

On the Development of Natural Fiber Composites of High-Temperature Thermoplastic Polymers

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ABSTRACT: A new method is presented for the development of natural fiber composites of high-performance thermoplastic polymers considering poly(phenylene ether) (PPE) and wood flour as an example system. The large gap between the high processing temperature of PPE, typically between 280 and 320°C, and the low decomposition temperature of wood flour, about 200°C, was reduced by using a reactive solvent, a low molecular weight epoxy. The epoxy formed miscible blends with PPE, which offered much lower viscosity compared to PPE and processing temperatures well below the decomposition temperature of wood flour. In addition, the epoxy component accumulated around the polar wood flour particles upon polymerization during the

fabrication step. The composite materials consisted of a thermoplastic continuous phase and two dispersed phases, one of polymerized epoxy and the other of wood flour particles coated with polymerized epoxy. These composites offered a significant reduction in density and better mechanical and physical properties when compared to commercially available grades of engineering polymer blends filled with short glass fibers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2159–2167, 2002

Key words: high performance polymers; reactive processing; phase separation; natural fillers; composites

INTRODUCTION

Reinforced polymers, filled with organic and inorganic fillers, provide much improved rheological, mechanical, physical, and thermal properties over unfilled polymers. A recent study indicated a yearly growth rate of 3% in the use of reinforced polymers in the United States alone, which will reach 4 billion pounds per year by 2005.¹ This presents tremendous growth opportunities for filler materials of natural origin if one considers reinforced polymer compounds with a typical filler content of 10–60% by weight.

Natural fillers, available in fiber or powder forms, are cellulosic in nature, lighter, and cheaper and provide much higher strength per unit weight than do most inorganic fillers.² Moreover, natural fibers are less abrasive and do not cause the wear of barrels and screws during processing. Also, natural fillers are biodegradable and are, therefore, environmentally benign.

In recent years, many natural fiber-filled polymer composites have been reported in the literature, although in conjunction with polymer systems with low-to-moderate processing temperatures.^{3–18} Thermosetting polymers such as polyesters,³ phenol-formaldehyde,^{4,5} and epoxy^{6–10} and thermoplastic polymers such as polypropylene,^{11–13} polyethylene,^{13–16}

PVC,¹⁷ and polystyrene¹⁸ have been compounded with wood flour, wood pulp, and cellulose fibers to form composites. The processing temperatures of these composites never exceeded 200°C, which is also the typical decomposition temperature of natural fibers.¹⁹

Low decomposition temperatures of natural fibers and poor bonding between hydrophilic fibers and hydrophobic polymer systems have been a deterrent to the development of natural fiber composites of engineering polymers, despite significant growth opportunities in automotive and aerospace industries. Although fiber-polymer bonding, in some cases, can be augmented by the use of coupling agents and precompounding surface treatment of fillers,^{7–10} new technologies are needed to reduce the gap between processing temperatures of engineering polymers and decomposition temperatures of natural fibers.

A spate of recent research activities has established the usefulness of reactive solvents in reducing the processing temperatures of many intractable thermoplastic polymer systems.^{20–27} Some studies also investigated the role of reactive solvents in promoting inorganic filler-polymer bonding, especially through the formation of coating layers around the filler particles.^{26,27}

In this study, we considered the development of a wood flour-reinforced composite of a high-temperature engineering polymer, poly(phenylene ether) (PPE), with the aid of a low molecular weight thermosetting liquid epoxy as the reacting solvent of PPE.

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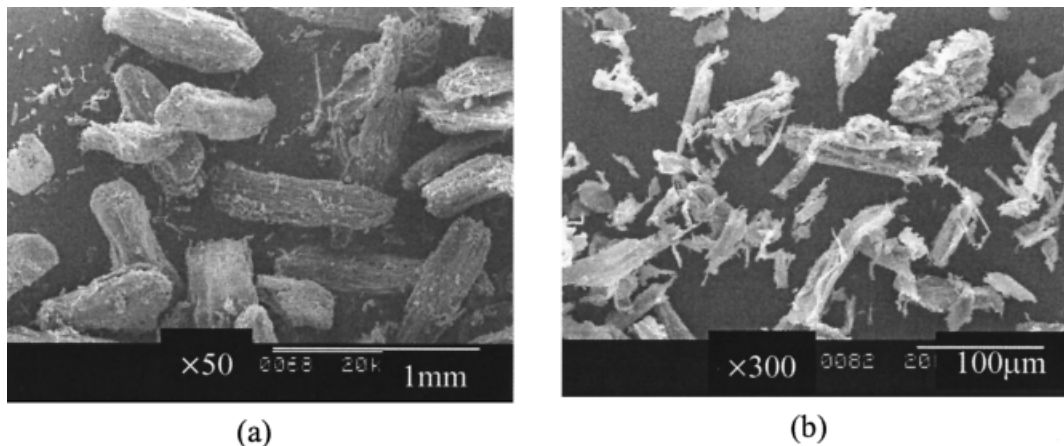


Figure 1 SEMs of wood flour after sieving: (a) 40 mesh; (b) 120 mesh.

