Modification of Rubber Wood with Styrene in Combination with Diethyl Allyl Phosphate as the Flame-Retardant Agent

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ABSTRACT: Rubber wood (*Hevea brasiliensis*) polymer composite was prepared using styrene as the monomer in combination with diethyl allyl phosphate (DEAP) to improve flame-retardant property. DEAP was synthesized, characterized and incorporated into wood with styrene. The polymerization was accomplished by catalyst heat treatment using AIBN as the catalyst. The properties of wood–polymer composites (WPC) like water absorption, swelling in water, hardness, modulus of elasticity (MOE), modulus of rupture (MOR) etc. were improved on treatment. The thermal degradation behavior of WPC was evaluated using thermogravimetric analysis (TGA) and the flammability of the WPC was evaluated using the limiting oxygen index (LOI) test. It was observed that fire retardancy of WPC improved on incorporation of DEAP. FTIR spectroscopy and SEM study showed the interaction between wood and the polymers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2461–2467, 2007

Key words: wood–polymer composite; diethyl allyl phosphate; fire retardancy; thermal properties

INTRODUCTION

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 exhibited enhanced strength properties, dimensional stability, and resistance to biodeterioration.[1–4] Besides modifying the physical and mechanical properties, the incorporated polymers can also affect the thermal behavior of wood.

Increased efforts to expand the use of wood products in institutional and commercial structures may require wood to be treated with fire retardants. Therefore, research on fire retardant treatments for wood has accelerated.

Although much research has been done on fire retardants for wood, there are many areas where improvements are needed. Progress for improving the leachability of fire retardants has been made in past decades. Several commercial treatments are available for exterior use. However, even these demonstrate some leaching of chemicals. Another research area is the reduction of smoke and toxicity of these chemicals besides increasing flame retardancy. Polymeric flame retardants can reduce the

leaching problem because of the high molecular weight.

Flame retardancy are generally imparted to woods by impregnating phosphate, silica, boron, etc., type of compounds into wood.[5–7] The thermal properties of five types of radiation-induced WPC based on rubber wood were studied by oxygen index measurement, differential thermal analysis, and thermogravimetric analysis. The composites impregnated with bis (2-chloroethyl) vinyl phosphonate showed maximum improvement in thermal stability.[8]

It was reported in the literature that the improvement in fire retardancy of wood was obtained on treatment with thiourea-formaldehyde resin and orthophosphoric acid.[9] Thermal properties of poplar wood composites with acrylonitrile as the monomer were evaluated using simultaneous differential thermogravimetric analysis (DTG–TG–DTA) in air. Wood composites showed resistance against thermooxidation.[10]

Halogenated compounds produce hazards in the form of emission of toxic gas such as halogen halides. Consequently, there is a continuing search for flame-retardant systems, which do not possess these disadvantages. Organic phosphorous containing compounds are believed to be very effective nontoxic flame retardants.

In this part of work, attempt was made to impregnate rubber wood (*Hevea brasiliensis*) with styrene as the impregnating monomer and diethyl allyl phosphate (DEAP) as the flame-retardant monomer. For

this, DEAP was synthesized, characterized, and then impregnated into wood. The utility of DEAP polymer (PDEAP) as a potent flame-retardant additive in polystyrene and poly(methylmethacrylate) has been established in one study.[11]

EXPERIMENTAL

Materials

Rubber wood (*Hevea brasiliensis*) was collected from a local forest in Assam, India. Styrene, obtained from Merck, India, was purified as per the procedure described elsewhere.[11] Allyl alcohol and phosphoryl chloride ($POCl_3$) were obtained from Merck, India. 2,2′-Azobis-(isobutyronitrile) (AIBN) was also obtained from Merck and used as received. All the other chemicals used were of analytical grade.

Sample preparation

The wood samples used for the study were prepared from clear defect free wood cut into blocks of different sizes for different experiments. The blocks having dimensions $2.5 \times 1 \times 2.5$ cm^3 (radial $\times$ tangential $\times$ longitudinal) for hardness, water uptake, swelling in water tests, $1 \times 1 \times 10$ cm^3 (radial $\times$ tangential $\times$ longitudinal) for bending strength, and $0.65 \times 0.3 \times 10$ cm^3 (radial $\times$ tangential $\times$ longitudinal) for limiting oxygen index (LOI) test were used.

