Composites from Benzylated Wood and Polystyrenes: Their Processability and Viscoelastic Properties

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SYNOPSIS

Utilization and conservation of raw materials are two of the main thrusts of our research. Several plasticized woods have been prepared from sawdust in our laboratory. They possess unique thermal, mechanical, and viscoelastic properties. In this study, benzylated wood was used to blend with polystyrene to prepare a wood/plastic composite. Its dynamic processability and viscoelastic properties were evaluated. The mixtures with different blending ratios (benzylated wood/polystyrene) were prepared by mixing them in an intensive mixing device. The specific energy required to do the processing work decreased with the increase of benzylated wood in the composite. The mixture can be molded or extruded easily. The study of the viscoelasticity of the compression-molded composite products using a dynamic mechanical thermal analyzer (DMTA) revealed, regardless of the mixing ratios, a single damping peak (tan δ). This suggested good compatibility between the two polymers. The glass transition temperature and the storage modulus of these composites decreased as the amount of benzylated wood increased. A composite with comparable mechanical properties of polystyrene was obtained from those composites with mixing ratios (benzylated wood/polystyrene) ranging from 0.4 to 0.6. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Wood is a composite material that is characterized by a high degree of diversity and variability in its properties. It has been recognized indisputably as a structural engineering material. Because of the shortage of high-quality wood, reconstituted wood materials, such as particleboard, plywood, and fiberboard, are important products of wood-based industry. Lately, chemically modified wood materials, using sawdust and wood residues, have drawn industrial interest, especially those moldable and extrudable wood products from a thermoplasticization process. The process renders the entire wood structure thermoplastic through chemical modification of wood residue, which means that lignin and hemicelluloses are modified and the cellulose decrystallized and modified. The unique process has reached commercialization with success. Recent development in thermoplasticization of wood has been reviewed by Shiraishi.[1] In short, thermoplasticization of wood can be achieved by (a) etherification,[2,3] (b) esterification,[4-6] and (c) grafting reactions.[7] In addition, many researchers have started to use wood fiber or cellulose for fiber-reinforced plastics.[8-11] This stems from both the availability (abundant, inexpensive) and the physical properties (strong, lightweight, nonabrasive, nonhazardous) of cellulose. However, the use of fiber properties to reinforce thermoplastics has not been successfully achieved, mainly for lack of compatibility between the hydrophilic lignocellulosic fibers and the hydrophobic thermoplastic matrices. Increasing the compatibility between fiber and thermoplastics would greatly facilitate the incorporation of such a valuable resource into a number of applications. There are several methods that can be used to enhance the interfacial reaction between lignocellulose and thermoplastics.[12-14] The use of dispersing agents and coupling agents, pretreatment of fibers by encapsulation or grafting, and coating fibers with chemicals have shown improvement of interfacial adhesion between

the composite components. Adhesives are sometimes incorporated to improve the interfacial adhesion.

To improve the compatibility between wood and thermoplastic, a different approach was undertaken in this study, i.e., thermoplasticized wood was blended with plastic. Wood was modified by benzylation to improve its thermoplasticity. Since benzylated wood contains a phenyl structure similar to that of polystyrene, it was anticipated that the thermodynamic compatibility between benzylated wood and polystyrene would be improved. Beyond this level of compatibility, it was hoped that greater attractive forces between benzyl and styrene groups would serve to enhance the resultant property profile. Hence, polyblends of benzylated wood and polystyrenes were prepared. The compatibility and dynamic processability of the polyblends were evaluated.

EXPERIMENTAL

Materials

Two different types of polystyrenes were used: A standard commercially available polystyrene was obtained from Amoco Foam Products Co. A rubber-modified high-impact polystyrene (styron R 478) was obtained from Dow Chemical Co., U.S.A. Benzylated wood was prepared as follows: Wood powder was dried under a vacuum at 60°C overnight before using. A fixed amount of wood powder was mixed with a fixed amount of 40% sodium hydroxide solution. The mixture was transferred into a three-neck flask and benzyl chloride was added. The flask, connecting with a condenser and a stirrer, was placed into an oil bath. The reaction was carried out at 110°C for 6 h to obtain a benzylated wood with a weight gain of 85%. Experimental details and the chemical reaction have been reported previously.[2]

Preparation of Polyblends

The homogeneous polyblends were prepared by the melt blending of benzylated wood and polystyrene with different weight ratios in an intensive mixing head (Plastic-Corder, PL-2000, C. W. Brabender Co.). To avoid thermal degradation for benzylated wood and polystyrene, the mixing temperature and time were set at 125°C and 20 min. The rotor speed was set at 25 rpm. The dynamic torque and the specific energy required to do the mixing were calculated directly from the Plastic-Corder.