PPE, with a processing temperature in the range of 280–320°C, was considered for this study due to its popularity in automotive industries in the form of blends with polystyrene (e.g., Noryl® of General Electric). Low moisture absorption, high elastic modulus, low linear thermal expansion coefficient, ant flame characteristics, and strong resistance to acids and alkali also make PPE a suitable host polymer in natural fiber composites.

Meijer et al.^{20–23} and Ishi and Ryan^{24,25} studied PPE–epoxy systems extensively and found miscibility at room temperature for an epoxy content of 30% or less by weight. The resultant thermoplastic–thermosetting miscible blends exhibited a substantial reduction in the processing temperature and viscosity compared to PPE and these features were exploited in the present study to facilitate the compounding of wood flour without decomposition. The epoxy component was polymerized in the composite fabrication step using suitable curing agents.

The rest of the article is organized as follows: In the second section, we present details of the experimental methodology. The results and discussion are presented in the third section. The last section presents the conclusions.

EXPERIMENTAL

Materials

PPE samples were obtained from GE Plastics (Pittsfield, MA) in powder form 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. Diglycidyl ether of bisphenol A (DGEBA), a bifunctional epoxy under the trade name EPON®828, supplied by Shell Chemical (Houston, TX), was used as a reactive solvent of PPE. EPON®28 shows 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. 4,4'-Methylenebis(3-chloro-2,6-diethylaniline) (M-CDEA) and 4,4'-methylenebis(2,6-diethylaniline) (M-DEA), both supplied by Lonza (Basel, Switzerland) in the form of a solid powder at room temperature, were used in stoichiometric amounts for polymerization of the epoxy.

Hardwood oak flour samples obtained from American Wood Fibers (Schofield, WI) in the form of 40- and 140-mesh powder were used as a natural filler. These filler particles, as received, contained 5% by weight of moisture, had a particle aspect ratio of 2.5–5.0, and bulk and particle density, respectively, of 12–18 and 39 lb/ft³. The particles were dried thoroughly in a vacuum oven at 60°C for 24 h before compounding with the polymer mixture. A close inspection of the as-received wood flour particles revealed a wide distribution of sizes and also a large excess of fines. These fines were removed by further sieving in our laboratory. Also, sieving yielded a narrower distribution in each of the 40- and 140-mesh categories, respectively, to a –40+50-mesh (mean size 360 μm) and –120+140-mesh (mean size 115 μm). Figure 1 presents scanning electron micrographs (SEMs) of wood flour particles after sieving.

Manufacturing of composites

The composite materials were manufactured in two steps: In the first step, PPE and epoxy were mixed in the weight ratio of 70:30 to yield a homogeneous material with a T_g of 105°C and a zero-shear viscosity of 10^5 Pa s at 200°C (PPE itself is in the glassy state at 200°C). PPE and epoxy were mixed in a 30-mm Japan Steel Works (JSW) twin-screw extruder at 100 rpm, with a feed rate of 4.0 kg/h and barrel set temperatures of 120°C in the feed zone and 150, 200, 220, and 220°C in the subsequent zones. At the listed conditions, the mean residence time was found to be ap-

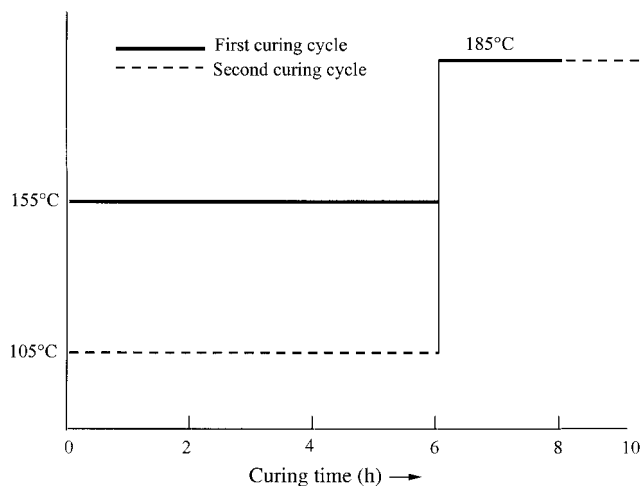


Figure 2 Curing cycles used for curing of composites using M-CDEA.

proximately 120 s. The weight ratio, 70:30, of PPE and epoxy yielded homogeneous material with the lowest viscosity. The viscosity increased with a higher PPE content, and if the epoxy content was increased beyond 30 wt %, two-phase mixtures, instead of homogeneous miscible blends, resulted at room temperature.

