

Natural Fiber Composites of High-Temperature Thermoplastic Polymers: Effects of Coupling Agents

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ABSTRACT: Our earlier paper (Jana, S.C.; Prieto, A. *J Appl Polym Sci* 2002, 86, 2159) on the development of natural fiber composites of high-performance thermoplastic polymers described a new methodology for the manufacturing of composite materials of a high-temperature thermoplastic polymer, poly(phenylene ether) (PPE) and wood flour, a cellulosic natural filler. A thermosetting epoxy, used as a reactive solvent, reduced the processing temperature of PPE/epoxy blends to well below the decomposition temperature of natural fillers. In addition, the epoxy component, upon polymerization, formed coating layers around the filler particles to provide resistance against moisture diffusion and attacks by acids and alkali. This article describes the results of an investigation on two outstanding issues: (1) the influence of cellulosic wood particles and coupling

agents on the speed of epoxy curing and reaction-induced phase separation and (2) the effects of coupling agents on the morphology of crosslinked epoxy at the surfaces of natural fillers and mechanical properties of the composites. It was found that wood particles expedited epoxy curing in the composites; the extent of epoxy curing, however, was reduced in the presence of coupling agents. Also, the coupling agents promoted complete coverage of wood flour particles by polymerized epoxy, although the mechanical properties deteriorated over systems without coupling agents. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2168–2173, 2002

Key words: high performance polymers; reactive processing; natural fillers; coupling agents; composites

INTRODUCTION

Natural fillers, such as wood flour, rice husk, and wheat straw, can potentially serve as cheap reinforcement of engineering polymers if compounded into polymers without decomposition. Natural abundance, much higher strength per unit weight than most inorganic fillers,¹ lower density, and a biodegradable nature make natural fillers more attractive than glass and carbon fibers for reinforcement of engineering thermoplastic polymer systems. However, most engineering polymers of interest process at temperatures much higher than the decomposition temperature of natural fillers (typically 200°C), for example, polyamides (PA) at 250–270°C, poly(butylene terephthalate) (PBT) at 260°C, and poly(phenylene ether) (PPE) at 270–300°C. Therefore, a critical need exists to develop new technologies, whereby engineering polymers can be combined with natural fillers at or below the decomposition temperatures of the latter component. One such technology based on the use of reactive solvents was presented in an earlier article of this journal,² where the development of wood flour-filled composites of a high-temperature engineering polymer, PPE, was reported. A reactive solvent in the form of a bifunctional epoxy of bisphenol-A, EPON® 828, was used to reduce

the processing temperatures of PPE–epoxy mixtures to well below the decomposition temperature of wood flour (approximately 200°C). Thus, a mixture containing 70 parts by weight of PPE and 30 parts by weight of epoxy was compounded with wood flour at 185°C. The epoxy component was polymerized during the composite fabrication step with a diamine curing agent and was found to form coating layers around wood flour particles (Fig. 1). These coating layers contributed to lower absorption of water, better thermal stability of wood particles, and better dimensional stability upon exposure to aqueous solutions of acid and alkali. The mechanical properties of the resultant composite materials were found to be comparable with many glass fiber-filled engineering polymer systems. A detailed description of the methodology used was presented elsewhere.³

In this article, the results of an investigation on two outstanding issues are presented. One such issue is the effect of wood particles and coupling agents on the speed of curing of epoxy and reaction-induced phase separation of crosslinked epoxy from mixtures with PPE. It was already seen in Figure 9 of the earlier article,² where measurements of the heat of reaction in DSC were reported, that the alcoholic—OH groups of cellulose react very slowly with epoxy and have stronger catalytic effects on epoxy–diamine reactions,⁴ leading to faster curing of epoxy. However, it was not investigated how such reactions might affect the shear viscosity of the materials during processing, for exam-

