High Performance Wood Composites from Highly Filled Polybenzoxazine

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ABSTRACT: Highly filled systems prepared by compression molding of *Hevea brasiliensis* woodflour filled polybenzoxazine composites with high mechanical properties and reduced water uptake has been developed. The effects of percent filler content and particle size of woodflour on the obtained composite's properties were examined. The low melt viscosity of BA-a type polybenzoxazine allows substantial amount of woodflour to be easily incorporated into the composites. The results showed that mechanical properties from dynamic mechanical analysis and flexural test at filler content below the optimum filler packing show approximately linear relationship with filler loading. The outstanding compatibility between the woodflour and the polybenzoxazine matrix is evidently seen from the large improvement in the composite's T_g and char yield. Scanning electron micrographs of the composite also reveals substantially strong interface between the woodflour filler and the polybenzoxazine matrix. Water absorption of the composites is greatly reduced with increasing the amount of polybenzoxazine due to the inherent low water absorption of the matrix. The polybenzoxazine is; therefore, a highly attractive candidate as high performance lignocellulosic binder or adhesive and other related applications. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1240–1253, 2006

Key words: highly filled system; wood composite; polybenzoxazine

INTRODUCTION

Many researches in recent years have used thermoplastics i.e., polyethylene,[1,2] polypropylene,[3,4] polystyrene,[5] polyvinyl chloride,[6] and ABS[7] as wood composite's matrices because of their promising ability to render improved composite performance on recycled materials.[8–13] However, a major problem encountered in using thermoplastic matrices is its rather poor interfacial adhesion between the untreated polar wood particles and the strongly hydrophobic characteristics of the polymeric matrix.[14] The polar nature of woodflour contributes to a relatively poor composite's strength, low stiffness, and high moisture sorption characteristics. Another significant shortcoming of this type of matrix is the relatively low filler content, typically less than 50–60% by weight, that can be added

into the matrix.[7,15] Recently, Takeyasu[7] reported woodflour-filled polyvinyl chloride composites at 55 wt % woodflour content and woodflour-filled polyethylene composites or polypropylene composites at up to 60 wt % woodflour content. To achieve greater filler content, modification of the interface between the wood particles and the matrix either by physical or chemical treatment is required.[11,13,16] However, the surface treatment of filler particles normally increases the steps and the cost of processing.

Based on thermosetting polymers, i.e., urea formaldehyde,[17,18] phenolics,[19] epoxy,[20] and polyester,[21] the second type of the matrix overcomes those problems encountered in the thermoplastic matrix. Urea-formaldehyde traditionally occupies the largest volume of the market due to its low cost and high cure speed. However, its poor hydrolysis resistance causes the loss of bond integrity and leads to the release of free formaldehyde, thereby, restricting its use to interior quality composites. Wood composites for exterior use are mostly based on phenolic resins, particularly the resole type.[22] The major advantages of phenolics are: heat resistance, flame retardancy, chemical resistance, dimension stability, and electrical insulation properties. However, traditional phenolic resins still have some shortcomings, including the need of acid or alkaline catalysts in the synthesis step, the release of by-product such as water or ammonia during the processing step, and their brittleness and short shelf-life.[23–25]
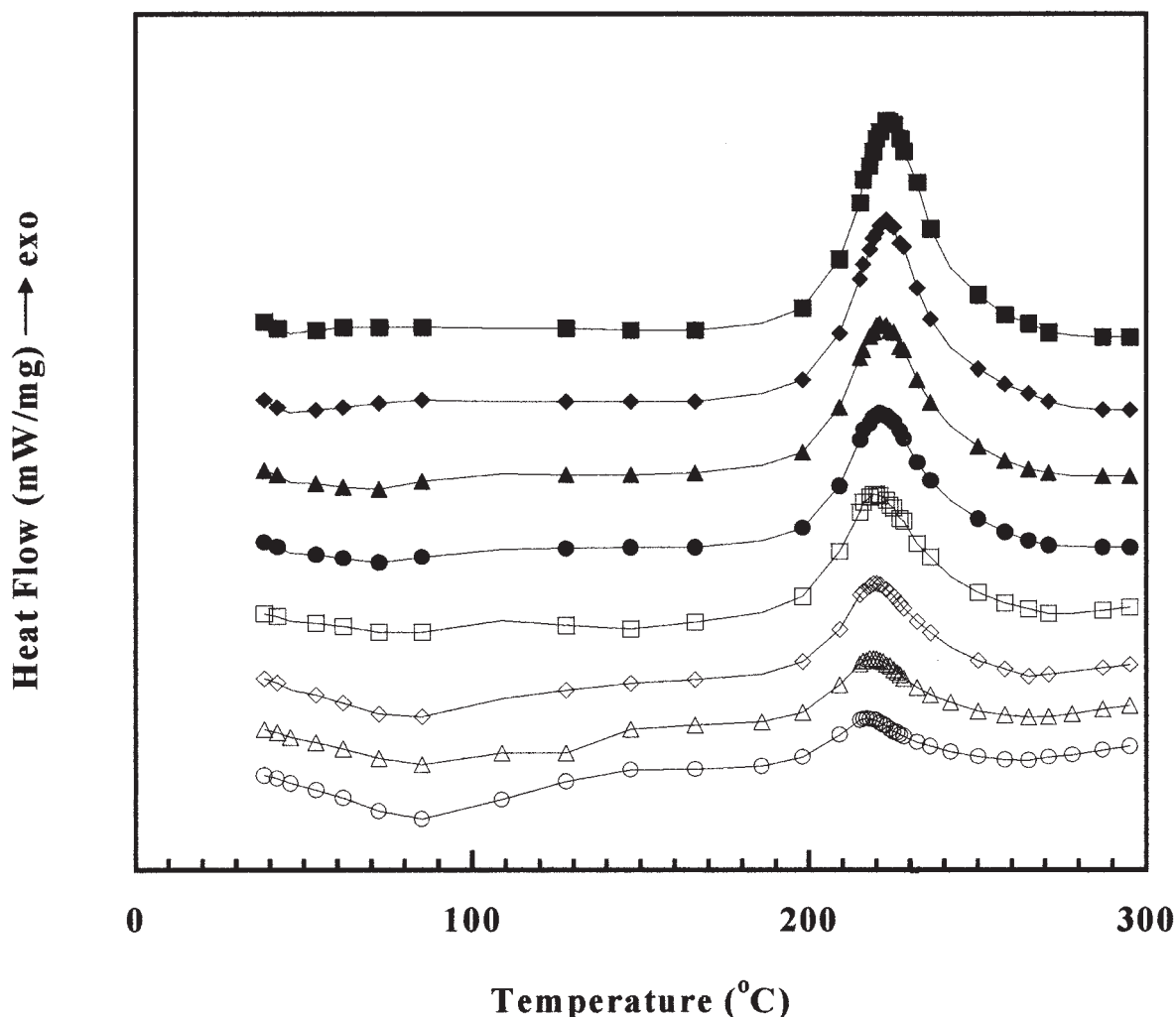
Figure 1 DSC thermograms of woodflour-filled polybenzoxazine composites at different filler contents: (■) neat resin, (♦) 8.1 vol %, (▲) 16.6 vol %, (●) 25.4 vol %, (□) 34.6 vol %, (◇)44.3 vol %, (△) 54.4 vol %, (○) 65.0 vol %.

Polybenzoxazine has been developed as a new class of phenolic resins with a wide range of mechanical and physical properties that can be tailored to specific needs. Polybenzoxazine can be synthesized using the patented solventless technology to yield a relatively clean precursor, without the need of solvent elimination or monomer purification.[26] The balanced properties of the material, including good thermal, chemical, electrical, mechanical, and physical properties, makes polybenzoxazine attractive as an alternative candidate for existing applications.[27] Its intriguing properties include low A-stage viscosity, near-zero shrinkage, fast development of mechanical properties as a function of curing conversion, and low water absorption in spite of having prevalent hydrophilic group in the structure.[28] The successful use of polybenzoxazine as a matrix for highly filled composite has been reported.[29]

Ishida and Rimdusit[29] examined the effect of particle size and its distribution on the thermal conductiv-ity of boron nitride-filled polybenzoxazine. The authors used large aggregates of flake-like boron nitride crystals and were able to make a composite with a maximum filler content up to 78.5 vol % (88 wt %). The extraordinary high thermal conductivity value of 32.5 W/mK was achieved at the maximum filler content.[30] In addition, the ability of benzoxazine resin to be alloyed with other polymers further expands its range of applications.[27,28] Consequently, the resin was chosen in this investigation to make wood composites with high performance and high processability.