Compression Molding

The uniformly blended polystyrene and benzylated wood was molded into broad-waisted dumbbelled specimens with a diameter of 6.4 mm and a gauge length of 25 mm. The mold was heated under 500 psi for 10 min and 1000 psi for an additional 15 min by a Dake Laboratory Press.

Dynamic Mechanical Properties Analysis

The storage modulus and thermal transition properties of the polyblends were determined using a dynamic mechanical thermal analyzer of Polymer Laboratories (PL-DMTA). Dual clamping was used. The strain was set at ×4. The single-scan frequency was set at 30 Hz. The testing temperature ranged from −100 to 200°C, and the heating rate was 4°C/min.

Mechanical Analysis

The mechanical property (tensile modulus) of the specimens was measured by an Instron tensile tester (Model 4204). Data were automatically computed using the Instron Series IX Automated Materials Testing program. The specimen gauge was set for 25 mm. The tests were run at room temperature at a strain rate of 2 mm/min. Tensile modulus was reported at 0.1% strain. Eight measurements were taken for each specimen.

RESULTS AND DISCUSSION

Polystyrene and high-impact polystyrene are transparent and opaque plastics, respectively. The color of benzylated wood is yellow. After intensive mixing of the polystyrenes and benzylated wood under heat (at 125°C), the polyblends exhibited a range of color from light brown to dark brown, depending upon the amount of benzylated wood present in the polyblends.

The specific energy required for mixing the polyblends as a function of polystyrene content is depicted in Figure 1. The results indicated that the specific energy requirement for the mixing increased as the polystyrene content increased. In other words, the specific energy requirement decreased as the benzylated wood content increased in the polyblends. The glass transition temperatures (T_g's) for polystyrene, high-impact polystyrene, and benzylated wood are 134.5, 129, and 102°C, respectively. Higher specific energy needed for polystyrene and
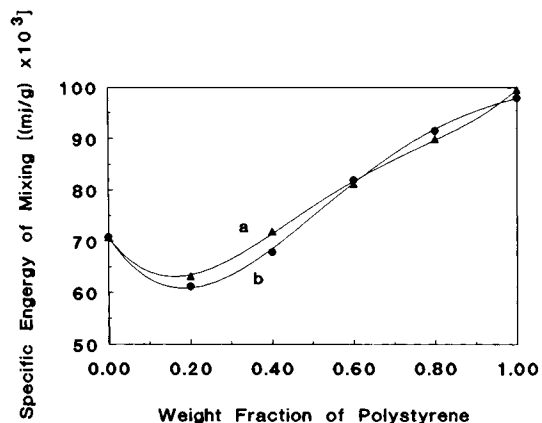
Figure 1   The mixing specific energy of compounding polymer/benzylated wood blended with different mixing ratios: (a) polystyrene/benzylated wood; (b) high-impact polystyrene/benzylated wood.

Figure 3   The loss tangent (tan δ) of polystyrene/benzylated wood blended with different mixing ratios: (a) 0% polystyrene (100% benzylated wood); (b) 20% polystyrene; (c) 40% polystyrene; (d) 60% polystyrene; (e) 80% polystyrene; (f) 100% polystyrene.

high-impact polystyrene may be due to the lower mixing temperature (i.e., 125°C), which is lower than their T_g's. As a result, more energy was needed to accomplish uniform mixing of the polyblends. It was noticed that the shearing between polymer molecules increased the temperature about 15°C in the mixing process in the first 10 mins.

The lowest mixing energy was obtained from the polyblends with the mixture ratio of 20 : 80 (polymer : benzylated wood), although the benzylated wood possesses a lower softening temperature than that of either polystyrene or high-impact polystyrene. This may be attributed to the excellent miscibility of the two polymer phases, resulting in reducing the energy requirement for mixing. Hence, the results
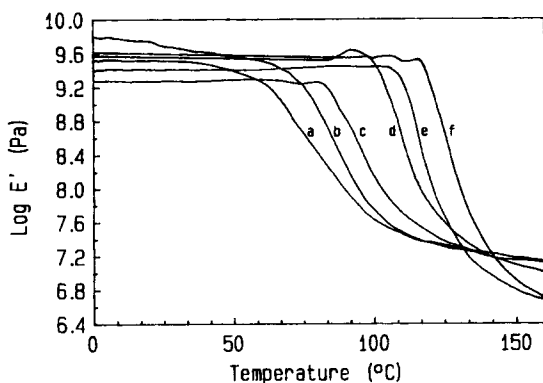
suggested that a lower processing energy may be used to process the polyblends in extrusion or other operation systems at such a mixing ratio.

