Studies on Dimensional Stability and Thermal Properties of Rubber Wood Chemically Modified with Styrene and Glycidyl Methacrylate

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ABSTRACT: Rubber wood (*Hevea brasiliensis*) was impregnated with styrene and glycidyl methacrylate (GMA) as the crosslinking monomer. After impregnation, the polymerization was accomplished by catalyst heat treatment. Water uptake (%) and water vapor exclusion (%) of the rubber wood were found to be improved on treatment. Dimensional stability expressed in terms of volumetric swelling in water vapor (90% relative humidity) as well as in liquid water and water repellent effectiveness (WRE) of the treated samples were determined and also found to be improved. The wood–polymer interaction was confirmed by FTIR spectroscopy. Thermal properties of untreated and treated wood samples were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetery (DSC) and an improvement in thermal stability was observed for the wood–polymer composites. The improvement in properties observed as more with styrene–GMA (1:1) combination. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1938–1945, 2004

Key words: wood–polymer composite; dimensional stability; crosslinker; glycidyl methacrylate; thermal properties

INTRODUCTION

Wood has been used as an engineering material for centuries. Wood is a heterogeneous material that is made up of two major components, carbohydrate and lignin, and two subcomponents that are organic extractives and inorganic minerals. Impregnating wood with polymerizable monomer formulation and then polymerizing it in place produces a wood–polymer composite (WPC). WPC could be more useful for more products, and have a longer life, because it is less susceptible to moisture-induced swelling, shrinking, and biodeterioration and has a harder surface.

Over the years, researchers have impregnated wood with a variety of chemicals to produce WPC. A few of these have found commercial applications, some for a limited time. There are many potential applications for the material. The preservation of wood can best be achieved by proper selection of consolident materials. The crucial point is, therefore, selecting a monomer that can protect and consolidate the wood. In principle, the consolident action can be effectively obtained if a polymer is fully compatible with the chemical constituents of the wood.[1]

Chemical modification of wood to improve its dimensional stability and to decrease its flammability depends on adequate distribution of reacted chemicals in the water-accessible regions of the cell wall. The chemicals used for modifying wood to facilitate penetration must react with the cell wall polymer hydroxyl groups under neutral or mild alkaline conditions at temperatures below 120°C.

Wood–plastic composites were prepared for the first time as a result of experimental work done at the University of West Virginia in 1962.[2] Wood treated with vinyl monomers followed by curing (radiation or catalyst) significantly improves the moisture resistance, hardness, etc.[3] WPC made with combinations of hexanediol diacrylate, hydroxyethyl methacrylate, hexamethylene diisocyanate, and maleic anhydride has reduced the rate of swelling in water as well as in water vapor.[4] Chemical modification of rubber wood with glycidyl methacrylate (GMA) and diallyl phthalate (DAP) has enhanced the properties of rubber wood significantly.[5,6] Impregnation of wood with vinyl or acrylic monomers shows less dimensional stability in the presence of moisture. This may be due to the confinement of monomer in cell lumen instead of cell wall.[7] Crosslinking of material in wood samples provides better dimensional stability to the wood–polymer composite.[8] The problem of limited adhesion

was extensively addressed in numerous reports on the effects of compatibilizers and coupling agents on the mechanical properties of composites.[9–13] Wood treated with styrene and GMA as the crosslinking monomer has shown improvement in properties.[14,15] The glycidyl group of GMA is capable of reacting with groups containing active hydrogens such as amino, hydroxyl, and carbonyl group.[16] The glycidyl group and terminal double bond of GMA can be exploited for reaction with hydroxyl groups of cellulose in wood and for copolymerization with vinyl or acrylic monomers.

Encouraged by our earlier study,[14] the present investigation was carried out to determine the effect of impregnation with styrene in the presence of a difunctional crosslinking monomer, GMA, on the water absorption, dimensional stability, and thermal properties of softwood.