The objective of this study is to develop a wood composite for high mechanical and thermal stability applications based on a highly-filled polybenzoxazine system. The effect of the particle size and the filler content on the thermal, mechanical, and other important physical properties of the resulting composites will be evaluated. The investigation utilizes a low-viscosity benzoxazine resin that offers an ability to add greater amount of filler while maintaining pro-
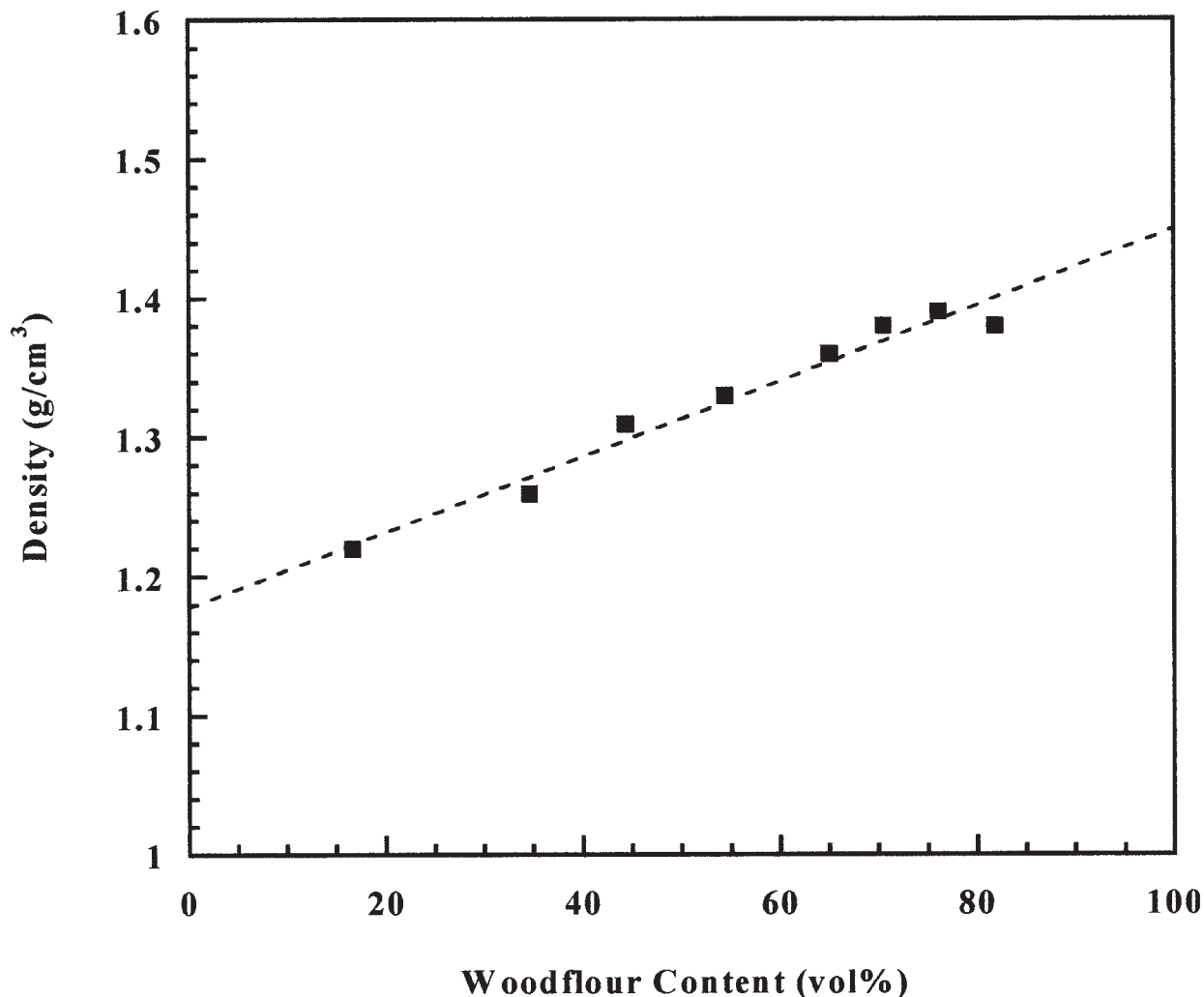
Figure 2   The packing density of woodflour-filled polybenzoxazine composite (particle size of *Hevea brasiliensis* woodflour <149 µm.).

cessability of the molding compound. The polar nature of both polybenzoxazine and woodflour are expected to render a substantial bonding between the two components, thus, achieving good overall composite properties.

EXPERIMENTAL

Materials

The bifunction benzoxazine monomer used is a bisphenol-A-aniline type.[27] The benzoxazine monomer was synthesized using three reactants, i.e., a ring-shaped phenolic derivative, paraformaldehyde, and primary amine. The monomer synthesis is based on the solventless method, which eliminates the need for undesirable solvents and dramatically improves the efficiency of the synthesis.[26] The obtained benzoxazine monomer was a light-yellow solid at room tempera-

ture. It was ground into fine powder and kept in a refrigerator.

The woodflour from *Hevea brasiliensis* tree was selected because of its abundance in Thailand. The density of the woodflour determined with a gas pycnometer is 1.49 g/cm^3. The fraction of particles that pass through a sieve of less than 149 µm, 250–297 µm, and 420–595 µm, respectively, were used. All woodflour fractions were dried at 105°C for 24 h in a vacuum oven and kept in the desiccator before use.

Processing method

Woodflour-benzoxazine resin molding compounds were prepared by manually mixing the calculated mass fractions of both in an aluminum container at 80°C for at least 15 min to ensure particle wet-out by the resin. Each compression-molded compound was shaped in a metal spacer of the desired dimensions at
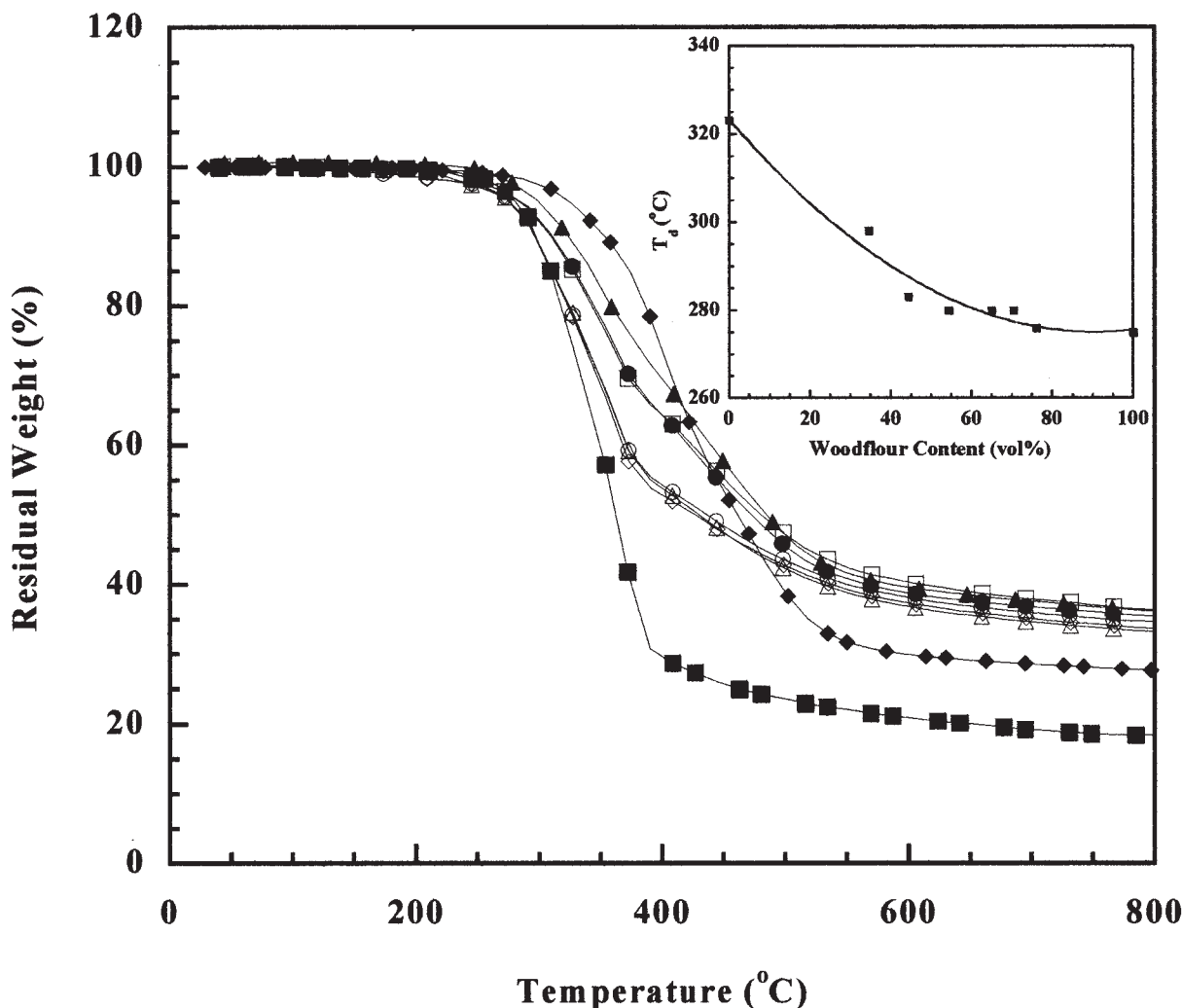
Figure 3 TGA experiments to determine suitable composition of woodflour-filled polybenzoxazine composite samples: (■) woodflour, (♦) neat resin, (▲) 34.6 vol %, (●) 44.3 vol %, (□) 54.4 vol %, (◇)65.0 vol %, (△) 70.5 vol %, and (○) 76.1 vol %.