In the second step, wood flour and the curing agents (M-CDEA and M-DEA) were compounded with the PPE-epoxy mixture at 185°C. A Brabender Plasticorder batch mixer was used to prepare compounds containing the M-DEA curing agent and M-CDEA-containing compounds were prepared in the JSW twin-screw extruder with the following operating conditions: screw speed of 100 rpm, feed rate of 4.0 kg/h, and barrel set temperatures of 120°C in the feed zone and 150, 185, 185, and 185°C in the subsequent zones.

The test specimens were prepared by injection and compression molding of composite compounds. M-CDEA-containing compounds were injection-molded at 185–195°C using a high injection speed. Compounds containing the faster curing agent M-DEA were prepared by compression molding and cured in the compression molds in one step at 185°C for 3 h. M-CDEA-containing test specimens, on the other hand, were cured in specially designed compression molds to retain their shape; two curing cycles, as presented in Figure 2, were used for the purpose. The first cycle consisted of a curing step of 6 h at 155°C followed by a postcuring step of 2 h at 180°C. The evolution of the heat of reactions, as measured by the DSC technique, revealed approximately 99% conversion of the epoxy under these conditions. In the second cycle, the composite was first cured at 105°C, the T_g of the PPE-epoxy blend, for 6 h, followed by post-

curing at 185°C for 4 h. The total curing times were 8 and 10 h, respectively, in first and second curing cycles.

All mechanical and physical properties were evaluated using test specimens containing 30% by volume or 22% by weight of wood flour not considering the curing agents; M-CDEA-cured composites contained 19% by weight of wood flour. A higher content of wood flour, such as 40 and 50% by volume, were used only for evaluation of the shear viscosity as reported in Figure 4.

Evaluation of mechanical properties

The tensile properties, such as yield stress, tensile strength, elongation at break, ultimate strength, and tensile modulus, were evaluated at room temperature following the ASTM D638 method with a crosshead speed of 5.0 mm/min. The ASTM D256 method was followed to evaluate the impact properties using a TMI-43-I Izod tester. All tests were carried out at room temperature and with a relative humidity between 25 and 50%.

Shear viscosity

The complex shear viscosity of the PPE-epoxy and PPE-epoxy-wood mixtures without the curing agents were measured at 185°C using an Alpha Technologies APA® 2000 cure meter using a twin-cone configuration. An ARES® Rheometrics rheometer was used to measure the viscosity of PPE at 260°C under a nitrogen atmosphere using a parallel-plate configuration.

Thermal properties and dimensional stability

The values of the glass transition temperature of various components and composites were evaluated by using a TA Instruments 2190 differential scanning calorimeter (DSC). All measurements were carried out under a nitrogen environment, with a scanning rate of 10°C/min.

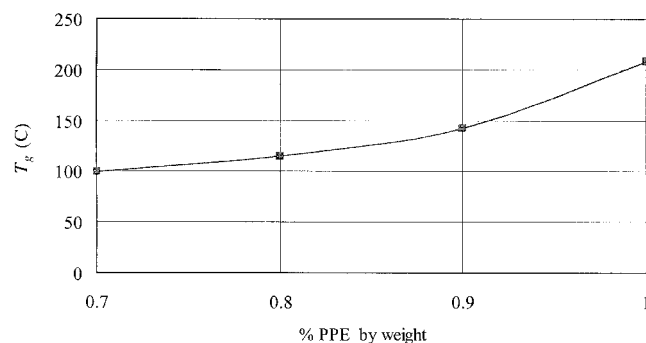


Figure 3 Glass transition temperature of PPE-epoxy system.