Preparation of diethyl allyl phosphate monomer

Diethyl allyl phosphate (DEAP) was prepared according to the procedure given in literature.[11] Freshly distilled ethanol (18.4 g, 0.4 mol) was slowly added from a dropping funnel to $POCl_3$ (34.4 g, 0.2 mol) at 5°C (approximately) in a 100-mL round-bottomed flask fitted with a condenser, mechanical stirrer, and a $CaCl_2$ guard tube. The reaction mixture was stirred at room temperature for 5 h. Diethyl chlorophosphate (DECP) thus formed was vacuum distilled (81°C, 6 mm of Hg). Dried allyl alcohol (4.04 g, 0.07 mol) was added drop wise to the cold ($\sim$ 5°C) DECP (12.09 g, 0.07 mol) under constant stirring and the reaction mixture was kept at room temperature for 5 h to yield the DEAP monomer. The reaction is shown in Scheme 1.

Impregnation procedure

All the samples were oven dried at 105°C to constant weight before treatment and 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 floatation during addition of monomers.
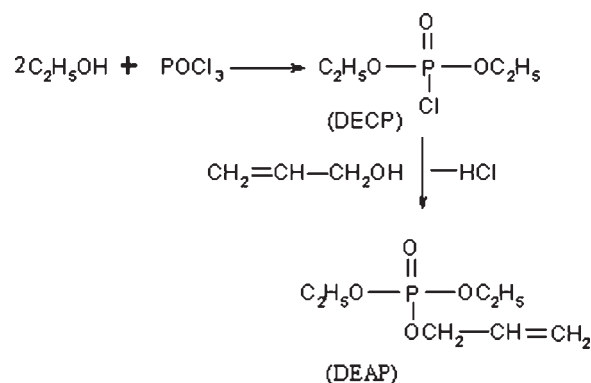
Scheme 1 Reaction scheme for preparation of diethyl allyl phosphate.

Vacuum was applied for a specific time period for removing the air from the pores of the wood before addition of monomers. After that, vacuum pump was disconnected. Now sufficient mixture of styrene and initiator or styrene–DEAP 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 an optimum polymer loading, which showed maximum overall improvement in properties. The condition of impregnation was varied by changing different parameters such as monomer concentration, initiator concentration, time of impregnation, vacuum, etc. After impregnation samples were taken out of the chamber and excess chemicals were wiped from the wood surfaces. The samples were then wrapped in aluminum foil and cured in an oven at 90°C for 24 h. This was followed by drying at 105°C in an oven 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

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

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

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

Water uptake test

Both untreated and treated wood samples were immersed in distilled water at room temperature (30°C) and weight was taken after 24 h. It is expressed as

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

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

Swelling in water

Dimensions of the oven dried samples were measured and conditioned at room temperature (30°C) and 30% RH. Final placements of the samples were done in distilled water and then dimensions were remeasured after 24 h.

In both the cases, swelling was considered as 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 untreated or treated wood after water absorption and V_o is the volume of the untreated or treated wood before water absorption.

Hardness

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

FTIR study

The treated and untreated samples were ground to a powder and FTIR spectra were recorded using KBr pellet in a Nicolet Impact 410 spectrophotometer.

Bending strength test

Bending strength test was performed by using Zwick Tensile Tester (model Z010) with a crosshead speed of 2 mm/min and by calculating modulus of rupture (MOR) and modulus of elasticity (MOE) of the wood samples according to ASTM D790 method.

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

where W is the ultimate failure load (N), L is the span between centers of support (m), b is the mean width (tangential direction) of the sample (m), and d is the mean thickness (radial direction) of the sample (m).

Thermal study

TGA was carried out in a thermogravimetric analyzer (model Universal V2. 5H) instruments at a heating rate of 20°C/min up to 800°C under nitrogen atmosphere.

Limiting oxygen index

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. The method was according to ASTM D-2863. The sample was placed vertically in the sample holder of the LOI apparatus. The total volume of the gas mixture ($N_2 + O_2$) was kept fixed at 300 cc. To begin with experiment, the volume of nitrogen gas and that of oxygen gas were kept initially at a maximum and minimum level. Now, the volume of nitrogen gas was decreased and that of oxygen gas was increased gradually. However, the total volume of gas mixture was kept fixed at 300 cc during the experiment. The ratio of nitrogen and oxygen at which the sample continued to burn for at least 30 s was recorded.