a curing temperature of 180°C for 2 h. In general, the curing or melting temperature should be kept below 200°C with the presence of woodflour, except for only a short period of time. A higher temperature can result in the release of volatile matter or odor, discoloration, and embrittlement of the wood component.[31] Finally, the samples were left to cool down at room temperature in the open mold before testing.

Differential scanning calorimetry

Curing behaviors and thermal transitions of the filled and unfilled samples were measured using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. Samples (5–10 mg.) were sealed in aluminum pans. The heating rate used was 10°C/min from room temperature to 300°C. The DSC experiment was performed under nitrogen purging.

Thermogravimetric analysis

The weight loss of a specimen as a function of temperature was monitored using a thermogravimetric analyzer (TGA) from Mettler-Toledo Co. (model TGA/SDTA851^e). The weight of the specimen was measured to be 15–20 mg. The specimens were heated at a rate of 20°C /min from 30 to 800°C under nitrogen atmosphere.

Composition and density measurement

The density of the woodflour-reinforced polybenzoxazine was measured by a water displacement method, ASTM D792–91 (Method A). The density of benzoxazine (BA-a) was also determined as a reference. The specimens were disk-shaped with 51 mm diameter and 3.2 mm thickness.
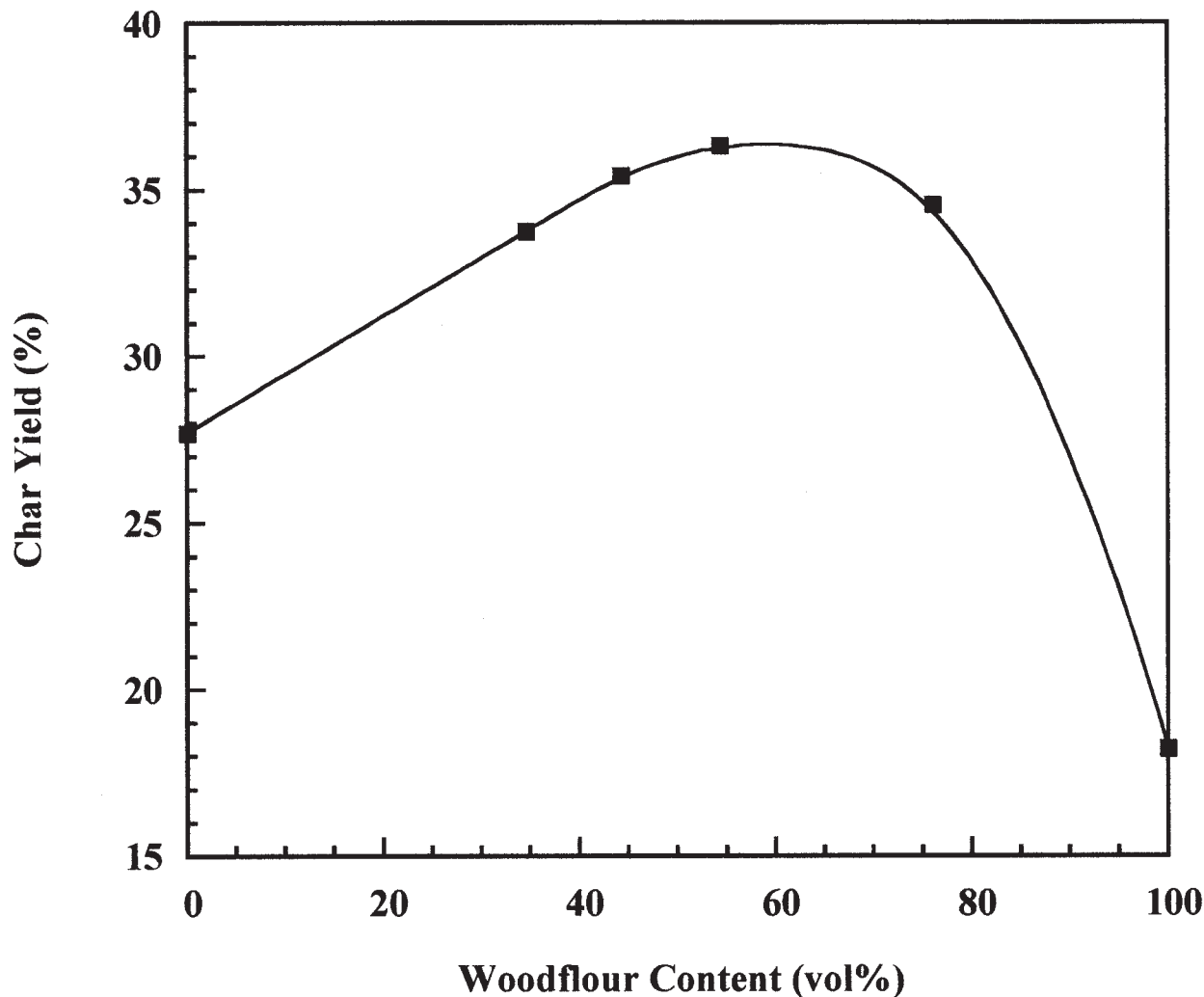
Figure 4 Effect of woodflour content on the char yield of the woodflour-filled polybenzoxazine composite (800°C under nitrogen atmosphere).

Dynamic mechanical analysis

Dynamic mechanical thermograms of the polybenzoxazine and its composites were obtained using a dynamic viscoelastic analyzer model DMTA MK 3 from Polymer Laboratories. The test was performed under the bending mode. The strain amplitude was 0.2% and the frequency used was 1 Hz. The specimen was heated at the rate of 2°C /min from room temperature to a temperature beyond its T_g. The samples were 25 $\times$ 5 $\times$ 2 mm^3. The storage modulus (G'), loss modulus (G''), and damping curve (tan δ) were determined. The glass transition temperature was taken as the maximum point on the loss modulus curve.

Bending test

Three point bending tests were performed to investigate the flexural properties of woodflour-filled polybenzoxazine composites. The specimens were tested according to ASTM D790–92 (Method I). Three specimens of each composite with dimensions of 60 $\times$ 25 $\times$ 2.4 mm^3 were tested. The modulus of elasticity in bending (E_B) and flexural strength (σ_B) were calculated from the obtained load-displacement curves.