Dynamic Mechanical Properties of Polyblends

The effect of the weight fraction of polymers on the storage modulus and damping factor, respectively, are shown in Figures 2 and 3 for polyblends of polystyrene/benzylated wood. Similar spectra were observed from a polyblend of high-impact polystyrene/benzylated wood. The maximum transition temperature and other thermal dynamic parameters of the polyblends with different mixing ratios are summarized in Table I.

Figure 2   The storage modulus (E') of polystyrene/benzylated wood blended with different mixing ratios: (a) 0% polystyrene (100% benzylated wood); (b) 20% polystyrene; (c) 40% polystyrene; (d) 60% polystyrene; (e) 80% polystyrene; (f) 100% polystyrene.
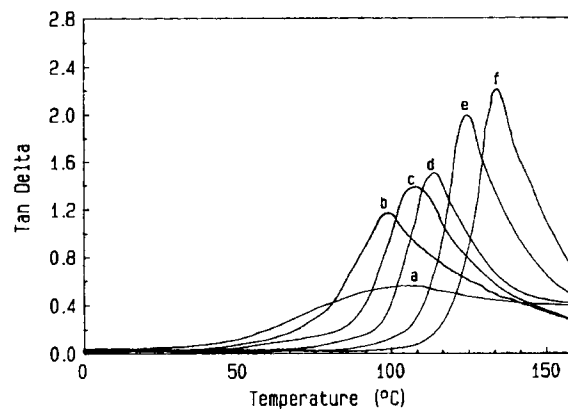
Table I   Peak Parameters of Polymer/Wood Blended with Different Mixtures

| Specimen | Polystyrene | | High-impact Polystyrene | |
	α-Peak Temp (°C)	W^a	α-Peak Temp (°C)	W
100[b]	134.5	10	128.5	12
80	125.5	11	120.0	14
60	114.5	15	115.0	15
40	107.5	18	104.0	20
20	97.5	24	95.0	22
0	102.0	28	102.0	28

[a] Width of α-peak at (tan $\delta)_{max}\sqrt{2}$.
[b] The percentage of polymer in the polymer/wood blends.

It is obvious that the storage modulus was not changed drastically at ambient temperature. Apparently, polyblends with more that 40% polystyrene have slightly higher storage modulus. Whereas benzylated wood started to lose its storage modulus at 30°C, pure polystyrene started to lose its storage modulus at 120°C. The changes of storage modulus of polyblends depended upon the amount of polystyrene present in the system. The more benzylated wood, the lower the temperature at which loss of modulus started.

The damping peaks of polyblends displayed the characteristics of the individual polymers. As a pure phase, polystyrene exhibited a single narrow peak, indicating that the polymer is homogeneous. On the contrary, pure benzylated wood exhibited a much broader single peak, indicating that the modified wood is heterogeneous. Since wood contains cellulose, hemicelluloses, and lignin in varying proportions, the heterogeneity is to be expected.

It is manifest in Table I that the glass transition temperature (T_g) of polystyrene, which corresponds to the α-relaxation, shifted to lower temperatures when the amount of benzylated wood increased. Since benzylated wood has a lower T_g than that of polystyrene, and the increase of benzylated wood lowered the T_g of the polyblends, it is suggested that benzylated wood acted like a polymeric plasticizer for polystyrene. Interestingly, the damping factor (tan δ) of polyblends showed a single peak for all specimens regardless of their blending ratios. This also suggested that the interaction between benzylated wood and polystyrene is good.