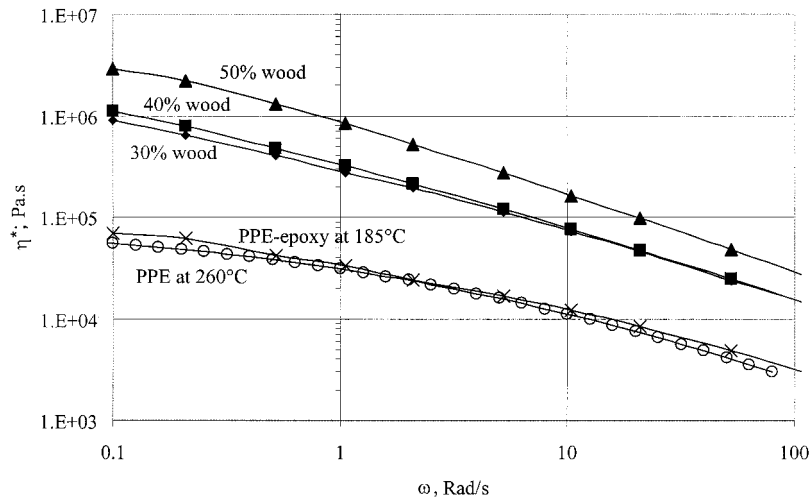


Figure 4 Shear viscosity of PPE-epoxy and PPE-epoxy-wood flour blends measured at 185°C with 1% strain in Alpha Technologies APA2000 cure meter. PPE viscosity was measured using ARES at 260°C under a nitrogen environment.

Thermogravimetric analysis (TGA) was used to determine the thermal stability of the composites under elevated temperatures. A TA Instruments thermogravimetric analyzer, TGA-2950, was used for the purpose. A heating rate of 10°C/min was used in all cases under a nitrogen environment with a flow rate of 40 mL/min.

The amounts of water absorbed by the composites and associated dimensional changes were determined by immersing the composite specimens in water separately at room temperature and under boiling conditions. An ASTM D570 method was followed; test specimens in the form of disks of 50.8-mm diameter and 3.2-mm thickness were immersed in water at room temperature for 24 h and at 100°C for 2 h. At the end of the experiments, test specimens were cloth-dried and weighed. Also, changes in the dimension in the thickness direction were noted.

The dimensional changes of the test specimens caused by exposure to acidic and alkaline environments were also determined following the ASTM D543 method. Composite materials of 50.8-mm diameter and 3.2-mm thickness were immersed for 7 days at room temperature in aqueous solutions of hydrofluoric acid (49% by weight) and sodium hydroxide (66% by weight) in closed containers. The changes in dimensions, cloth-dried weight, and external appearance were noted.

Morphology

The morphology of the composite materials, especially the surface of the wood particles and the location of crosslinked epoxy in reference to the wood particles, was inspected by an SEM, Hitachi S-2150. Samples were prepared by fracturing composite specimens in

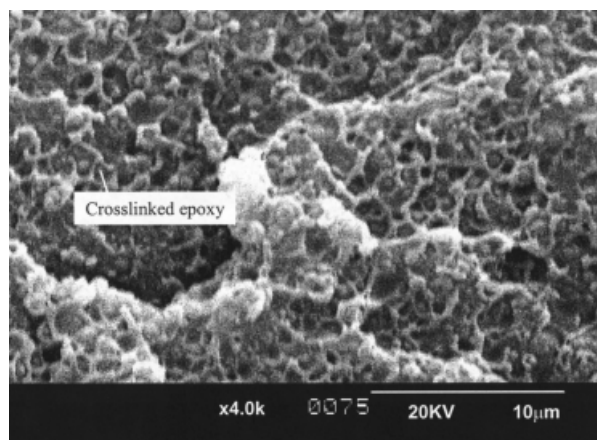


Figure 5 SEM of M-CDEA-cured PPE-epoxy blend, cured at 105°C for 6 h and postcured at 185°C for 4 h.

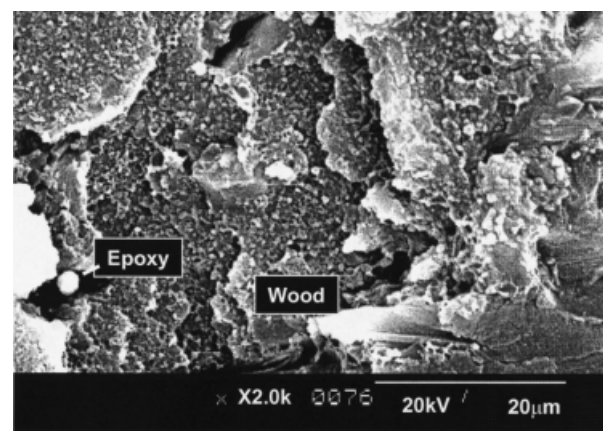


Figure 6 SEM of cold-fractured surface of M-CDEA-cured composite containing 30% by volume of wood flour cured at 185°C for 4 h.