Water absorption measurement

Water absorption measurement was conducted following ASTM D570–95, using three disk-shaped specimens having a 51 mm diameter and a 3.2 mm thickness. All specimens were conditioned in an oven at 50°C for 24 h, cooled in a desiccator, and were weighed again to the accuracy of the analytical balance to 4 decimals. The specimens were then immediately immersed in distilled water and were weighed periodically. Based on the initial conditioned mass of each specimen, the amount of water absorbed was calculated from the following formula:
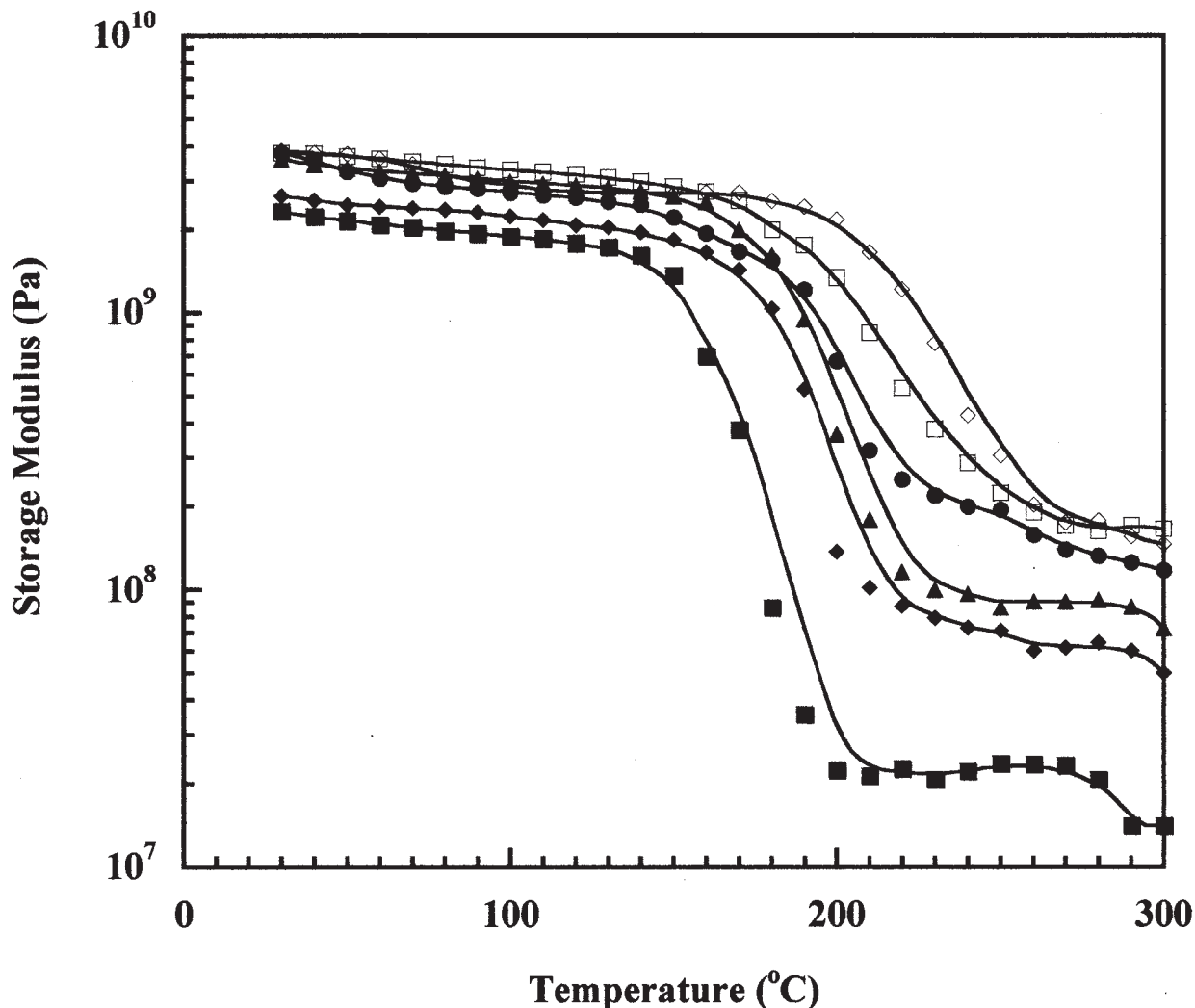
Figure 5 Storage modulus of woodflour-filled polybenzoxazine composites as a function of temperature at different filler contents: (■) neat resin, (♦) 34.6 vol %, (▲) 44.3 vol %, (●) 54.4 vol %, (□) 65.0 vol %, (◇)70.5 vol %.

$$WA(\%) = [(M_e - M_0)/M_0] \times 100 \qquad (1)$$

Here M_e and M_0 are the masses of the specimen after and before immersion.

Scanning electron microscopy

The fractured surface of the composite specimen was observed with an ISM-5400 scanning electron microscopy (SEM) from JEOL Ltd. at an acceleration voltage of 10 kV. The micrograph was used to investigate the surface of woodflour and the adhesion between woodflour filler and polybenzoxazine matrix. The specimens were the fractured surface of a 10% by weight of woodflour-filled polybenzoxazine composite. All specimens were coated with a thin film of gold, using a JEOL ion sputtering device model JFC-1100E for 4 min to obtain a thickness of ~300 Å.

RESULTS AND DISCUSSION

Molding compound characterization

The effect of woodflour content on curing reaction of benzoxazine resin was exhibited in the DSC thermograms of Figure 1 Benzoxazine resin is a self-polymerizable resin, on the application of heat. Under DSC scan at 10°C/min, the materials normally show an exothermal peak at about 220–240°C depending on the purity of the monomer.[32] Our as-synthesized resin shows the same feature as evidently seen in Figure 1 The thermograms at different woodflour content showed the curing exotherms with similar peak maxima of 220°C, implying that the woodflour content has insignificant effect on the curing process of the benzoxazine monomers.

Density measurement

One major goal of this investigation is to utilize a suitable polymeric system that can accommodate a
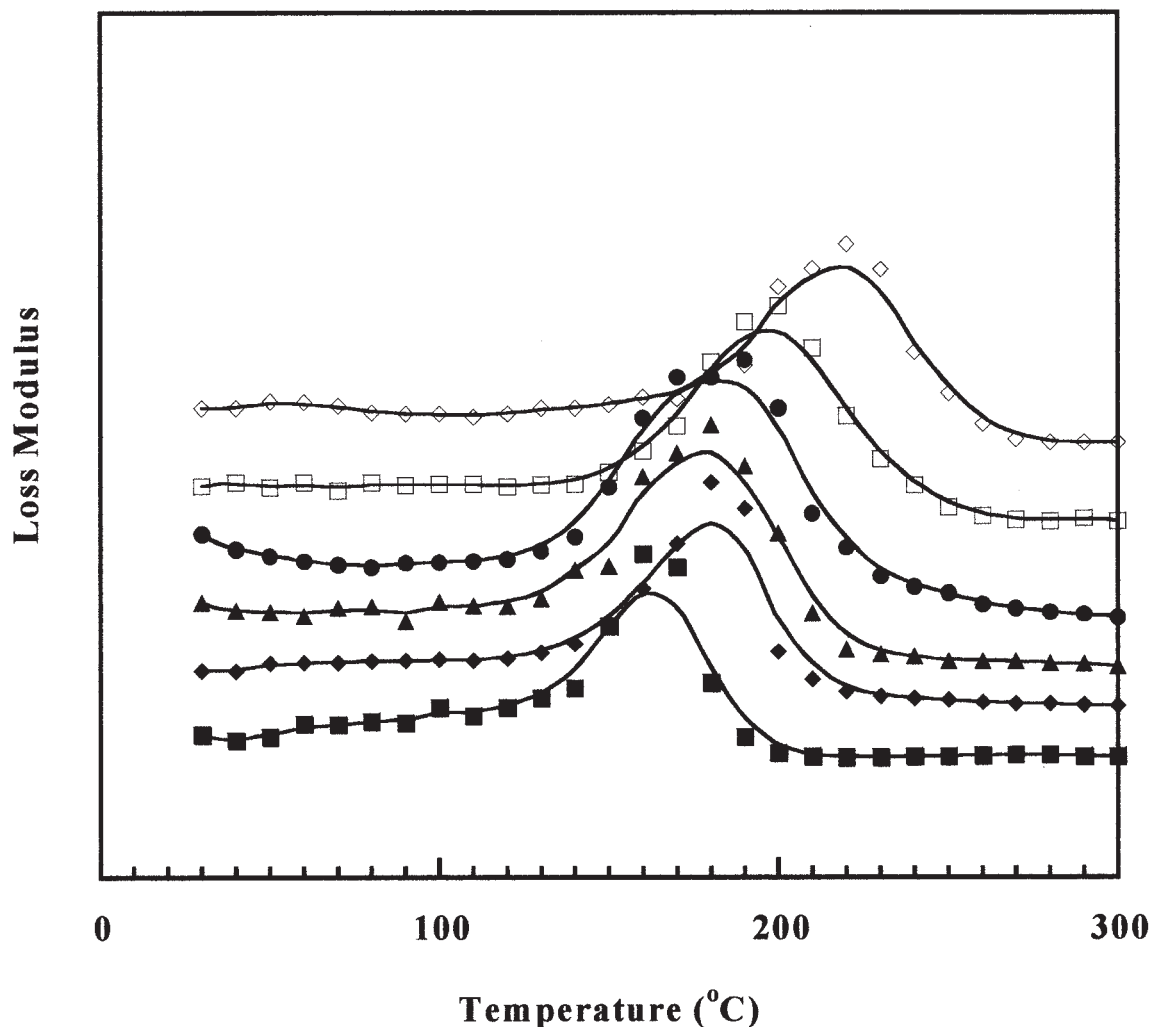
Figure 6 Loss modulus of woodflour-filled polybenzoxazine composites as a function of temperature at different filler contents: (■) neat resin, (♦) 34.6 vol %, (▲) 44.3 vol %, (●) 54.4 vol %, (□) 65.0 vol %, (◇)70.5 vol %.