EXPERIMENTAL

Materials

Rubber wood (*Hevea brasiliensis*) was collected from a local forest in Assam, India. Styrene, obtained from Merck (Mumbai, India), was purified by following standard procedure.[17] GMA and 2,2'-azobisisobutyronitrile (AIBN) obtained from Merck 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 clear, defect-free wood cut into blocks of $2.5 \times 1 \times 2.5$ cm^3 for water uptake, water vapor exclusion, water-repellent effectiveness, and dimensional stability test.

Impregnation procedure

All 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 to prevent them from floating during the addition of monomers. Vacuum was applied for a specified time period to remove the air from the pores of the wood before addition of monomers. Now sufficient mixture of styrene, GMA, and initiator, or mixture of styrene and initiator, or that of 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 im-

provement in properties. The condition of impregnation was varied by changing different parameters such as 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 aluminum 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 the dimensions were measured by using a slide caliper and weights were taken.

Measurements

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, expressed as

$$\text{water uptake (\%)} = \left[\frac{W_t - W_d}{W_d} \right] \times 100 \qquad (1)$$

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

Water vapor exclusion test

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 is expressed as a percentage of moisture absorbed based on oven dry weight.[4]

Water repellent effectiveness (WRE)

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

$$\text{WRE} = \left[\frac{(D_0 - D_t)}{D_0} \right] \times 100 \qquad (2)$$

where D_0 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.
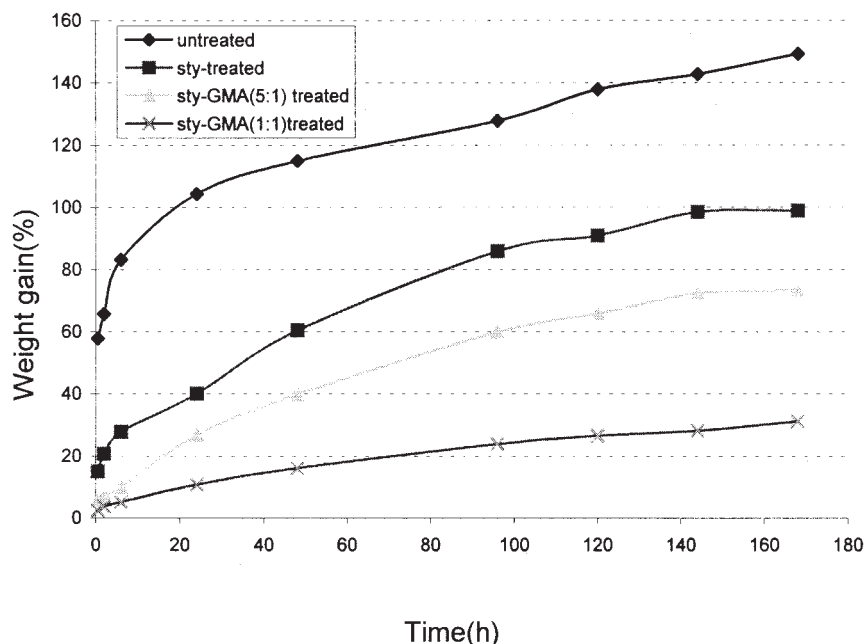
Figure 1 Weight gain of WPC in water at 30°C.

Dimensional stability test

Dimensional stability test was performed by using a procedure described elsewhere.[4]

Swelling in water vapor. 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. The dimensions were remeasured after 0.5, 2,4, 8, 24, 48, 96, 120, and 168 h.

Swelling in water. Dimensions of the oven-dried samples were measured and conditioned at room temperature (30°C) and 30% RH. Final placement of the samples as done in distilled water and then dimensions were remeasured after 0.5, 2, 6, 24, 48, 96, 120, 144, and 168 h.

