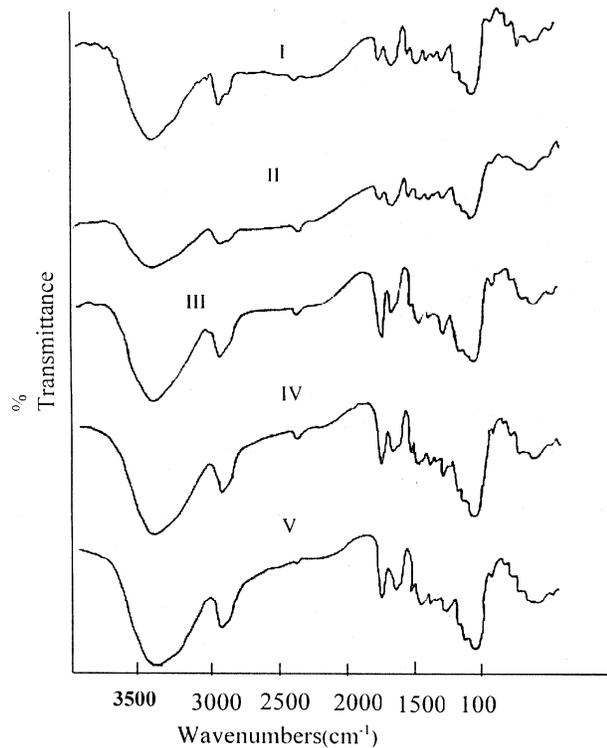


Fig. 3—FT-IR spectra of (I) styrene treated, (II) untreated, (III) GMA treated, (IV) styrene-GMA (1:1) treated and (V) styrene-GMA (2:1) treated pinewood

also increased on treatment. These results indicated a strong interaction between wood and styrene by incorporation of GMA.

The fine structures of wood and the compatibility between wood and the polymers were investigated by scanning electron microscopy (SEM). The photographs were taken from the fracture surfaces of some selected samples. Fig. 4(a), (b) and (c) represents SEM photographs of untreated, styrene treated and styrene-GMA (1:1) treated samples, respectively. The cells swelled (arrow marked) due to treatment as shown in Fig. 4b and 4c.

Conclusions

The work demonstrated that the properties of pinewood were enhanced due to chemical modification with styrene and glycidyl methacrylate (GMA). Swelling on impregnation increased with increasing GMA concentration. Properties such as water absorption, swelling in water and hardness etc. improved on treatment with styrene-GMA compared with styrene only. Water vapour exclusion and swelling in water vapour (at 90% RH) were also found to improved due to modification. FT-IR

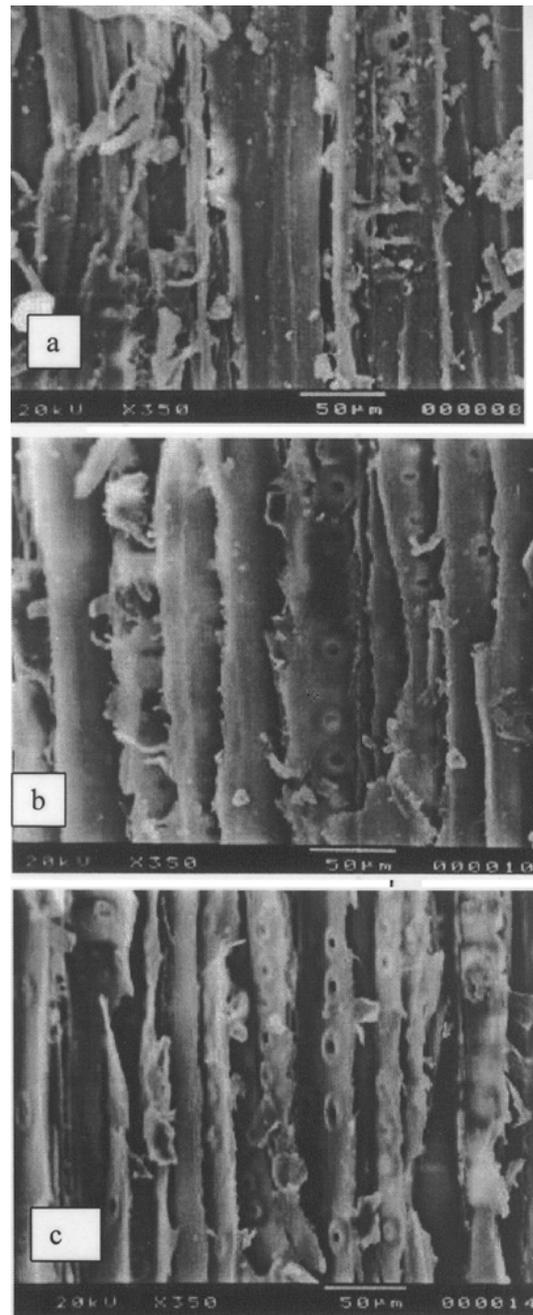


Fig. 4—SEM photographs of (a) untreated, (b) styrene treated and (c) styrene-GMA (1:1) treated pinewood.

spectroscopy and SEM studies reveal the evidence for the interaction between the wood and the polymers.

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