maximal quantity of the woodflour filler to yield high performance and cost-competitive wood composites. In our previous investigation of highly filled boron nitride (BN)-polybenzoxazine composites, the low melt viscosity of the benzoxazine resin provided an outstanding filler wet-out, with good mechanical integrity of the resulting cured specimens even at up to 78.5% by volume of the BN filler. The type of BN filler used was large aggregates of flake-like BN crystals with an average size of 225 μm, which is comparable to the size of woodflour particle used in this investigation.[29] In addition, the presence of the phenolic structure in the lignin fraction of woodflour and the abundance of hydroxyl moieties in the filler is believed to provide a composite system with strong interfacial bonding to the polybenzoxazine, a class of phenolic resin as well. One measure to determine the optimum packing of the filler in the polybenzoxazine matrix is by composite density measurement.[29,33]

The densities of woodflour-filled polybenzoxazine composites as a function of the woodflour content are shown in Figure 2. The experimental results at filler contents in the range of 16.6–70.5% by volume (20–75% by weight) show a linear relationship between the density value and the filler loading. The predicted densities of the neat polybenzoxazine matrix and the woodflour filler were extrapolated to be 1.180 g/cm^3 and 1.442 g/cm^3, respectively. These values are remarkably close to the experimentally obtained densities of the neat resin and the woodflour, i.e., 1.185 g/cm^3 and 1.490 g/cm^3 respectively.

Thermal characterization

The TGA thermograms of neat polybenzoxazine and woodflour-filled polybenzoxazine at different woodflour contents were depicted in Figure 3. As evidently seen in the thermograms, the degradation temperature at 5% weight loss under nitrogen atmosphere of the composites was shifted to a lower temperature with increasing the woodflour content. In other
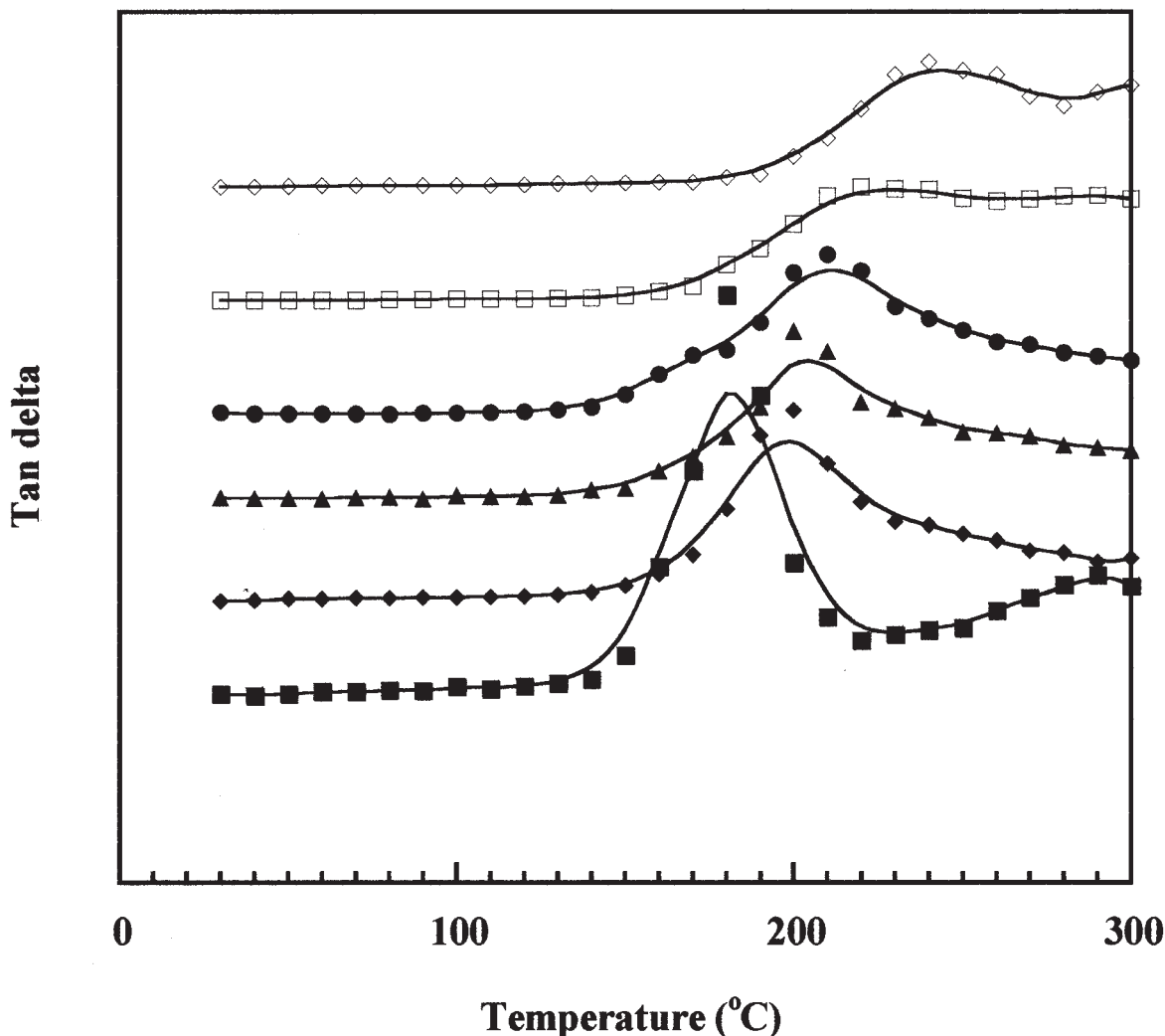
Figure 7 Tan δ of woodflour-filled polybenzoxazine composites as a function of temperature at different filler contents: (■) neat resin, (♦) 34.6 vol %, (▲) 44.3 vol %, (●) 54.4 vol %, (□) 65.0 vol %, (◇)70.5 vol %.

words, the presence of polybenzoxazine helps stabilize the thermal degradation of the *H. brasiliensis* wood. The degradation temperature of the woodflour used is 275°C, which is lower than the 323°C of the neat polybenzoxazine, thus, causing a decrease in the degradation temperature from 298 to 276°C as the woodflour content increased from 34.6 to 76.1% by volume respectively, (see the inset in Fig. 3). The effect of filler connectivity on the degradation mechanism in these highly filled systems is one possible cause of the observed degradation behavior.

Another interesting feature in the TGA thermograms (Fig. 3) is the percent residue at 800°C, the char yield, of the polybenzoxazine wood composites as clearly illustrated in Figure 4. Positive deviation in the composite's char yield (synergism) was observed in the polybenzoxazine wood, i.e., the char yields of the filled systems show the values greater than those of the neat polymer and the woodflour filler. Moreover, the TGA thermograms indicated that the char yields of