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

$$\% \text{ Swelling} = \left[\frac{V_{t,u} - V_0}{V_0}\right] \times 100 \qquad (3)$$

where $V_{t,u}$ is the volume of the untreated or treated wood after water absorption; and V_0 is the volume of the untreated or treated wood before water absorption.

FTIR study

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

Thermal study

Thermal properties of the untreated and treated wood samples were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC study was carried out in a differential scanning calorimeter (model Metler TA 4000) at a heating rate of 10°C/min up to 500°C. TGA was carried out by using a thermogravimetric analyzer (model Metler TA 4000) at a heating rate of 20°C/min up to 500°C.

RESULTS AND DISCUSSION

For the water uptake, water vapor exclusion, and dimensional stability measurements, the treated samples chosen were more or less of similar polymer loading and each result presented in figures or tables was taken from the average of five samples.

Water uptake test

The results of water uptake for treated and untreated samples were shown in Figure 1. In both treated and untreated samples up to the time period studied, water absorption increased with an increase in time and untreated samples absorbed more water compared to treated samples. Styrene–GMA (1 : 1) treated samples showed the least water uptake throughout the time period studied. With an increase in time, the capillaries and void spaces were getting more time to become filled up with water, which in turn leads to an increase in the water uptake. In treated samples, the decrease in spaces, available to hold water due to filling up of the same by
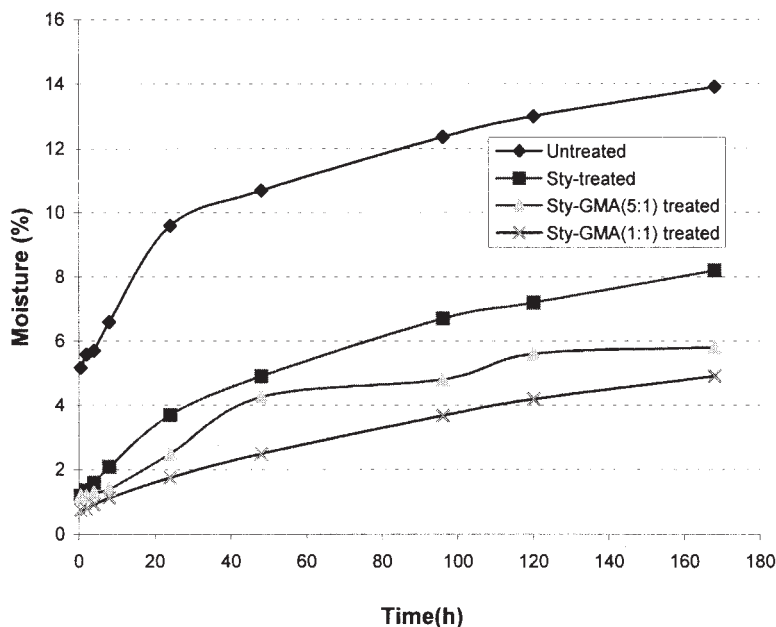
Figure 2 Weight gain of WPC in water vapor at 90% RH and 30°C.

polymer, was responsible for lowering in water absorption. The water absorption decreased further because of the crosslinking formed by the interaction of glycidyl group and double bond of GMA with hydroxyl group of wood and styrene, respectively.

Water vapor exclusion

In a series of water vapor exclusion study in 90% RH and at 30°C for various time periods, treated samples absorbed less water vapor than untreated samples (Fig. 2). The absorption of water vapor followed the trend untreated > styrene treated > styrene–GMA (5 : 1) treated > styrene–GMA (1 : 1) treated samples. The reason for this trend could be explained as earlier.

Water repellent effectiveness

Table I showed the results of the WRE values for treated and untreated wood samples in water at room temper-

ature (30°C). An improvement in WRE values was observed for treated samples, particularly on incorporation of GMA. In all the cases, water repellency decreased initially at a faster rate and finally at a slower rate. A similar type of observation was reported in the literature.[8,18] The improvement in WRE could be explained by the same reason as stated earlier.