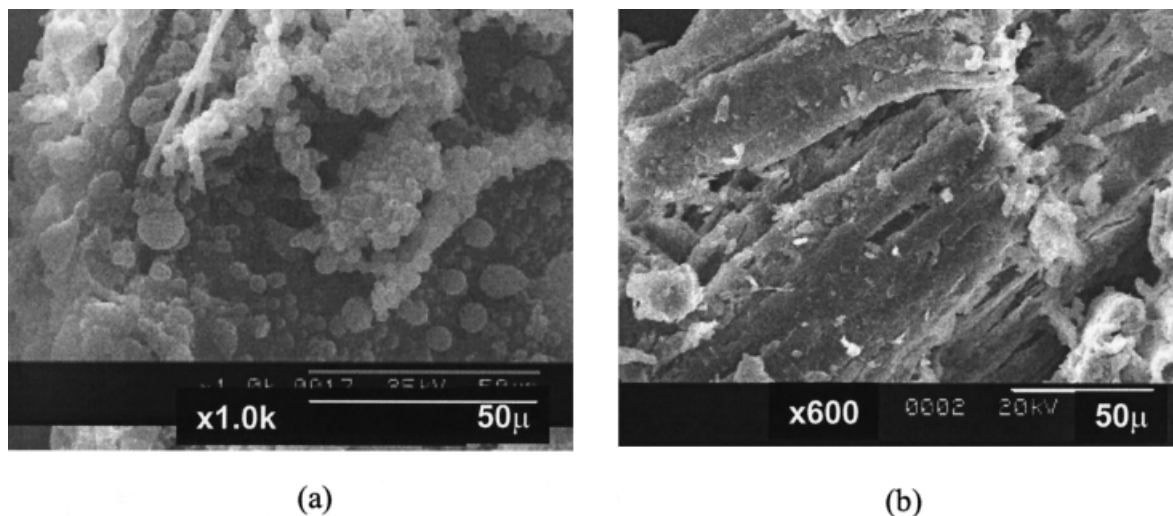


Figure 7 SEM of wood flour-cured epoxy after extraction of PPE phase with chloroform for 6 h: (a) M-CDEA-cured composite, cured following curing cycle 1 of Figure 2; (b) M-DEA-cured composite, cured at 185°C for 3 h.

liquid nitrogen; in some cases, fractured specimens were further treated in oxygen plasma to provide better resolution.

RESULTS AND DISCUSSION

Processability

The glass transition temperatures of the PPE–epoxy mixtures were found to be significantly lower than that of PPE, as can be seen in Figure 3. A reduction in the processing temperature of approximately 100°C was, therefore, achieved by using 30% by weight of epoxy. This facilitated the compounding of wood flour particles with the PPE–epoxy mixture at 185°C without degradation. The zero-shear viscosity of the PPE–epoxy blend, $\eta = 7 \times 10^4$ Pa s at 185°C also showed a marked decrease compared to the viscosity of neat PPE, which was glassy at temperatures below 208°C. The zero-shear viscosity of PPE was measured to be 6.3×10^4 Pa s at 260°C, as shown in Figure 4. Figure 4 also shows the effect of wood flour addition on the shear viscosity of composite materials, minus the curing agents. It can be noted that the composite materials exhibited a power-law-type behavior similar to the PPE–epoxy mixture, indicating the absence of yielding in this composition range. As expected, the zero-shear viscosity gradually increased from 7×10^4 Pa s to 8×10^5 , 1.2×10^6 , and 3×10^6 Pa s as the wood particle content was increased from 0% by volume to 30, 40, and 50% by volume, respectively. The composites with 40 and 50% by volume of wood flour offered very high viscosity and were found to be difficult to extrude through stranding dies. Therefore, the rest of the article is concerned with only 30% by volume of wood flour.

Analysis of morphology

Figure 5 presents an SEM of a PPE/cured epoxy blend exhibiting a two-phase morphology of a PPE continuous phase and a dispersed phase of crosslinked epoxy. Epoxy was cured using M-CDEA following the second curing cycle and formed a separate phase upon reaction-induced phase separation from an initially miscible system.^{21–26}

The composite materials with wood particles, however, revealed two dispersed phases after curing of the epoxy—one of crosslinked epoxy and the other of wood flour particles—as shown in Figure 6. The morphology of the wood flour particles, especially at the interface between the wood flour and the polymer, was not immediately apparent from Figure 6 and, therefore, the PPE–phase was extracted using chloroform in a Soxhlet extraction device. Figure 7 shows SEMs of the surface of the wood flour particles after extraction of PPE. In view of the initial morphology of the wood flour particles as in Figure 1, it can be concluded that the nodular morphology in Figure 7(a)

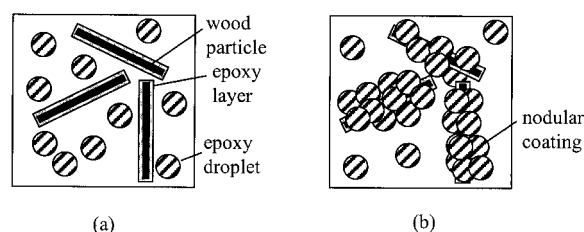


Figure 8 Model of formation of nodular coating of epoxy on wood flour particles: (a) liquid epoxy droplets and epoxy coating layers are formed at the onset of reaction-induced phase separation; (b) liquid epoxy droplets adhere to the coating layers, cure, and harden to form nodular coating.