the composites increase with the woodflour content up to 54.4% by volume (60% by weight) and then decreases at a higher loading. More specifically, the composite char yields at 34.6–54.4% by volume of woodflour content range from 33.8 to 36.3% and decrease to 33.7% in the 65% by volume filled system (70% by weight), compared with that of the neat woodflour and the polybenzoxazine that have the values of approximately 18 and 28%, respectively. The observed synergistic behavior in the char formation of this composite system may be attributed to the substantial chemical bonding between the woodflour filler and the polybenzoxazine matrix because of their similar phenolic nature and their relatively high availability of the free OH group. An excess amount of the woodflour filler beyond 54.4% by volume; however, negated the effect of the strong chemical bonding on the char yield enhancement and the value started to approach the 18% char residue of the pure woodflour. This kind of synergism in char yield formation was
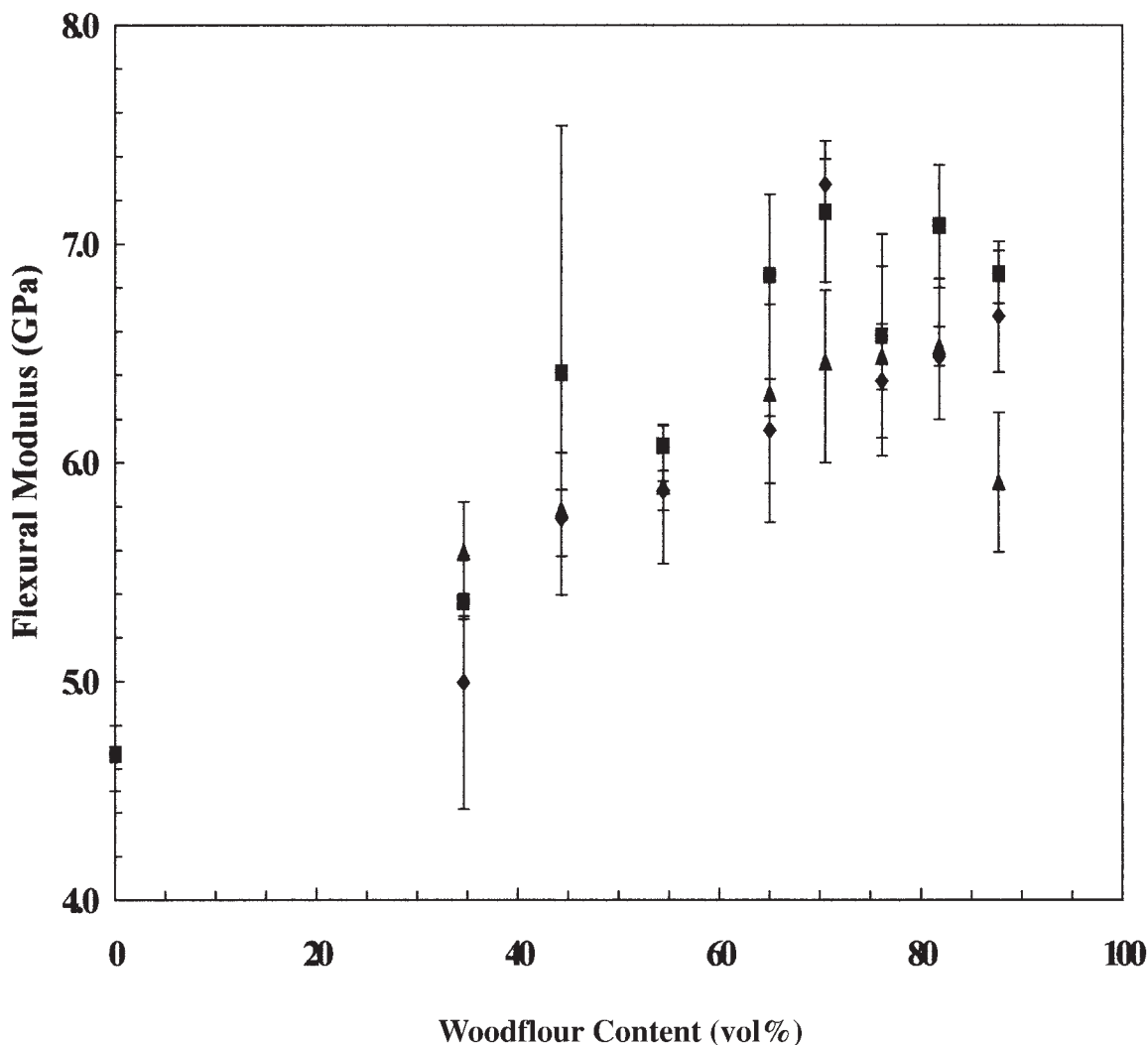
Figure 8 Flexural modulus of woodflour-filled polybenzoxazine composites at different filler contents: (■) 420–595 μm, (♦) 250–297 μm, (▲) < 149 μm.

recently reported in the system of polybenzoxazine and polyimide polymer hybrids.[34]

Mechanical characterization

Dynamic mechanical analysis

Figure 5 exhibits the storage moduli at the temperature ranging from 30 to 300°C of the neat polybenzoxazine and woodflour-filled polybenzoxazine composites with filler contents ranging from 34.6 to 76.1% by volume. As expected, the storage modulus (G') of the composites increases with the amount of a more rigid woodflour up to 70.5% by volume. Beyond 70.5% by volume, the composite's modulus is observed to decrease throughout the whole temperature range. The room temperature modulus of the woodflour-filled polybenzoxazine at the filler content of 70.5% by volume exhibits a significantly higher value of 3.85 GPa than the 2.33 GPa of the neat polybenzoxazine.

Substantial improvement in the rubbery plateau modulus of the polybenzoxazine wood composites over the neat polymer was clearly seen in Figure 5, thus, confirming the significantly strong chemical bonding between the two phases.

Figure 6 is a plot of the loss moduli, G'', of the unfilled and filled polybenzoxazines as a function of temperature. The peak positions of the loss moduli were used to indicate the glass transition temperature (T_g) of the specimens. In Figure 6, the systematically shifting of the peak maxima with the content of the woodflour to higher temperature signifying the increase in T_g of our wood composites with the filler loading. This trend was similarly observed as in the curves of loss tangent with temperature in Figure 7. A glass transition temperature of 220°C was observed in 70.5% by volume of the woodflour filled polybenzoxazine. This makes benzoxazine resin highly attractive as a binder or matrix for this woodflour as it helps
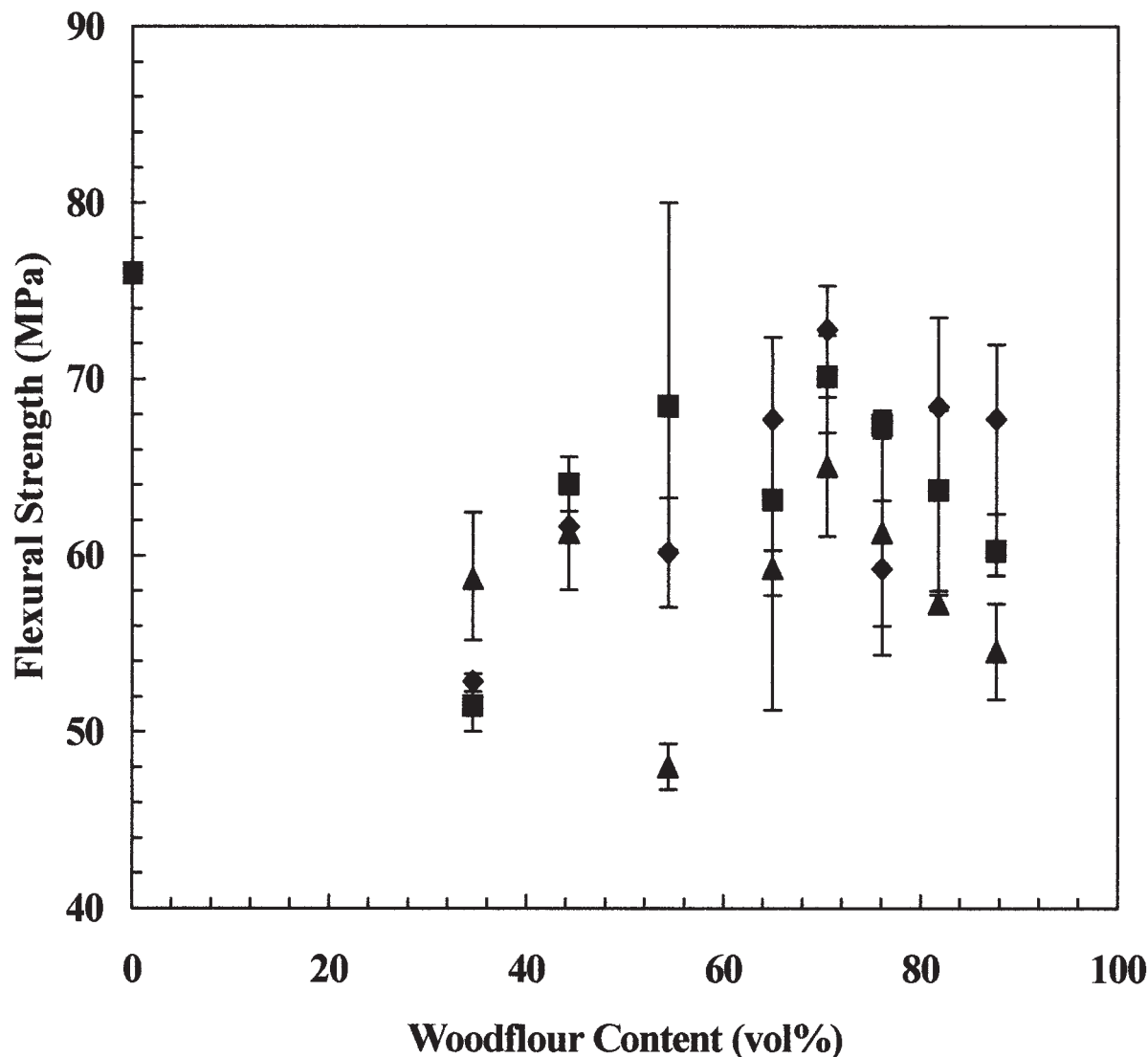
Figure 9   Flexural strength of woodflour-filled polybenzoxazine composites at different filler contents: (■) 420–595 μm, (♦) 250–297 μm, (▲) < 149 μm.

improve the service temperature of the composites. Indeed, this T_g enhancement of up to 60°C is hardly found in other filled polymeric systems. The excessive presence of the more rigid woodflour filler together with the substantial adhesion between the woodflour and the polybenzoxazine resulted in a restriction of the molecular mobility of the polymer and, thereby, the substantial enhancement in the T_g of the composite materials.