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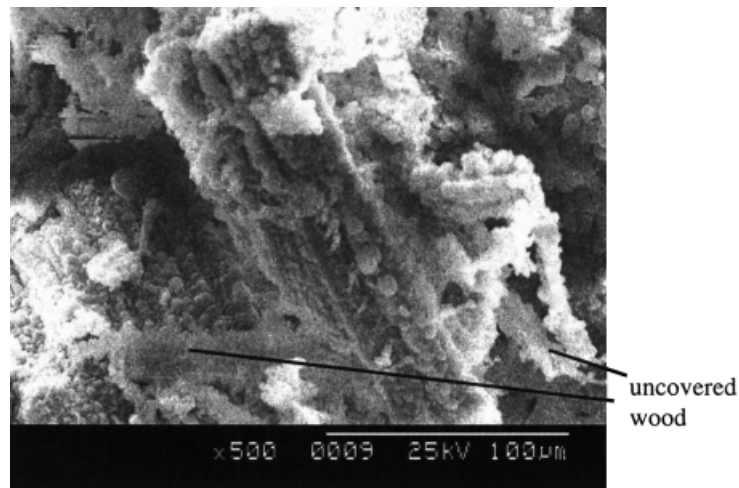


Figure 1 Scanning electron micrograph of morphology of crosslinked epoxy particles on the surface of wood flour particles, showing incomplete coverage. The composite was cured with M-CDEA at 185°C for 4 h. No coupling agent was used.

ple, in injection molding. In addition, coupling agents may also influence the cure kinetics of epoxy.

Another issue is the lack of uniform coating of crosslinked epoxy around wood flour particles, as seen in Figure 1, which we suspect may be a deterrent to achieving the best properties from these composites. Even though these composites, as reported in the earlier paper,² offered strong mechanical properties, it is interesting to determine if the mechanical properties can be further improved by using coupling agents. A survey of the literature^{5–7} revealed that coupling agents have been proved to be useful in augmenting fiber–polymer bonding in epoxy–wood composites.

EXPERIMENTAL

Materials

Powdered PPE with a glass transition temperature (T_g) of 212°C, weight-average molecular weight of 25,200 (as measured by GPC), and zero-shear viscosity of 6.3×10^6 Pa s at 260°C were obtained from GE Plastics (Pittsfield, MA). A bifunctional epoxy, EPON® –828, a diglycidyl ether of bisphenol A with a T_g of –18°C, boiling point of 315°C, density of 1.16 g/cm³, epoxy equivalent weight of 185–192, and a zero-shear viscosity of 11–15 Pa s at 25°C was supplied by Shell Chemical (Houston, TX). A slow epoxy curing agent, 4,4'-methylenebis(3-chloro-2, 6-diethylaniline) (M-CDEA), and a fast curing agent 4,4'-methylenebis(2, 6-diethylaniline) (M-DEA), both supplied by Lonza (Basel, Switzerland) in the form of solid powder at room temperature, were used in stoichiometric amounts for curing of the epoxy.

Two silane coupling agents, Silquest® A-1100 and A-2120, with chemical formulas, respectively, of $H_2NCH_2CH_2CH_2Si(OCH_2CH_3)_3$ and $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(CH_3)(OCH_3)_2$, supplied by OSi Specialties (South Charleston, WV), were used. Silquest® A-1110, a clear, colorless liquid with a molecular

weight of 221.3, and Silquest® A-2120, also a clear, straw color liquid at room temperature, were sprinkled until wet on previously dried wood flour. Wood flour was further mixed in a tumbler and dried at room temperature in a vacuum oven. The third coupling agent, hydroxymethylated resorcinol, was produced first by mixing 90.4 parts of deionized water, 3.3 parts of crystalline resorcinol, 3.8 parts of a 37% aqueous formaldehyde solution, and 2.4 parts of a 3 molar aqueous solution of sodium hydroxide and adding 0.5 parts of sodium salt of dodecyl sulfate. The solution was sprinkled on wood flour particles until wet; the soaked wood flour was mixed in a tumbler and dried in a vacuum oven at room temperature until a constant weight was reached, typically in 48 h. A 40-mesh sample of hardwood oak flour provided by American Wood Fibers (Schofield, WI) with particle aspect ratio of 2.5–5.0 and bulk and particle density, respectively, of 12–18 and 39 lb/ft³ was used.