Limiting oxygen index (LOI)

$$= \text{Volume of } O_2/\text{Volume of } (O_2 + N_2)$$

Scanning electron microscopy study

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

RESULTS AND DISCUSSION

Standardization of impregnation conditions

The optimum condition for impregnation at which maximum improvement in properties observed was optimized by varying vacuum, time of impregnation, monomer concentration, and catalyst concentration. DEAP as such was not compatible with styrene. The

TABLE I
Effect of Variation of DEAP Concentration on Polymer Loading (WPG %) and Other Properties

Samples[a]	Styrene : THF 88 : 22	DEAP (mL)	WPG (%)	Volume increase (%)	Weight gain in water (%)	Swelling in water (%)	Hardness (Shore D)
Untreated	–	–	–	–	104.4	3.9	46.6
Treated	Styrene : THF 88 : 22	–	11.0	Negligible	42.8	5.6	58.0
Treated	Styrene : THF 88 : 22	0.5	8.1	5.1	64.9	7.1	54.5
Treated	Styrene : THF 88 : 22	1.0	8.4	5.6	60.0	7.3	57.6
Treated	Styrene : THF 88 : 22	1.5	9.0	7.1	43.8	3.4	62.5
Treated	Styrene : THF 88 : 22	3.0	10.8	10.4	44.7	4.2	58.1
Treated	Styrene : THF 88 : 22	5.0	12.9	10.3	44.9	4.4	57.8

Styrene–THF (v/v) = 88 : 22; AIBN = 0.5% (by weight); time = 4 h; vacuum = 5 in. of Hg; temperature = $(30 \pm 1)^\circ$C.
[a] Each value represents the average of five samples.

minimum ratio (V/V) of styrene and THF (a solvent for both styrene and DEAP) to form a miscible mixture with DEAP was 4 : 1. The final optimized impregnating conditions were as follows: vacuum: 5 in. of Hg, time of impregnation: 4 h, AIBN (by weight): 0.5%, styrene (mL): 88, tetrahydrofuran (mL): 22, and DEAP (mL): 0.5–5.0.

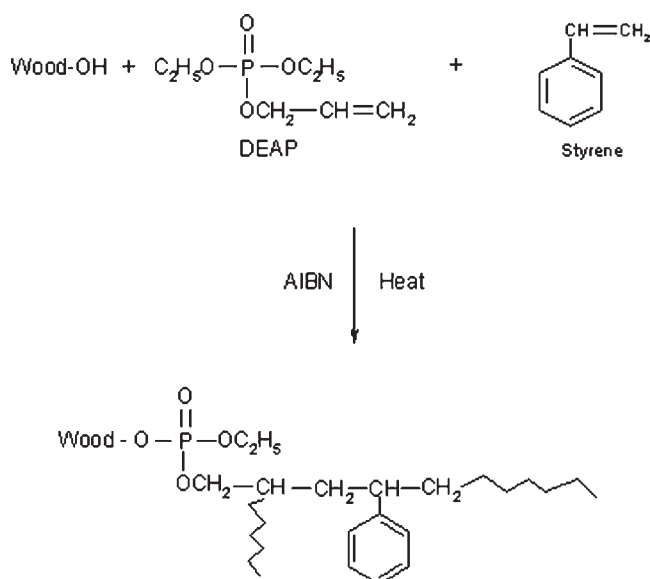## Effect of variation of DEAP concentration on WPG (%) and other properties

Effect of variation of DEAP concentration on WPG (%) and other properties is shown in Table I. Polymer loading (WPG %) was found to increase with the increase in DEAP concentration. With the increase in the concentration of DEAP, an increase in the volume (%) was observed. Both water uptake (%) and swelling in water decreased first and then leveled off. Hardness showed a rising trend initially followed by a decreasing trend later. The improvement was more at (88 : 22 : 1.5) styrene : THF : DEAP ratio. Improvement in hardness for MMA and

silane-treated radiata pine (softwood) and black butt (hardwood) was reported in the literature.[12]

Improvement in dimensional stability and hardness was due to the deposition of polymer into the void spaces and capillaries of wood. This prevented the cell wall from shrinking in response to water absorption. Further DEAP treatment might form crosslinks with wood and styrene through its alkoxy linkage and double bond resulting in further reduction of water absorption. Scheme 2 shows the probable interaction between wood, styrene, and DEAP.