Static mechanical analysis

Generally, the strength of reinforced composites depends mainly on the properties of their constituents and interfacial interactions between the filler and the matrix. However, when the flexural properties are considered, the homogeneity of the overall composite needs to be taken into account. The extent of homogeneity is largely affected by the spatial distribution and wetting of the filler. One most important factor is the viscosity of the matrix that indicates the penetrability of the resin into the hollow lumens in woodflour/wood fibers. Figure 8 shows the flexural moduli of the woodflour-filled polybenzoxazine composites at different filler contents. The flexural moduli were found to increase with the filler contents from 34.6% by volume to the optimum value at 70.5% by volume, and then slightly decreased at higher filler content due to the insufficient amount of the polymer matrix to wet all the filler particles. The results are consistent with those obtained from our dynamic mechanical analysis. At a filler content of greater than 70.5% by volume, the load transfer from the matrix to the filler becomes less effective because of the presence of voids
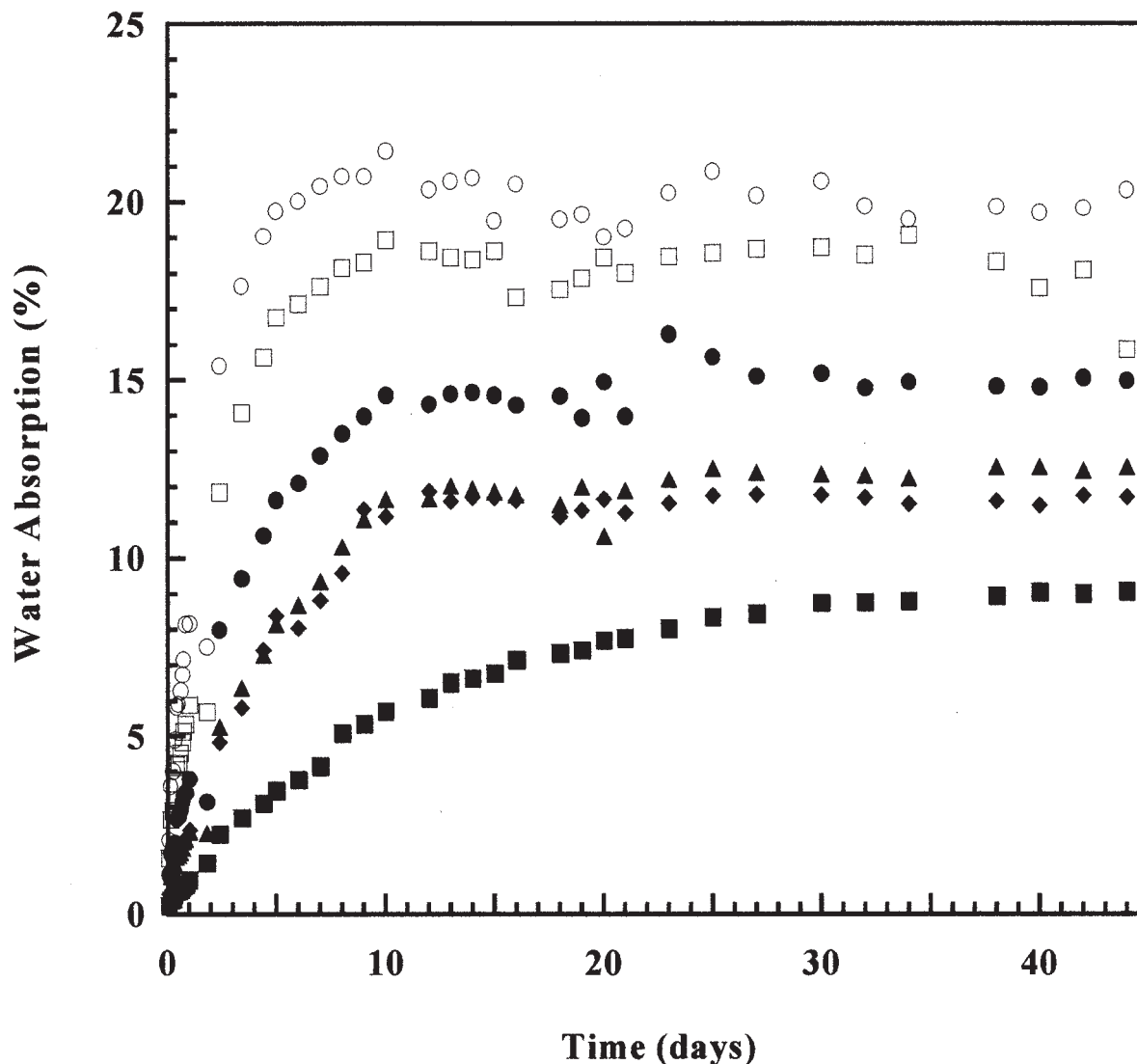
Figure 10 Water absorption of woodflour-filled polybenzoxazine composites at different filler contents: (■) 34.6 vol %, ([daif]) 44.3 vol %, (▲) 54.4 vol %, (●) 65.0 vol %, (□) 70.5 vol %, (O) 76.1 vol %.

that, in addition, can act as stress concentrators in the specimen, resulting in a significant drop in the flexural properties. At 34.6% by volume (40% by weight) of woodflour, our composite provides a flexural modulus of 5.60 GPa, which is comparable to those of wood polymer composites of the thermoset-type in other related works, i.e., wood-unsaturated polyester/styrene that has a flexural modulus of 5.44 GPa.[16] However, at the optimum packing of 70.5% by volume of woodflour, our polybenzoxazine wood possesses a substantially higher flexural modulus up to 6.9 GPa compared with 9.7 GPa of the Heavea wood.[35] The value is more than two times the modulus of typical PVC wood at its highest woodflour content.[31]