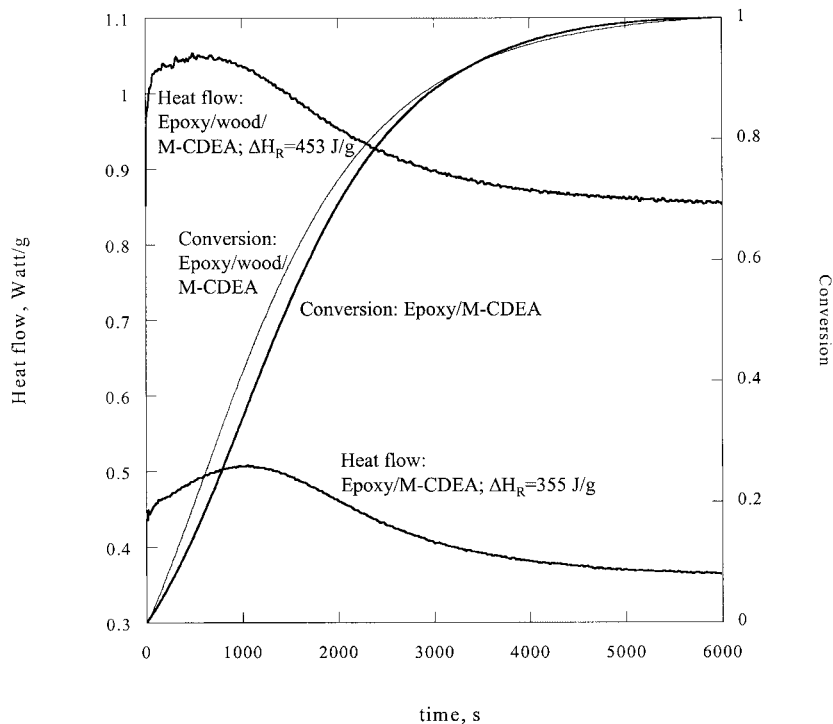


Figure 9 Evolution of reaction heat and conversion of epoxy with M-CDEA with and without wood. Curing reactions were carried out at 185°C in a DSC cell. Epoxy and M-CDEA were mixed using a magnetic stirrer at room temperature. Epoxy, wood, and M-CDEA were mixed at 185°C for 5 min.

presents strong evidence of the formation of epoxy coating layers around wood flour particles, as was already observed in studies involving inorganic fillers.^{26,27} The nodular form of coating with a typical size of 5–10 μm , rather than smooth layers, was a direct consequence of the reaction-induced phase separation of epoxy. As the nodular epoxy particles were found to be adhered to the wood particles, a model, as presented in Figure 8, can be proposed for their accumulation and adhesion, especially in view of chemical reactions between the epoxy and cellulosic components of the wood flour particles.²⁸ The DSC thermograms in Figure 9 show that epoxy crosslinking reactions were faster in the presence of wood particles and produced a larger heat of reaction than in the absence of wood particles. A similar DSC experiment with wood and epoxy in the same ratio as in the composite revealed a slow release of a very small heat of reaction. In view of this, it can be argued that epoxy first preferentially accumulated around the wood flour particles at the onset of the reaction-induced phase separation due to polar–polar interactions between the epoxy molecules and the cellulosic ingredients of the wood flour particles, thereby forming thin coating layers [Fig. 8(a)]. These layers of coating then chemically were attached to the wood particles through cellulose–epoxy reactions and/or cured through epoxy–amine reactions. Simultaneously, phase-separated epoxy domains, still in the liquid/rubbery state,

coalesced to the coating of epoxy on the particles [Fig. 8(b)], thereby producing a nodular form as seen in Figure 7(a). If epoxy crosslinking reactions were fast enough, as in the case of the M-DEA-cured composites, the phase-separated epoxy domains hardened before attaching to thin layers of the epoxy on the wood particle surface and nodular epoxy particles were not formed, as seen in Figure 7(b). Although an immediate advantage of using a faster curing agent such as M-DEA is to achieve reduction of the curing time, the lack of nodular epoxy coating eventually led to poor

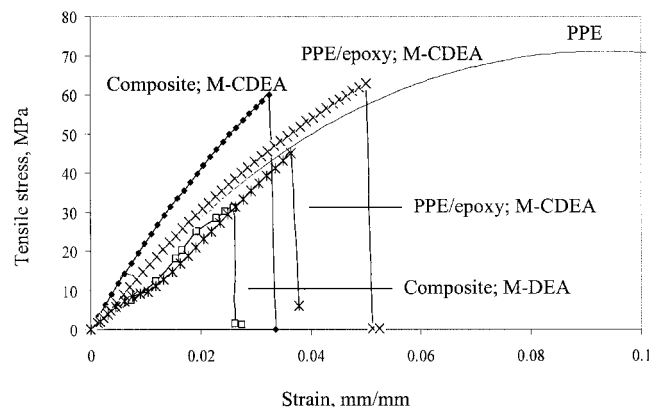


Figure 10 Tensile stress versus strain diagrams of composites cured with M-CDEA (second curing cycle) and M-DEA (3 h at 185°C).