Bending test

MOE and MOR values of DEAP–styrene–THF-treated WPC were evaluated and compared with untreated or styrene–THF-treated WPC. From Table II, it was observed that MOE value increased on incorporation of DEAP, while MOR values decreased. The increment in MOE value was due to increased interaction of DEAP with styrene and wood as shown in Scheme 2.

FTIR study

FTIR spectra of polymer impregnated wood

The FTIR spectra of DEAP, untreated rubber wood, DEAP treated, and of styrene–DEAP-treated rubber wood are presented in Figure 1. The peak at 3395.02 cm^{-1} of untreated wood [Fig. 1(b)] shifted in the region 3422–3427 cm^{-1} when either DEAP or sty-

Scheme 2 Reaction between wood, styrene, and DEAP.

TABLE II
MOE and MOR Data for Styrene–DEAP Rubber Wood Composites

Samples[a]	MOE (MPa)	MOR (MPa)
Untreated	3680.5	53.5
Treated with		
Styrene–THF	4589.0	61.2
Styrene–THF–DEAP (1.5 mL)	4790.8	50.5
Styrene–THF–DEAP (3.0 mL)	4920.3	48.2

[a] Each value represents the average of five samples.
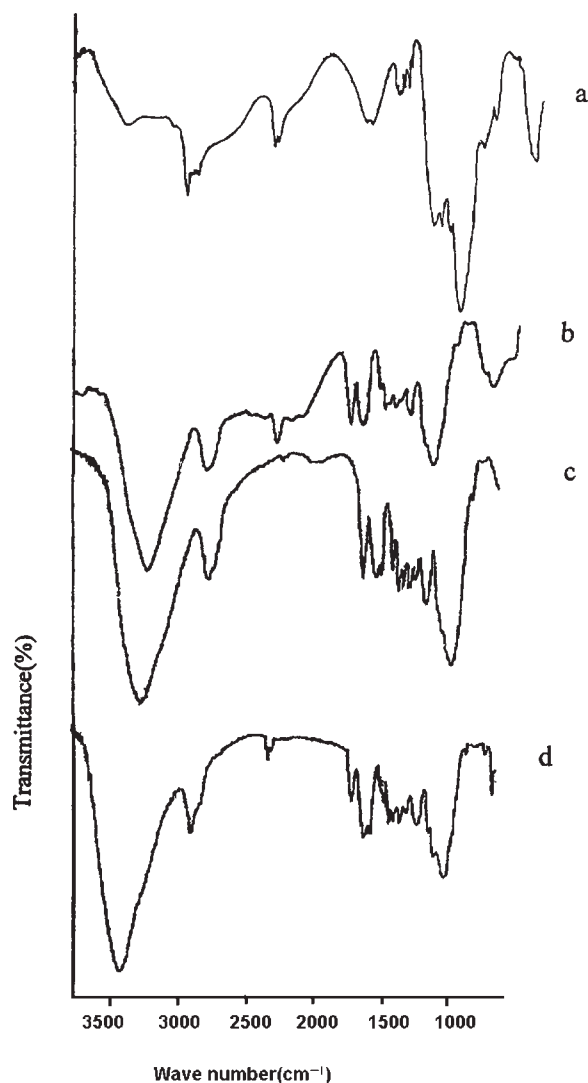
Figure 1 FTIR spectra of DEAP (a), untreated (b), DEAP treated (c), and styrene–DEAP treated (d), rubber wood samples.

rene–DEAP was incorporated into wood [Fig. 1(c,d)]. The peak appeared in DEAP spectrum [Fig. 1(a)] at 1033.42, 1166, 1690.02, and 2987.46 cm^{-1} were due to P—O—C aliphatic stretching vibration, P=O (aliph),

C=C stretching, and aliphatic C—C stretching vibration.[13] The peak at 1058.41 cm^{-1} of untreated wood was found to shift towards P—O—C aliphatic stretching vibration when wood was treated with DEAP. The peak appeared at 3000 cm^{-1} in the wood–styrene–DEAP-treated sample was due to aromatic C—H stretching vibration. These results confirmed that interaction improved between styrene and wood due to incorporation of DEAP.