Dimensional stability

Swelling in water vapor

The results showing the effect of swelling in water vapor at 90% RH and room temperature (30°C) up to 168 h were presented in Figure 3. As expected, treated samples, particularly those where GMA was incorporated, showed more reduction in swelling.

Swelling in liquid water

The effect of swelling in liquid water at room temperature (30°C) for untreated and treated wood samples

TABLE I
Water Repellent Effectiveness (WRE) (%) of Wood Polymer Composites

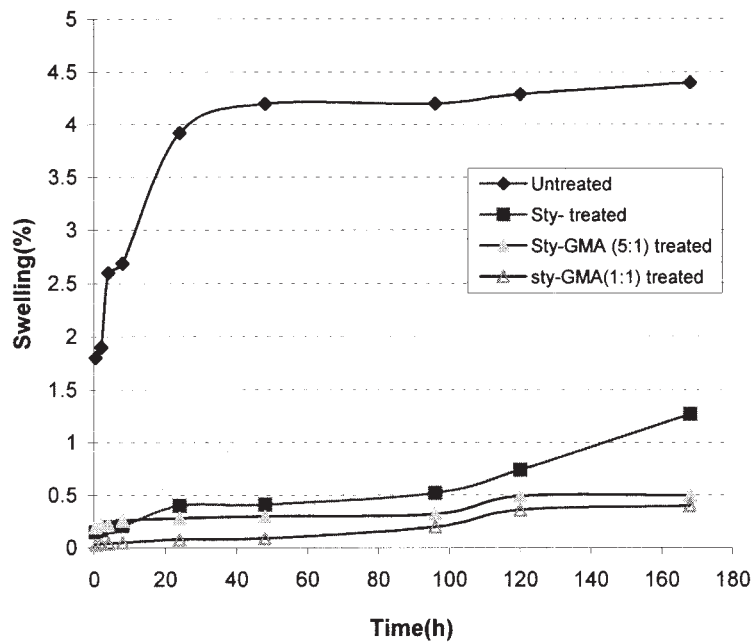| Time (h)	Styrene-treated wood	Styrene–GMA (5 : 1) treated wood	Styrene–GMA (1 : 1) treated wood
0.5	73.9	90.15	95.68
2	68.3	89.05	94.07
6	66.5	87.88	93.76
24	61.5	74.3	89.5
48	47.4	65.4	85.9
96	32.7	53.12	81.3
144	30.9	49.25	80.26
168	33.6	50.77	79.03

Figure 3   Swelling of WPC conditioned at 90% RH and at 30°C.

for different time periods was shown in Figure 4. Samples treated with styrene–GMA (1:1) combination showed the least swelling compared to either untreated or other treated samples. Samples treated with styrene or styrene–GMA (5 : 1) showed less swelling than the untreated samples up to a certain time (105–120 h); beyond that swelling increases. The reason for this was not clear. Overall, due to treatment, the reduction in swelling was noticed.

The reduction in rate of swelling in the above cases could be explained with the help of the combined effect of crosslinking by GMA and filling of void space by polymers.

