

POLYPROPYLENE COMPOSITES FILLED WITH STEAM-EXPLODED WOOD FIBERS FROM BEETLE-KILLED LOBLOLLY PINE BY COMPRESSION-MOLDING

Suzhou Yin

Associate Professor
College of Wood Science and Technology
Nanjing Forestry University
Nanjing 210037, China

Siqun Wang^{†*}

Associate Professor
Forest Products Center

Timothy G. Rials[†]

Professor
Forest Products Center

Kevin M. Kit

Associate Professor
Department of Materials Science and Engineering

and

Marion G. Hansen

Professor
Department of Materials Science and Engineering
University of Tennessee
Knoxville, TN 37996

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ABSTRACT

Beetle-killed loblolly pine chips were steam-exploded (SE) with a severity factor of 4.8 in a batch reactor into a fibrous mass followed by a sieve step to remove oversize pieces (>16 mesh). The sieved SE fibers (<16 mesh) contained 5%–10% water-soluble materials and were mainly composed of fiber fragments with lignin droplets on their surfaces. Composites were prepared by firstly compounding sieved SE fibers and polypropylene (PP) with or without maleic anhydride grafted polypropylene (MAPP) as a compatibilizer, and then by compression-molding the mixtures at 195°C. The MOE of the composites increased greatly, and the yield stress σ_y was decreased slightly by inclusion of 50% SE fibers with no compatibilizer. Addition of 2.5% MAPP improved significantly the flexural properties of the composites, especially the σ_y which was eventually superior to that of neat PP. DMA and DSC measurements revealed that the SE fibers increased the crystallinity of PP by forming more crystalline fractions around wood fibers or fiber fragments. Addition of MAPP resulted in a reduction in the damping and an increase in the heat of fusion of the PP in the composites, suggesting a stronger interface between the matrix and SE fibers. The better interfacial adhesion was also demonstrated by SEM observations showing fiber breakage occurring on the fractured surfaces of the PP composites with MAPP as a compatibilizer.

Keywords: Beetle-killed pine, steam explosion, polypropylene composite, compatibilizer, flexural properties.

[†] Member of SWST.

* Corresponding author (swang@utk.edu)

INTRODUCTION

Beetle-killed timber is low-quality material left in the forest because it is not economical to remove, or local facilities to process it do not exist. There are many beneficial forest management reasons why this material should be removed, including reducing fire hazards, altering the stand species and quality mix to a more desirable composition, providing healthier wildlife habitat, and protecting watersheds (LeVan-Green and Livingston 2001). However, the lack of processing methods dominates the challenge in the cost-effective and value-added uses of this material. Typically, beetle-killed southern pine is comprised of juvenile wood and is characterized by a high bark/wood volume ratio and by some degree of decay. The production of traditional wood composites, such as OSB or particleboard, requires stable raw material composition and supply, prohibitive capitalization and infrastructure, and therefore is not able to accommodate beetle-killed timber as a raw material. In order to find economical and value-added uses for this material, current strategy is focusing on using rural-community-based approaches to generate small businesses that can serve local markets with value-added products (Forest Products Laboratory 2000).

Wood-plastic composites (WPCs) have attracted great attention since the early 1990s as a technique of utilizing wood and plastic wastes and preparing water-resistant wood-based materials without using formaldehyde-based adhesives. The production of WPCs requires less capital investment than traditional wood composites and for this reason is more attractive as a rural-community-based enterprise. The current important applications of WPCs are in construction as non-structural building products, e.g. decking, fencing, siding, window parts, doors, landscape timber, and molding (Clemons 2002). For the most part, WPCs are produced by profile extrusion with approximately 50% wood flour or very short fibers as filler. Because WPCs absorb less moisture and do so more slowly than wood, they have better fungal resistance and dimensional stability when exposed to moisture. On

the other hand, their mechanical properties such as creep resistance and strength are consistently lower than those of solid wood and composite wood panels (Clemons 2002). Hence, there is a strong need in research towards engineered WPCs with greater structural performance and more efficient design.