Thermogravimetric analysis

Thermal results are shown in Tables III and IV. Table III shows the values of (i) initial decomposition temperature (T_i) at 5% weight loss, (ii) the temperatures of the first and second exothermic peak, and (iii) the char yield. It was observed that T_i value decreased on incorporation of DEAP with styrene. The higher the percentage of DEAP, lower was the T_i value. Char yield (%) increased with the increase in the concentration of DEAP. Char yield was calculated at two temperatures namely 450 and 600°C. Styrene-treated wood produced char yield similar to that of untreated wood at both the temperatures. The highest char yield (%) of 34 (at 450°C) and 27 (at 600°C) were obtained with DEAP amount of 3.0 mL.

It was observed that polystyrene alone did not produce any char. The char yield of polydiethyl allyl phosphate (PDEAP) was compared to that of PS and PDEAP blend. The higher percent of char yield (not shown in table) produced in the blend compared to PDEAP alone indicated a significant interaction between PS and PDEAP during degradation process. Both PDEAP and its blend with PS should produce similar char yield in absence of any interaction. It was reported[11] that char yield (%) of PS and PDEAP blend was more at lower degradation time and less at higher degradation time compared to those of PDEAP alone.

It was reported that polyphosphate polymers were generally produced char through formation of phos-

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

Sample particulars[a]	T_i (°C) at 5% weight loss	T_{m_i}[b] (°C)	$T_{m_{ii}}$[c] (°C)	RW (%) 450 (°C)	600 (°C)
Untreated	90	309	360	22	6
Treated with					
Styrene–THF	90	360	425	22	7
Styrene–THF–DEAP (0.5 mL)	70	349	–	25	10
Styrene–THF–DEAP (1.5 mL)	70	350	–	28	12
Styrene–THF–DEAP (3.0 mL)	65	352	–	34	27

[a] Each value represents the average of three samples.
[b] T_m value for the first step.
[c] T_m value for the second step.

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

Sample particulars[a]	Temperature of decomposition (T_D) in °C at different weight loss (%)					
	20	40	60	70	80	90
Untreated	302	338	370	397	475	550
Treated with						
Styrene–THF	305	340	368	410	465	560
Styrene–THF–DEAP (0.5 mL)	300	340	370	428	520	645
Styrene–THF–DEAP (1.5 mL)	294	342	370	425	530	645
Styrene–THF–DEAP (3.0 mL)	310	340	385	530	680	–

[a] Each value represents the average of three samples.

phoric acid.[14] The low char yield in the blend at higher degradation time indicated that DEAP monomer produced from decomposition of PDEAP did not decompose fast enough to produce acids in presence of styrene derived from decomposition of polystyrene. However, a thorough investigation is necessary to find out the exact mechanism.

To understand the mechanism of char formation, the ^{31}P NMR spectra of PDEAP, char of PDEAP, and char PS/PDEAP blend were recorded (using H_3PO_4 as external standard) and reported.[11] The peaks appeared at δ 3.4 ppm in both the char were due to phosphoric acid monoester.[15] Monoester of phosphoric acid could be considered to be the intermediate before formation of phosphoric acid. Phosphoric acid alters the pyrolytic decomposition reactions of the wood components, resulting in a higher carbonaceous char yield.[16] Similar types of results were reported by Chan et al.[8]

The lowering of initial decomposition temperature (T_i) might be because of the removal of water from wood components by the phosphoric acid produced from the decomposition of PDEAP.

Table IV shows the temperatures of decompositions (T_D) at different weight loss percentages. T_D values of treated wood samples were higher than untreated samples. The observed high values might be due to the decreasing chance of elimination of

small molecules such as CO, CO_2, etc., with the formation of crosslinks (shown in Scheme 2), verified experimentally by swelling, which act as an infusible support and provided thermal resistance to the wood fibers.

On the basis of these observations, it was concluded that DEAP could be used as a flame-retardant monomer because of its ability to lower the initial decomposition temperature as well as to maintain a high char yield. Thermal stability of wood fibers could also be improved by incorporation of DEAP with styrene.