FTIR study

The FTIR spectra of untreated and treated wood samples were presented in Figure 5I–III. From the FTIR spectra, it
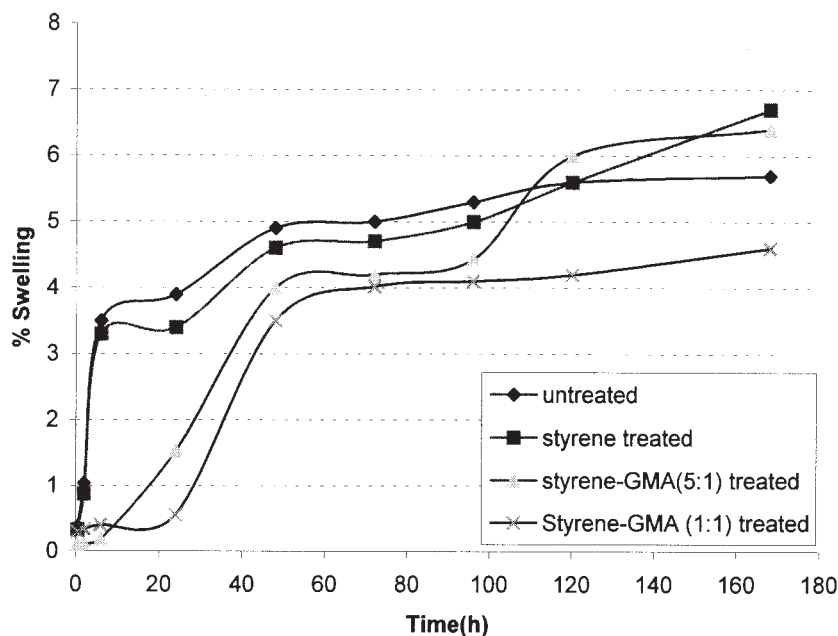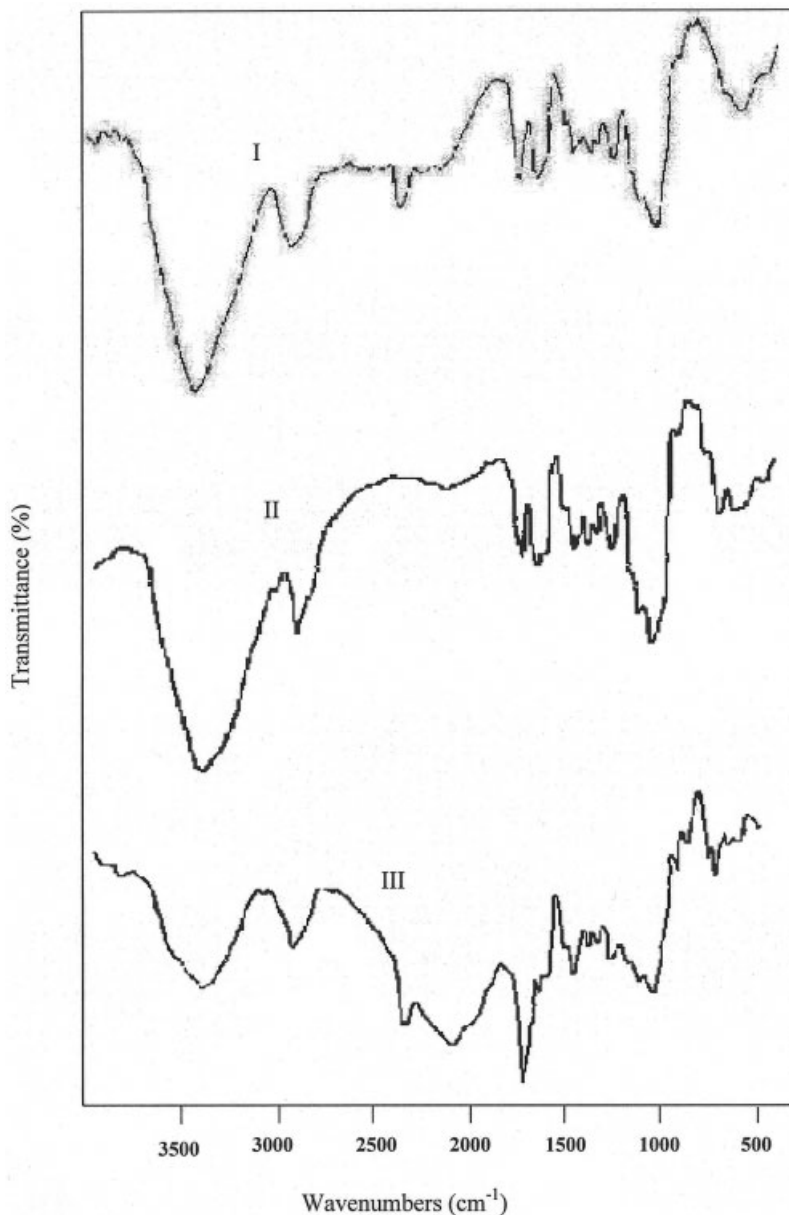

Figure 4   Volumetric swelling of WPC in water.