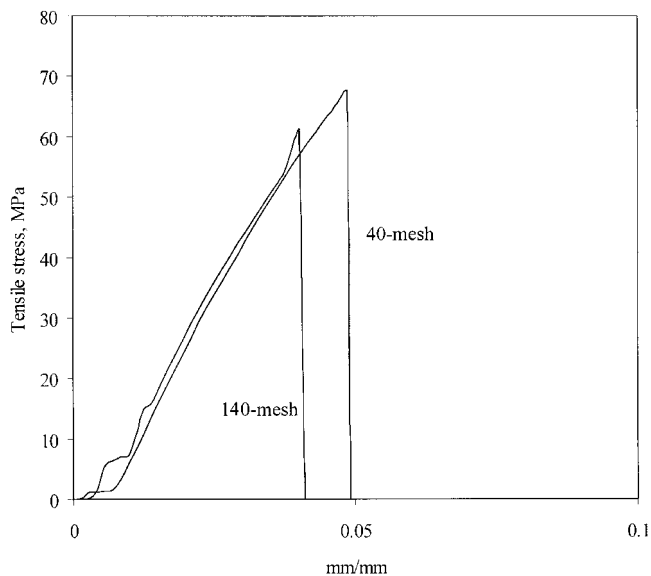


Figure 11 Stress-strain diagram of M-CDEA-cured composites with 40- and 140-mesh wood flour (second curing cycle).

mechanical performance, as will be seen in the next section.

Epoxy coating layers on the wood flour particles were also observed in the M-CDEA-cured composites using the second curing cycle, although much smaller nodules (1–2 μm) were obtained. As the onset of epoxy polymerization in the second curing cycle was set right about the glass transition temperature of the uncured PPE-epoxy blend, phase separation was thought to have occurred by a nucleation and growth mechanism. Consequently, the growth of the cured particles was impeded and many crosslinked epoxy particles with a very small diameter were formed at the onset.

Mechanical properties

Figure 10 shows tensile stress versus tensile strain diagrams of the cured composites and the PPE-epoxy blends cured using M-CDEA and M-DEA. It is seen that the elongation at break of all the blends and composites decreased dramatically and the tensile

strength of the cured materials also showed a substantial reduction when compared with neat PPE. These can be explained on the basis of the two-phase nature of PPE/cured epoxy blends and the three-phase nature of the cured composites. The presence of wood flour in the composite reduced the ductility of the samples, although the tensile strength and the modulus were improved over those of PPE/epoxy in the case of the M-CDEA-cured materials. The M-DEA-cured composites exhibited a more brittle nature, probably due to a higher degree of crosslinking in the epoxy phase than with M-CDEA and a lower tensile strength and a lower modulus than those of the PPE/epoxy blends, thus endorsing the observation that there were not much wood-epoxy interaction in the M-DEA-cured composites, as already seen from the examination of the morphology in the previous section.

Composites fabricated using 40-mesh wood flour exhibited a slightly higher tensile strength than did those filled with 140-mesh as presented in Figure 11. Such a slight increase may not have any physical significance considering the errors in measurements as well as the small aspect ratio of 3–5 of the particles. In addition, no significant difference was observed in the tensile modulus of these materials.

Table I presents a comparison of the tensile and impact strengths of the composites with those of PPE and Table II compares the mechanical properties of the PPE-epoxy-wood flour composites with wood flour-filled composites of conventional thermoplastic polymers such as PS, PE, and PVC. As is evident, the new composites offer much higher strength than that of the conventional natural filler composites and meet the criteria of many filled engineering polymers, such as glass-filled PBT. Additionally, these natural composites were found to be much lighter, with a density of 0.99 g/cm^3 , than was glass-filled PBT with a typical density of 1.3 g/cm^3 .