Even though the T_g's of polystyrene and benzylated wood are quite different (more than 27°C apart), the mixing of these polymers gave a sharp single damping peak, indicating that both polymers have nearly the same solubility parameter. Hence,
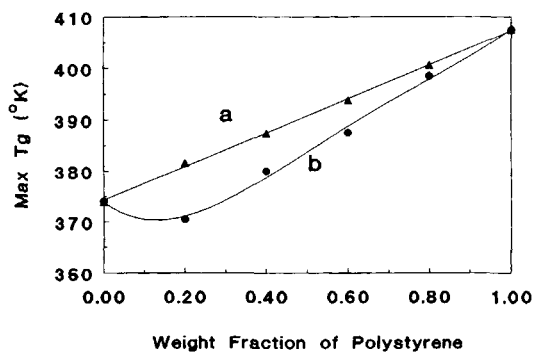

Figure 4 (a) The calculated and (b) experimentally obtained T_g of polystyrene/benzylated wood blended with different mixing ratios.
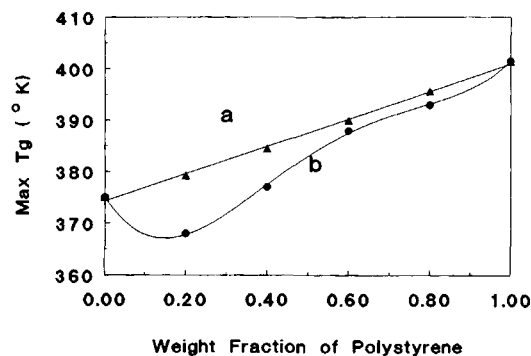

Figure 5 (a) The calculated and (b) experimentally obtained T_g of high-impact polystyrene/benzylated wood blended with different mixing ratios.

the slopes in the storage modulus curves remain steep and the modulus just shifted on the temperature scale in proportion to the relative concentration of the two polymers. This characteristic implied that polystyrene and benzylated wood are compatible and miscible in one another.

To further evaluate the miscibility between the polymers and benzylated wood, the Fox equation is used for predicting the glass transition temperature of the miscible mixture.[15] The Fox equation is shown as follows:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

where W is the weight fraction and subscripts 1 and 2 denote benzylated wood and polystyrene, respectively. The calculated and experimental T_g's of polystyrene/benzylated wood blends and high-impact polystyrene/benzylated wood blends with different mixing ratios are shown in Figures 4 and 5, respectively. The difference between experimental and calculated T_g's became larger when the amount of benzylated wood increased in the polyblends. The differences between experimental and calculated T_g's were about 2–12°C. As discussed earlier, the broadening damping factor of the polyblends displayed the heterogeneity of wood. Although the benzylated portions of wood appeared to be compatible with polystyrene, other unbenzylated portions of wood might present incompatibility with polystyrene, hence contributing to the difference.

Tensile Modulus

The influence of benzylated wood on mechanical properties of polyblends was studied. The effect of benzylated wood on the tensile modulus is shown in Figure 6. The results demonstrated that the tensile
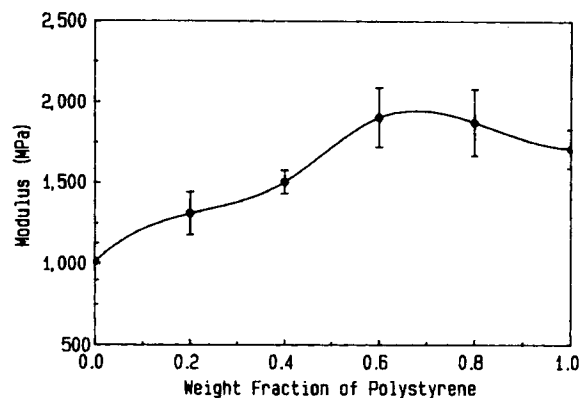
Figure 6 The Young's modulus of polystyrene/benzylated wood with blended different mixing ratios.

strength of polyblends did not diminish when 40% of benzylated wood was present in the polystyrene. A slight diminishing of tensile strength may be observed from the high-impact polystyrene blends. Therefore, it is obvious that although benzylated wood functions as a plasticizer in the polyblends, incorporation of 40% of benzylated wood in the polyblends did not cause any adverse effect on tensile modulus.

CONCLUSIONS

Benzylated wood possesses thermoplasticity and is miscible with polystyrene. The DMTA study revealed the shift of glass transition temperature to a lower temperature of polystyrene and high-impact polystyrene when they were blended with benzylated wood. This study suggested that benzylated wood functions as a polymeric plasticizer in the polyblend. The DMTA study also revealed a single damping peak of the polyblend regardless of the blending ratios between polystyrene and benzylated wood. It appeared that polystyrene and benzylated wood could achieve a good dispersion system. In addition,

the compatibility between these two polymers appeared to be good. Addition of up to 40% of benzylated wood in the polyblend had no adverse effect on the tensile modulus of polystyrene. Hence, it is evident that benzylated wood is a good plasticizer for polystyrene. It can improve the dynamic processability of polystyrene for extrusion and compression molding.

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