Figure 5 FTIR spectra of untreated (I), styrene-treated (II), and styrene–GMA-treated (1 : 1) (III) rubber wood samples.

was found that the peak at 1733 cm^{-1}, which was due to carbonyl stretching vibration, became more pronounced on treatment with styrene–GMA. The position of the peak at 3428.38 cm^{-1} (OH stretching) for untreated wood remained unchanged by incorporation of styrene. The peak shifted to 3432.39 cm^{-1} for styrene–GMA (1 : 1). The intensity of C—O stretching vibration (1113.56 cm^{-1}) of untreated wood was also found to increase on treatment with styrene and GMA. All these, as stated above, confirmed the interaction between wood, styrene, and GMA.[6,14,15,19,20]

Thermal properties

For the study of thermal properties, treated samples chosen were of approximately similar polymer loading.

TABLE II
Thermal Analytical Data for Untreated Wood and Polymer-Treated Wood Samples

Sample particulars	T_i (°C)	Tm_i[a] (°C)	Tm_{ii}[b] (°C)	RW (%)
Untreated	270	315	368	31.55
Styrene treated	272	363	433	27.39
Styrene–GMA (5 : 1) treated	280	356.3	414.7	28.05
Styrene–GMA (1 : 1) treated	295	341.3	384.7	23.84
GMA treated	289	349	418	16.83

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

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

	Temperature of decomposition (T_D) in °C at different weight loss (%)						
Sample particulars	20	30	40	50	60	65	70
Untreated	302	326	350	363	380	430	—
Styrene treated	303	330	352	370	417	432	455
Styrene–GMA (5 : 1) treated	308	328	350	364	405	420	440
Styrene–GMA (1 : 1) treated	310	330	348	369	390	396	414
GMA treated	310	328	344	350	372	389	400

TGA study

Table II shows the initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m), and residual weight (RW) for untreated and polymer-treated wood samples. T_i and T_m values for both stages of pyrolysis in treated samples were higher than untreated samples. RW value is observed higher in the case of untreated wood samples compared to those of treated ones.