Thermogravimetric analysis

Figure 12 presents the results of the thermogravimetric analysis of the cured composites. It is seen that

TABLE I
Mechanical Properties of PPE-Epoxy-Wood Flour Composites

Material	Tensile strength (MPa)	Tensile strain at break (mm/mm)	Tensile modulus (MPa)	Notched-Izod impact strength (J/m)
PPE	72.2	1.08	2381	38.5
PPE/epoxy (M-CDEA-cured)	63	0.06	1174	37.4
PPE/epoxy/40-mesh wood (M-CDEA-cured)	70	0.03	2264	38.5
PPE/epoxy/40-mesh wood (M-DEA-cured)	34.2	0.03	1531	36.21

Standard deviation in case of impact strength varied between 8 and 18%.

TABLE II
Comparison of Mechanical Properties of the Composites Developed in This Study with Other Wood-Fiber Composites and Some Popular Engineering Thermoplastic Polymer Blends

Composite	Specific gravity	Tensile strength (MPa)	Tensile modulus (GPa)	Notched Izod impact strength (J/m)	Source
M-CDEA-cured composite; 19% by weight 40-mesh wood flour	0.99	70.0	2.264	38.5	This study
HDPE-wood flour (40% by weight)	1.08	34.2	2.5	37	[29]
PP-wood flour (40% by weight)		27.9	2.4	26.1	[30]
PP-calcium carbonate		21.8	2.2	19.0	[30]
PP-talc (40% by volume)	1.27	30	3.7	75.0	[31]
PP-glass fiber (40% by volume)	1.23	105	11	110	[32]
Epoxy-flax fiber (26% by weight)	1.19	193	22		[33]
PS-wood flour (10% by weight)		24	1.3	17	[34]
PPE-HIPS (Noryl®EN185, extrusion grade)	1.08	43.0		160	Product Literature, GE Plastics
PBT-glass fiber (VALOX® 325E)	1.31	51.7		53.4	Product Literature, GE Plastics
ABS (Cyclocac® GPM5500)	1.04	44.8	2.28	294	Product Literature, GE Plastics
PA66 (Zytel® 101)	1.14	82.7		53	Product Literature, Du Pont

wood flour started losing weight considerably after 220°C, while neat PPE lost weight above 450°C and cured epoxy withstood gradual heating without losing weight up to 325°C. The composite performed much better than did wood, showing stability to about 300°C. It is clear that the continuous PPE phase and the coating of epoxy on the wood particles improved the thermal stability of the wood component. While wood flour lost considerable weight about at 220°C in an inert environment, the composite filled with wood flour withstood temperatures to 300°C before losing weight.

Dimensional stability, water absorption, and resistance to chemicals

The results showed a 0.57% weight gain and a 0.7% increase in the thickness in M-CDEA-cured sample

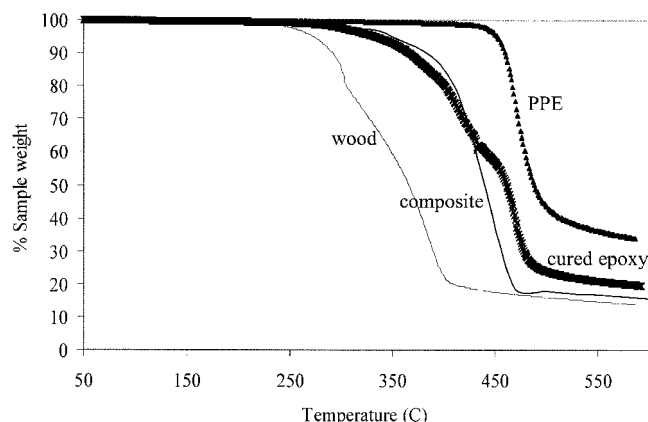


Figure 12 TGA of wood, PPE, cured epoxy, and M-CDEA-cured composite under a nitrogen environment. M-CDEA-cured composite using second curing cycle.

specimens upon immersion in room-temperature water for a period of 24 h. Composites cured with M-DEA showed the highest water uptake, 0.87%, in a 24-h test period, and as is found in Figure 7(b), the epoxy did not properly coat the wood particles. The 2-h boiling water test produced similar results with M-CDEA- and M-DEA-cured composites, absorbing, respectively, 0.84 and 1.11% by weight water. In comparison, natural filler composites of PP and PVC showed much greater water absorption, 1–4 wt %, as presented in refs. 35–37. The M-CDEA-cured composites performed well in acid and alkaline medium as well, gaining, respectively, 0.01 and 0.58% in weight in alkali and acid solutions.

CONCLUSIONS

This study established that thermosetting liquid epoxy resins can be a useful reactive solvent for combining wood flour particles with a high-temperature thermoplastic polymer, PPE. The new composite materials, especially the ones cured with M-CDEA, showed lower water absorption and provided much higher strength than those of other natural fiber-filled composites and compare very well with some glass-filled engineering polymers. These materials will be very suitable for applications in the automotive industry.

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