Manufacturing of composites

First, a homogeneous material with a T_g of 105°C and a zero-shear viscosity of 7×10^4 Pa s at 200°C was obtained by combining PPE and epoxy in a weight ratio of 70:30 in a 30-mm JSW twin-screw extruder. Dried wood flour treated with a coupling agent and curing agents were mixed with the PPE–epoxy mixture at 185°C in a JSW twin-screw extruder or Brabender Plasticorder batch mixer. All materials containing M-DEA and some containing M-CDEA were prepared in the batch mixer at 50 rpm with total mixing time of 25 min, of which only the last 5 min were used to mix the curing agents. The typical residence time for mixing of the curing agents and wood particles in the twin-screw extruder was of the order of 2 min.

Test specimens were prepared by injection molding at 185–195°C using a high-injection speed and cured

for 4 h at 185°C in specially designed molds to retain the shape. The final composite contained 19% by weight of wood flour.

Evaluation of mechanical properties

The tensile properties, such as yield stress, tensile strength, elongation at break, ultimate strength, and tensile modulus, were evaluated following the ASTM D 638 method with a crosshead speed of 5.0 mm/min. An ASTM D 256 method was followed to evaluate the impact properties using a TMI-43-I Izod tester, with potential energies ranging from 2 to 10 in. lbs. All tests were carried out at room temperature and with relative humidity between 25 and 50%.

Curing in rheometer

The effect of wood particles and coupling agents on the speed of epoxy curing was investigated under an oscillatory shear flow at 185°C using an Alpha Technologies APA2000 cure meter, with a twin-cone setup. Materials prepared in the batch mixer were used for this purpose.

Morphology and dimensional stability

The morphology of crosslinked epoxy on surfaces of wood particles was inspected by a scanning electron microscope (SEM), Hitachi S-2150, after extracting the PPE phase in chloroform. Samples of the cured materials obtained at the end of the viscosity measure-

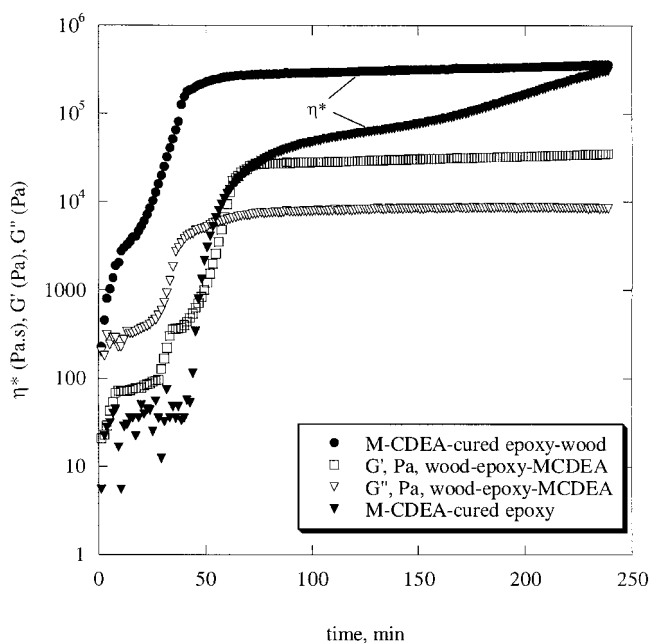


Figure 2 Effect of wood flour on the evolution of complex viscosity (η^*), storage modulus (G'), and loss modulus (G'') during curing of epoxy-wood mixture using M-CDEA at 185°C in oscillatory shear flow with 1% strain and 100 rad/s.