Table III shows the T_D values at different weight losses for different samples. It was observed that T_D values of treated wood samples were higher than the untreated samples, up to 60% decomposition; beyond that, the value decreased. The increasing trend might be due to the decreasing chance of elimination of small molecules such as CO and CO_2, etc., with the formation of crosslinking, verified experimentally by swelling, which act as an infusible support and provided thermal resistance to the wood fibers. The decreasing trend might be due to the earlier decomposition of polystyrene chain at higher temperature compared to wood fibers. Again, a decreasing trend in T_D values were observed in the treated samples when GMA was added. The higher the percentage of GMA, the lower was the T_D value. The higher decomposition rate of GMA polymer at higher temperature might be responsible for the lower stability of wood treated with styrene–GMA combination.
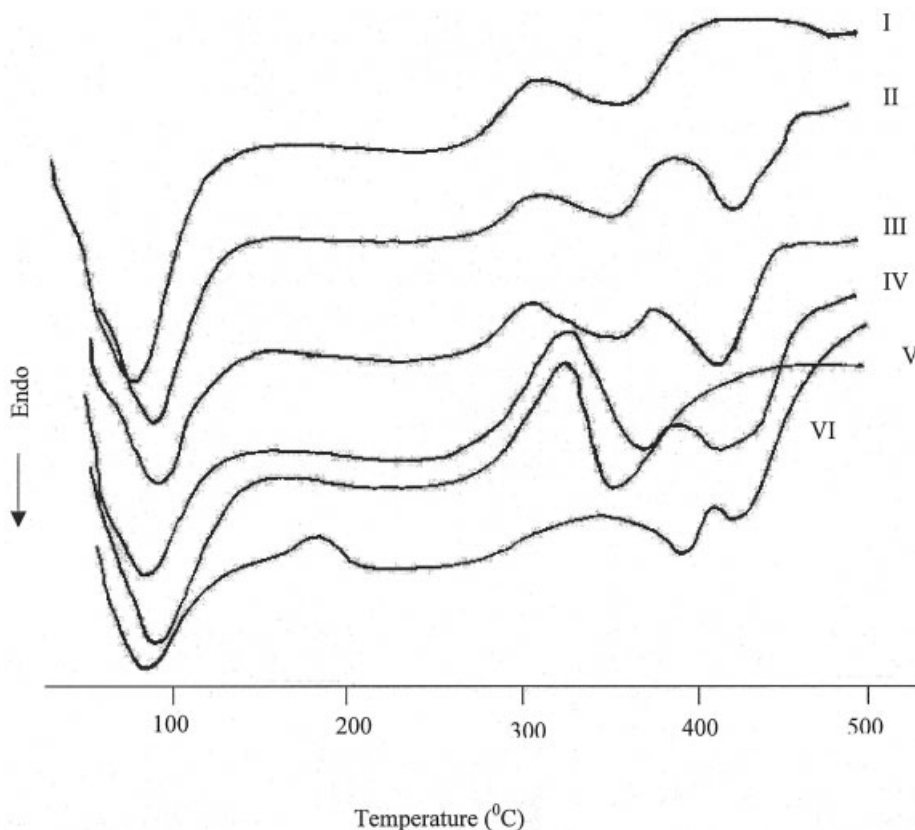

Figure 6 DSC thermograms of untreated (I), styrene treated (II), styrene–GMA (5 : 1) (III) treated, styrene–GMA (1 : 1) (IV) treated, and GMA (V) treated and physical mixture of styrene–GMA (5 : 1) (VI) treated rubber wood samples.

DSC study

Figure 6 I–VI shows the DSC results of untreated and treated wood samples. Untreated wood (curve I) shows a single endothermic peak at 360°C, which was due to the thermal decomposition of wood fibers. Wood treated with GMA (curve V) also showed one endothermic peak at around 351°C. Styrene and styrene–GMA impregnated wood samples (curves II–IV) showed one endothermic peak in the range 354–370°C and another endothermic peak in the range 416–432°C. The double endothermic peaks exhibited in DSC thermograms were due to the thermal decomposition of wood fibers and filled polystyrene in the wood. The position of one peak, which was due to the decomposition of wood fibers, remains almost unchanged with the exception of styrene–GMA (1 : 1) impregnated samples (curve IV), where it shifted to higher temperature. The other peak, which was due to the decomposition of filled polystyrene, shifted to lower temperature. Curve VI showed the thermograms of a physical mixture of wood, polystyrene, and poly(GMA). Polystyrene and poly(GMA) were mixed in a ratio of 5 : 1 and mixed with wood flour similar to that of polymer loading in sample (curve III) to prepare the physical mixture. These DSC results indicated that there may be some chemical interaction between wood, polystyrene, and poly(GMA). These results also support a low compatibility in thermal properties in relation to wood and styrene polymer.

CONCLUSION

From the study, it was found that incorporation of glycidyl methacrylate, a crosslinker, into wood improves more the various properties such as water absorption, water vapor exclusion, dimensional stability in water, as well as in water vapor compared to those of either untreated or styrene-incorporated wood samples. Further, the improvement observed is more in (1 : 1) styrene–GMA combination samples. FTIR spectra confirm the interaction between wood, styrene, and GMA. Impregnation with styrene and GMA also improves thermal stability, as revealed by thermal analysis.

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