The filler used in current WPCs is generally wood flour obtained by grinding sawdust and industrial wood waste that requires high energy consumption. The particulates of flour typically have a size of 10 to 80 mesh and an aspect ratio of 1 to 2. The reinforcement potential of wood flour is limited due to the small aspect ratio of particulates, which does not allow efficient stress transfer from the matrix to the particulates. Previous studies have shown that wood fibers are more efficient than wood flour in improving the mechanical properties of WPCs, such as strength, elongation, and impact energy (Clemons 2002). In the case of beetle-killed trees, preparing wood fibers or fibrous material is achievable. However, in order to compete economically with wood flour, alternative approaches should be considered that require less energy consumption than grinding.

Steam-exploded (SE) wood has long been used for the preparation of plastic-like pressed wood products, although the technology is not widely used today (Stamm and Harris 1953). The steam-explosion (SE) process for wood defibrillation consists of chip softening at high pressure and temperature, usually around 200°C, followed by an explosive decompression. It is very effective as a means of fiber separation with low energy consumption (Kokta and Ahmed 1998) and allows a rather selective separation of wood into its main components, namely cellulose fibers, amorphous lignin, and hemicelluloses (Josefsson et al. 2002a). The last two substances can then be removed if needed by simple washing or stirred extraction, and fibers or fiber fragments with a high content of cellulose are finally produced.

The steam explosion process affects all constitutive polymers of wood (Tanahashi 1990). The hemicelluloses are hydrolyzed to oligosaccharides and monosaccharides, which become

water-extractable. The molecular weight of lignin is reduced and the amorphous cellulose is partially depolymerized. This treatment also causes ultrastructural changes (Donaldson et al. 1988), such as the aggregation of lignin and an increase in the porosity of SE wood. As a result of SE treatment, the remaining SE fibers have a reduced hygroscopicity and a higher content of crystalline and/or paracrystalline cellulose (Anglès et al. 1999; Josefsson et al. 2002b). This gives a number of advantages to the SE fibers as reinforcing filler for improving the strength, dimensional stability, and durability of plastic composites.

In exploring a use for beetle-killed timber, SE treatment was proposed in this study as a technique to transform beetle-killed pine into a fibrous mass that may take advantage of the unique characteristics of wood fibers. Considering the great severity of the steam explosion process, it is possible to remove some of the decay in beetle-killed timber by this treatment, which would be another benefit for the utilization of this process on partially decayed wood. Composite panels were made by compression-molding mixtures of SE fibers and polypropylene (PP). To improve the interfacial adhesion between the SE fibers and the PP matrix, a commercially available maleic anhydride grafted polypropylene (MAPP) was selected as a compatibilizer. Morphology of the SE fibers from beetle-killed pine was examined by scanning electron microscope (SEM). The impact of SE fiber inclusion to the performance of PP composites was investigated by testing their flexural properties. Thermal analysis techniques were employed to get insight into the structure of composites and to elucidate the interactions of the SE fibers and PP.

EXPERIMENTAL

Materials

Loblolly pine (*Pinus taeda* L.) trees of 15–18-cm diameter at breast height were harvested at the University of Tennessee Forestry Experimental Station. The beetle-killed pine trees had

been dead for 2–4 years, with slight decay and little remaining bark when they were cut down. A mobile chipper (Vermeer Brush BC1000XL) was used to reduce logs of beetle-killed pine (dead pine–DP), debarked live pine (LP) into chips. The chips were then dried in a kiln to 3%–6% moisture content and sieved using a screen with opening size of 12.7 × 12.7 mm to remove oversized and powder-like fine particles. The dimension range of chips used for SE treatment was ca. (6–25) × (3–6) × (3–6) mm.

Polypropylene was provided by FiberVisions, Inc. (Covington, GA) in the form of fiber bundles (FiberVisions® Create WL, Type 153, 10 mm in length and 3 deniers). The compatibilizer was a maleic anhydride-modified polypropylene provided by Eastman Chemicals, Epolene G-3003, with an acid number of 8 and an average molecular weight $M_w = 52000$ ($M_n = 27200$).

Pulp fibers and lignin were used as reference materials. Bleached pulp was obtained from Kimberly-Clark (Knoxville, Tennessee) in the form of sheets. Pulp fibers were regenerated by cutting sheets into small pieces and then by refining these pieces in a kitchen blender. Kraft lignin powder was Mead-Westvaco's Indulin-AT, donated by Oak Ridge National Laboratory.