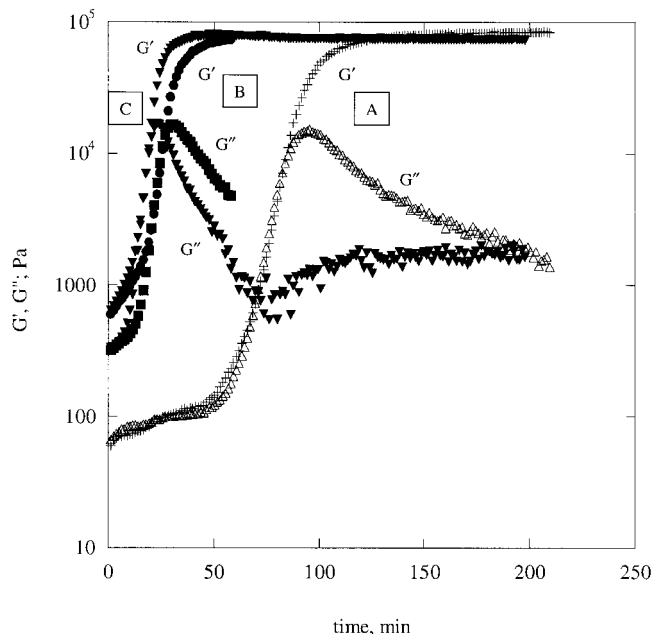


Figure 3 Effect of wood flour on the evolution of the storage and loss moduli during curing at 185°C in an oscillatory shear flow with 1% strain and 100 rad/s: (A) PPE-epoxy blend cured with M-CDEA; (B) composite cured with M-CDEA; (C) composite cured with M-DEA.

ments in the Alpha Technologies APA2000 cure meter were used for this purpose.

The dimensional changes in the test specimens caused by exposure for 7 days at room temperature to a 49% by weight aqueous solution of hydrofluoric acid and a 66% by weight aqueous solution of sodium hydroxide were determined following the ASTM D-543 method using composite specimens of 50.8-mm diameter and 3.2-mm thickness. The specimens of the same size were dipped in water at room temperature for 24 h and in boiling water for 2 h following the ASTM D-570 method.

RESULTS AND DISCUSSION

Effects of wood particles and coupling agent on speed of epoxy curing

The epoxy component in various blends was cured under an oscillatory shear flow at 185°C with 1% strain and a frequency of 100 rad/s. Figures 2–4 present time evolution of the complex viscosity. It is observed that the viscosity of each material increased sharply after an initial time interval. Figure 2 shows the effect of wood particles on the speed of curing of epoxy using M-CDEA as the curing agent. These samples were prepared by mixing the ingredients at room temperature. An higher initial viscosity of the wood-epoxy mixture was due to the presence of wood particles and the initial scatter in the epoxy-M-CDEA system reflected too low initial torque values. In each case, the viscosity rose due to gelation of the epoxy

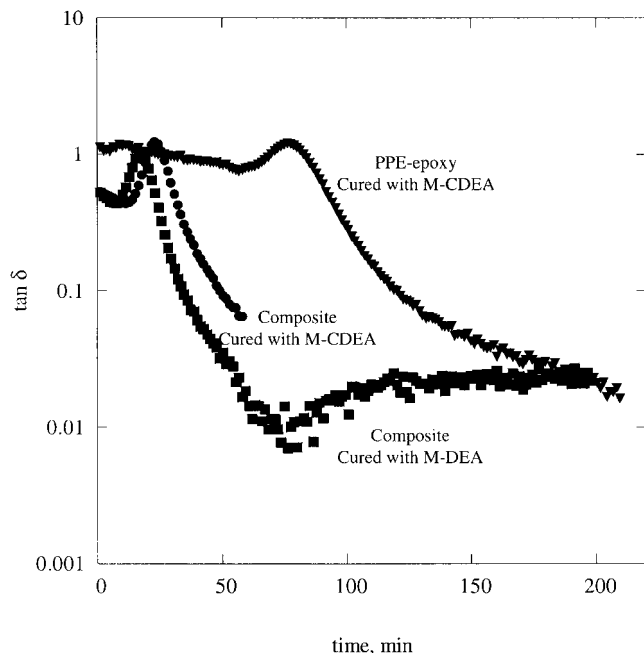


Figure 4 Effect of wood flour on the evolution of loss tangent during curing at 185°C in an oscillatory shear flow with 1% strain and 100 rad/s.

networks. It is worthwhile to note here that the T_g of the completely cured system was of the order of 180°C, slightly below the curing temperature of 185°C. It is evident that a period of about 50 min was needed for the epoxy–M-CDEA system for the onset of the viscosity increase, which was shortened to about 25 min in the case of the epoxy–wood–M-CDEA system. The gel time, measured from the crossover point between the storage modulus (G') and the loss modulus (G'') in the case of the epoxy–wood–M-CDEA system, was found to be about 60 min. A parallel experiment with a wood–epoxy mixture (no M-CDEA), containing the same ratio of wood and epoxy as that of the composites, revealed negligible heat generation in DSC cells over a period of 3 h. In view of this and Figure 2, it is inferred that the viscosity increase in the wood–epoxy–M-CDEA system was due mainly to catalytic effects of wood particles, catalyzing epoxy–amine reactions with alcoholic—OH groups.