As shown in Figure 9, the flexural strength of the polybenzoxazine wood was found to decrease as the particle size of the wood filler decreased. A rather lower aspect ratio of the woodflour filler observed in the smaller particle size is probably responsible for the weaker reinforcement compared with that of the fibrous filler.[5] Nevertheless our composite had a flexural strength of 50–60 MPa at the filler content of 34.6% by volume (40% by weight) compared with the flexural strength of 44.2 MPa of woodflour-filled polypropylene composite at 40 wt % filler content reported by Pinchot.[36] For wood-based composites and panel products, an optimal flexural strength is required[31] i.e., 3.0–23.5 MPa for particleboard grade requirements, 11.0–19.5 MPa for particleboard flooring-product grade requirements, and 14.0–34.5 MPa for medium-density fiberboard (MDF). Our composites show flexural strength up to 60.0–70.0 MPa, which is more than sufficient for high strength wood-substituted products.
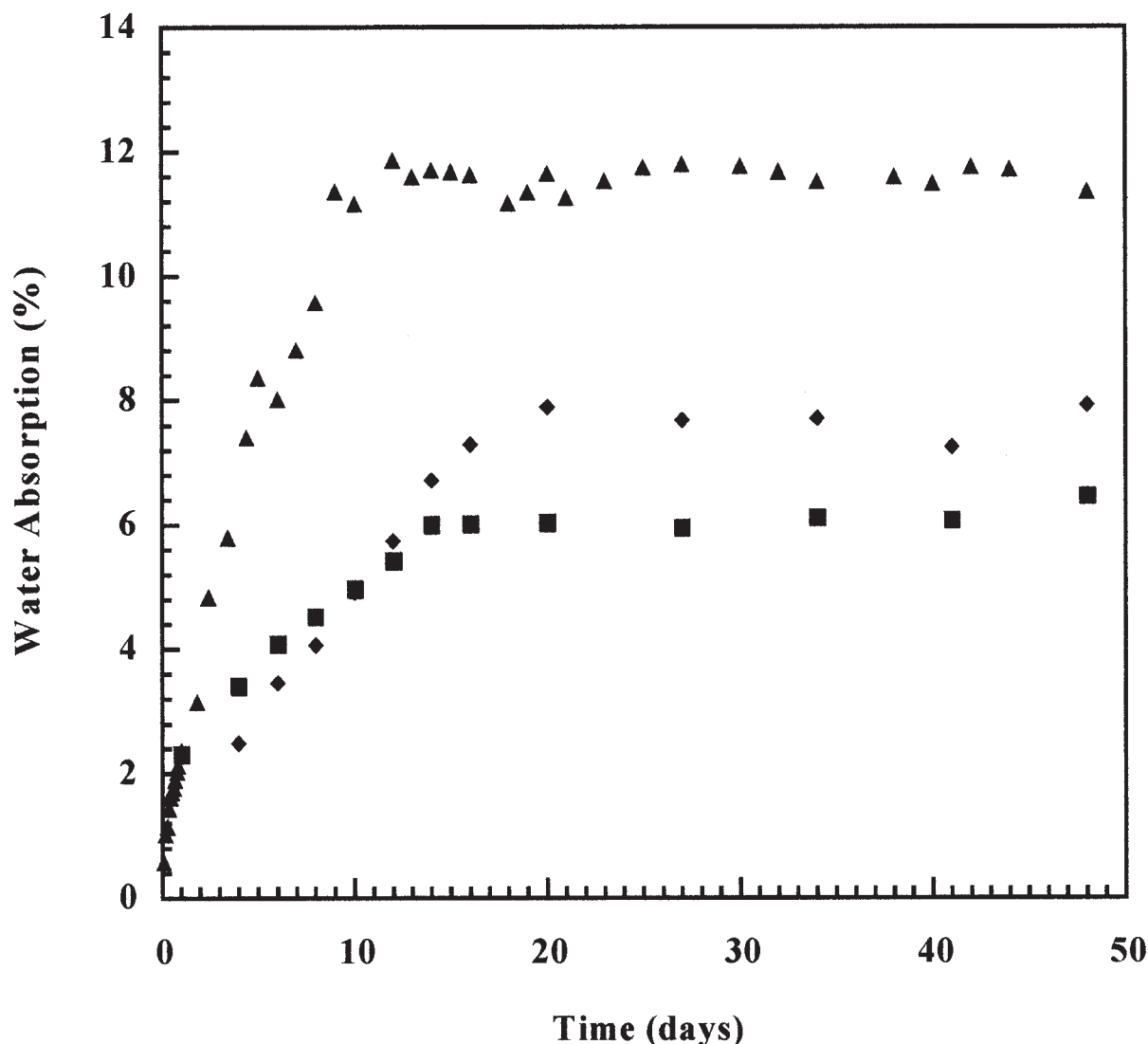
Figure 11 Water absorption of woodflour-filled polybenzoxazine composites at 50 wt % of woodflour with different particle sizes: (■) 420–595 μm., (◆) 250–297 μm, (▲) < 149 μm.

Water absorption

Figure 10 shows the water absorption capacity of the woodflour-filled polybenzoxazine with woodflour contents ranging from 34.6 to 76.1% by volume and up to 45 days. As expected, the water absorption increases as the woodflour content increases. Typically, the water absorptivity of the woodflour based composites largely depends on the availability of the hydrophilic groups, i.e., the free —OH and —COOH groups, on the surface of the reinforcing woodflour. Logically, an increase in the water absorption should result from an increase in the amount of woodflour. Figure 11 shows an example of the effect of the particle size of the woodflour filler on the water uptake capacity at steady state when the woodflour content is fixed at 44.3% by volume (50% by weight). It was evident that the water absorption increase with decreasing the

filler's particle size because of a larger surface area of the smaller size particles resulting in a greater availability of the polar —OH and —COOH groups in the systems.[4]

Interfacial characterization

The dispersion of woodflour/fibers in the polybenzoxazine matrix, the wettability of the filler by the matrix, and the interfacial adhesion between the woodflour/fibers and the matrix were inspected with scanning electron microscopy (SEM) technique. The SEM technique typically revealed the appearance of three types of interfacial adhesion, i.e., woodflour/fibers pull-out, woodflour/fibers breakage, and fibrillation. The woodflour/fibers pull-out morphology corresponds to poor adhesion of the two phases. On the
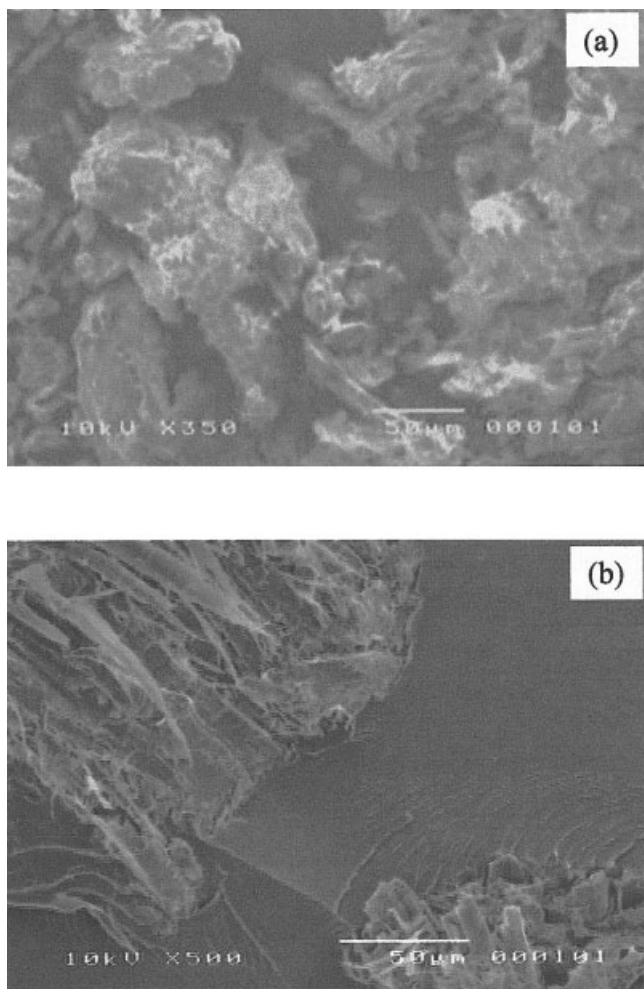
Figure 12 SEM micrographs (a) untreated woodflour particles, (b) fracture surface of polybenzoxazine matrix at 10 wt % of woodflour.

other hand, the breakage and fibrillation of woodflour/fibers were observed on the fractured surface, which implies the existence of substantial degree of adhesion between the two components.

Figure 12(a) shows the morphology of untreated woodflour particles, all of which are below 149 μm in size. Figure 12(b) shows the tight interfaces between the woodflour filler and the polybenzoxazine matrix. Both the woodflour/fiber breakage and the fibrillation of the woodflour are observed. These observations confirm good interfacial adhesion between the woodflour filler and the polybenzoxazine matrix. The property represents one of the significant load transfers, which contribute to the high modulus values of the composite materials. Figure 12(b) also illustrates good miscibility of the two phases, which enhanced mechanical mixing and led to the improved dispersion of the woodflour in the polybenzoxazine matrix. As mentioned above, the woodflour contains cellulose and hemicellulose, which have strongly polar hydroxyl groups and C—O—C links in their structures.

This makes the woodflour highly compatible with polar acidic or basic polymers such as the polybenzoxazine.

CONCLUSIONS

The effects of the woodflour content and particle size on the thermal, mechanical, and some other important physical properties of polybenzoxazine wood may be summarized as follows. The storage modulus (G') of the polybenzoxazine wood composites was found to increase with the woodflour content and reached an optimum value at 70.5% by volume (75% by weight) of the woodflour. Above 70.5% by volume, the storage modulus instead decreases because of the insufficient woodflour wetting in the obtained composites. The glass transition temperature of the composites was found to increase with the woodflour content, i.e., from 160°C in the case of the unfilled system to 220°C in the case of 70.5% by volume of the woodflour. On the other hand, the degradation temperature at 5% weight loss was expectedly observed to decrease with the woodflour content. The char yield of the polybenzoxazine wood showed synergistic characteristics with the peak value of 36%, compared with 28% of the neat resin and 18% of the woodflour. The flexural modulus at room temperature of the *H. brasiliensis* wood is 9.7 GPa compared to the woodflour-filled polybenzoxazine composite with 70.5% by volume filler which shows the modulus value of 6.8–7.3 GPa. Scanning electron micrographs show tight interfaces between the filler and the matrix, which further confirm good interfacial adhesion between the woodflour filler and the polybenzoxazine matrix.

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