Limiting oxygen index

The results of limiting oxygen index (LOI) measurements are presented in Table V. The LOI test assumes that inherently less flammable materials require greater oxygen concentrations to produce the heat necessary for the continued production of flammable volatiles and flame propagation. Rubber wood treated with styrene–DEAP system exhibited improved flame retardancy as evident from higher LOI value. Effective flame retardancy was associated with localized flame, minimal smoke or fume generation, high char yield, etc. It was known that decomposition of the cellulose fraction and solid state oxidation of lignin fraction was primarily responsible for the flaming combustion and glowing reactions.[16] Wood treated with styrene–DEAP produced small smoke; localized flame and high char yield leading to improved flame retardancy. Similar types of results were also reported.[8,17]

Scanning electron microscopy study

Scanning electron microscopy (SEM) was used to examine the interaction of the polymer with the cell walls of the wood. Figure 2(a) shows the void spaces in untreated rubber wood. Figure 2(b,c) shows the micrograph of WPC treated with styrene and styrene–DEAP, respectively. From Figure 2(b,c) (arrow marked), it was observed that there was swelling of the cell wall. The interaction between wood and polymer increased when DEAP was introduced [Fig. 2(c)]. Elvy et al.[12] observed and reported that

TABLE V
Limiting Oxygen Indices and Flaming Characteristics

Samples[a]	WPG (%)	LOI (%)	Flame description	Smoke and fumes	Char
Untreated	–	26	Candlelike, localized	–	Little
Treated with					
Styrene–THF	11.4	27	Strong flame	Tall stream of smoke	Little
Styrene–THF–DEAP (1.5 mL)	10.2	30	Small localized flame	Small and black smoke	Higher
Styrene–THF–DEAP (3.0 mL)	10.8	32	Small localized flame	Small and black smoke	Higher

[a] Each value represents the average of five samples.
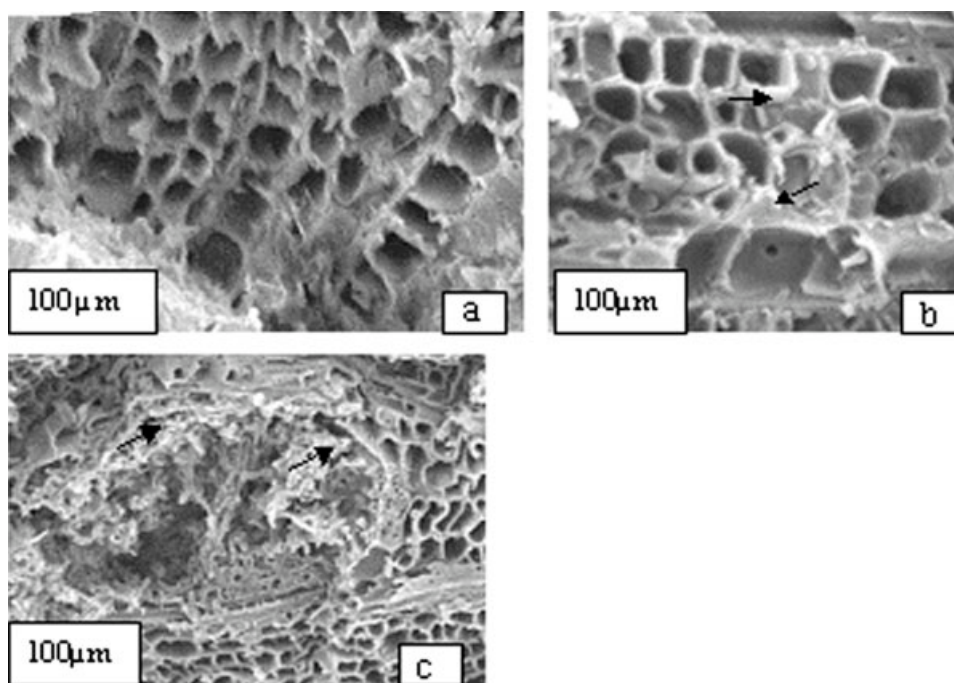
Figure 2 SEM micrograph of (a) untreated (magnification ×230); (b) styrene–THF treated (magnification ×330), and (c) styrene–THF–DEAP-treated (magnification ×140) rubber wood samples.

the gaps between the polymer strand and the cell decreased because of increased adhesion caused by silane-coupling agent.

CONCLUSIONS

From the study, it was observed that the incorporation of DEAP improved the various properties such as dimensional stability, hardness, mechanical properties, etc. The introduction of DEAP into wood decreased the initial decomposition temperature and increased the char yield as revealed by the TGA. LOI study also indicated that the flame-retardancy behavior of rubber wood was improved due to incorporation of DEAP. SEM study showed the interaction between wood, styrene, and DEAP.

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