Figures 3–5 present similar behaviors, but they are the results of a different physical scenario. In the case of PPE–epoxy systems cured with M-CDEA and M-DEA, the viscosity increase can be attributed to vitrification of the continuous PPE phase, as established by Ishi and Ryan.¹³ The epoxy component lost solubility in PPE with the progress of the crosslinking reactions and formed a separate dispersed phase.^{8–15} Consequently, the viscosity and the glass transition temperature (T_g) of the PPE-rich continuous phase gradually increased until the vitrification point, whereby the T_g of the PPE-rich continuous phase increased to the curing temperature of 185°C. A gel point still can be

defined based on the crossover between G' and G'' , as seen in Figure 3, or as the time at which $\tan \delta$ reached a value of 1.0, as in Figure 4. It is believed that the wood particles in the composites, through catalytic effects on epoxy–amine reactions, accelerated phase separation of the epoxy and contributed to a faster gelation of the epoxy domains that formed around the wood particles. Gel times calculated from Figure 4 are as follows: PPE–epoxy cured with M-CDEA, 70 min; M-CDEA-cured composites, 22 min; and M-DEA-cured composites, 8 min.

As seen in Figure 5, the M-CDEA-cured composite reached a plateau viscosity within 50 min, although the composite with the same composition, except with wood flour treated by coupling agents, took much longer to reach the plateau viscosity values. For instance, the composite with resorcinol–formaldehyde-treated wood flour took about 1 h to reach the maximum viscosity. The time to reach the maximum viscosity increased to 70 min in the case of Silquest® A-1100 and 90 min in the case of Silquest® A-2120.

This delay in epoxy curing in the presence of coupling agents can be explained on the basis of reactions between coupling agents and the—OH groups of cellulose. For example, the dimethoxy groups of Silquest® A-1100 hydrolyze and produce alkoxy-silanol, which, in turn, react with the—OH groups on the cellulosic material or other alkoxy-silanol.¹⁶ Consequently, a lower number of cellulosic—OH groups were available for catalyzing epoxy–amine reactions. Wood flour particles treated with Silquest® A-1100 exhibited higher reactivity toward epoxy than did Silquest® A-2120, as the latter contained trimethoxy groups, which resulted in a higher concentration of silanol groups upon hydrolysis, thereby effectively reducing the number of cellulosic—OH groups for

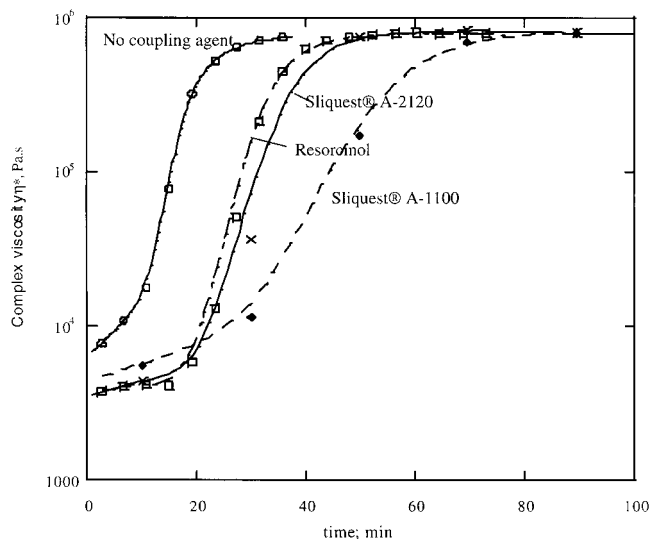


Figure 5 Effect of coupling agents on complex viscosity of various composites cured with M-CDEA under an oscillatory shear flow at 185°C, 1% strain, and 100 rad/s.

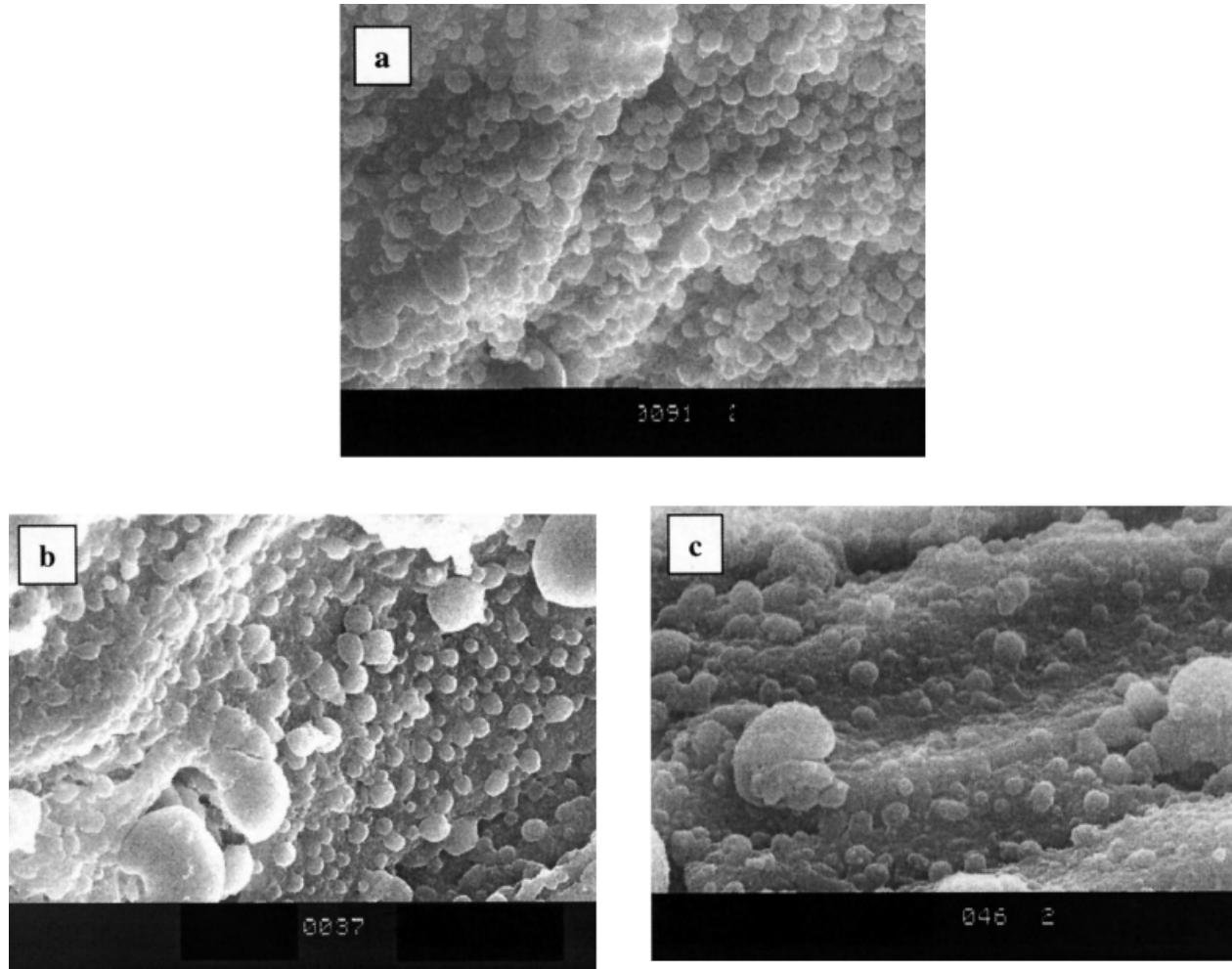


Figure 6 Effect of coupling agents on the morphology of epoxy-coated wood particles. Epoxy was cured with M-CDEA under an oscillatory shear flow at 185°C, 1% strain, and 100 rad/s: (a) resorcinol-formaldehyde; (b) Silquest® A-1100; (c) Silquest® A-2120.

reactions with the epoxy. Composites with hydromethylated resorcinol-treated wood flour also exhibited delayed curing behavior.

An interesting observation about processing of these composites can be drawn from Figure 5. Although coupling agents were used for the purposes of improvement of adhesion between epoxy and wood flour, they can be useful as an effective viscosity modifier and to delay premature curing of epoxy.

Effects of coupling agents on morphology

Figure 6 shows the morphology of epoxy-coated wood particles after extraction of the PPE phase for three coupling agents. As evident, nodular epoxy particles are visible around the wood flour particles and all wood particles appeared completely coated by epoxy, in contrast to Figure 1. A likely scenario is that the coupling agents, although they reduced the number of cellulose—OH groups for catalyzed epoxy curing, participated locally in reactions with epoxy purportedly through unreacted phenolic—OH in resorcinol

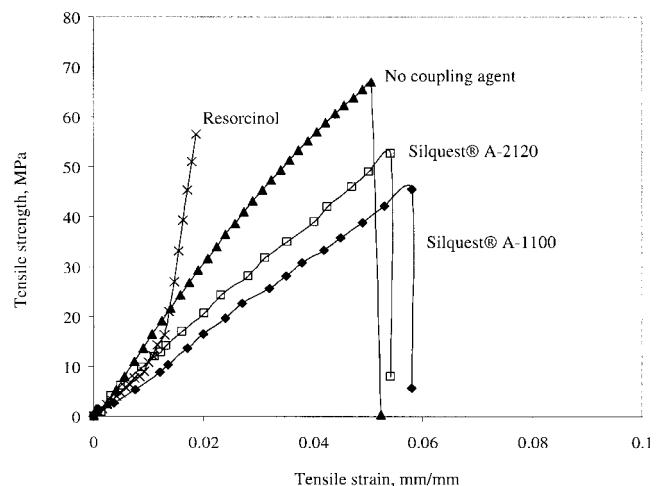


Figure 7 Stress-strain diagram of composite materials filled with wood flour treated by various coupling agents. Composites cured with M-CDEA at 185°C in a compression mold.

TABLE I
Dimensional Changes and Water Absorption (by Weight) by Composite Samples

Material	Water uptake 24-h water immersion	Water uptake 2-h boiling water	Water uptake in acid	Water uptake in alkali	Dimensional change 24-h water immersion	Dimensional change 2-h boiling water
M-CDEA-cured composite	0.57%	0.84%	0.58%	0.01%	0.67%	0.92%
Resorcinol-treated composite cured with M- CDEA	0.36%	0.52%	0.63%	0.01%	0.60%	0.76%

and NH₂ groups in Silquest®, thereby promoting accumulation of epoxy around the wood particles.

The epoxy particles in the case of resorcinol were found to be of a more uniform size, of the order of 5 μm, than with aminosilane coupling agents. The epoxy particles in the latter are found to be coarse, with their size varying between 5 and 40 μm.

Mechanical properties

Figure 7 shows stress–strain curves of composites containing wood flour, treated with coupling agents. The silane coupling agents made the composites somewhat more ductile, although both the tensile modulus and the tensile strength decreased in comparison to composites without coupling agents. The resorcinol coupling agent, on the other hand, rendered the composites more brittle and much stiffer. A point to note here is that the sample specimens were dried in a vacuum oven at room temperature for 24 h before evaluation of their mechanical properties. The use of coupling agents also reduced the impact strength of the composites as can be judged from the following values of notched Izod impact strengths: 38.5, 14.0, 11.3, and 20.3 J/m, respectively, for composites with no coupling agents, resorcinol, Silquest® A-1100, and Silquest® A-2120.

Dimensional changes

Table I compares changes in the dimensions of sample specimens and the percentage water uptake due to immersion in water at room temperature for 24 h, in boiling water for 2 h, and in aqueous solutions of acid and alkali. The results associated with resorcinol coupling agents are reported here. These results suggest the effectiveness of the resorcinol coupling agents in reducing the rate of moisture diffusion into the composite. A good bondage between the hydrophilic wood flour and the thermosetting resin by means of the resorcinol–formaldehyde solution improved the barrier to diffusion of water molecules to the surface

of wood flour particles. Besides, the main component, PPE, has an intrinsic barrier to diffusion of moisture.

CONCLUSIONS

The effects of three coupling agents on the morphology of epoxy coating on wood flour particles and the mechanical and physical properties were investigated. All three coupling agents slowed the epoxy curing reactions and promoted complete coverage of wood flour particles by crosslinked epoxy, although a hydroxymethylated resorcinol coupling agent provided better morphology around wood flour particles; much smaller-size epoxy particles of a more uniform size were formed. Nevertheless, both tensile and impact strengths were reduced due to the use of coupling agents.

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