Steam explosion treatment

SE wood fibers were produced in a batch reactor at the Steam Explosion Pilot Plant of Virginia Tech. Moisture contents of the chips were 3%–6% before steam explosion. Based on previous experiences and the output of trial runs, the appropriate severity factor was determined to be $\log(R_0) = 4.8$, with a temperature of 228°C and a retention time of 10 min. The factor R_0 combines the process parameters of time and steam pressure (temperature) into a single variable and is defined as $R_0 = t \exp [(T-100)/14.75]$ with T in °C and t in minutes (Overend and Chornet 1987). All the SE fibers were dried in a kiln at 70°C to a moisture content of 2%–4% and then sieved using a screen of 16 mesh (opening 1.19 mm). Only the components passing through the screen (<16 mesh) were used for

the characterization of SE fibers and for the preparation of PP composites in this study.

Preparation of composites with PP and SE fibers

Mixing wood and plastic.—Two processes were employed to mix the SE fibers and PP, namely, dry-blending and compounding. In both processes, the ratio of wood/PP/MAPP was either 50/50/0 or 50/47.5/2.5.

Dry-blending was performed at room temperature in a food processor equipped with two whisks. The total mass of SE fibers and PP fibers was ca. 60 g, and the blending time was 5 min.

Compounding was carried out in a Brabender compounder at 195°C with a rotation speed of 40 rpm. For each batch, the total mass of materials was ca. 40 g. PP fibers were added first into the mixing chamber and melted gradually; this step took ca. 3 min. Once the polymer melted, SE fibers and MAPP were added and the compounding continued for 15 min. Each mixture type was recovered manually with a spatula from the mixing chamber, and after cooling, the solidified pieces were reduced into small granulates with a double-bladed kitchen blender.

To prepare a composite panel by compression molding, a mixture of 40 g (compounded) or 60 g (dry-blended) was put into an aluminum molding die. The die was composed of three separate parts, one female mating ring with an inside diameter of 159 mm to confine radial flow of the polymer melt and fibers, one top and one

bottom plug, both with an outside diameter of 159 mm, to apply load uniformly over the polymer-fibers mixture. Target density of the composite panels was 1000 kg/m³. Target thickness was either 2 mm for compounded panels or 3 mm for dry-blended panels.

The consolidation was performed in a Wabash press at 195°C. The mold was first heated for 5 min under a minimum pressure (<0.5 MPa) to melt the PP. The pressure was then increased gradually to 5.5 MPa in 5 min and held for another 4 min (2-mm-thick panels) or 5 min (3-mm-thick panels). This was followed by introducing cold water into the hot plates to cool down the mold to 40°–50°C. Three to five panels were consolidated for each formulation of composites and neat PP (Table 1 and Table 2).

Characterization of SE fibers

Cold- and hot-water-soluble materials in the sieved SE fibers from beetle-killed pine (DP) were determined according to TAPPI T207 Water Solubility of Wood and Pulp. Two replicates were performed for each procedure, and the reported values were the average of two determinations.

Morphology of the DP SE fiber from dead pine was examined using a Hitachi S-3500 scanning electron microscope. The specimens were oven-dried and coated with gold on an ion sputter coater. The SEM microscope was operated at 5 to 10 kV and various magnification levels, depending on the need to obtain a good image.

TABLE 1. *Flexural properties of PP and PP composites (compounding)*.*

Formulation	MOE (MPa)	MOR (MPa)	0.2% yield stress (MPa)	0.2% yield strain (%)
No. 1 PP	1367 (59)	44.41 (2.17)	24.76 (1.10)	2.39 (0.14)
No. 2 PP-DP	2651 (152)	27.86 (2.43)	22.93 (1.39)	1.28 (0.07)
No. 3 PP-MAPP-DP	3008 (161)	36.88 (2.44)	33.29 (2.27)	1.55 (0.04)
No. 4 PP-LP	2765 (165)	28.50 (1.77)	22.33 (3.09)	1.19 (0.12)
No. 5 PP-MAPP-LP	2826 (176)	37.11 (2.85)	33.06 (1.88)	1.61 (0.13)
No. 6 PP-Lignin	1361 (77)	18.33 (1.91)	12.94 (1.00)	1.35 (0.10)
No. 7 PP-MAPP-Lignin	2171 (49)	26.61 (0.99)	24.70 (0.67)	1.60 (0.07)
No. 8 PP-Pulp	3110 (170)	21.03 (2.69)	20.56 (2.46)	1.03 (0.12)
No. 9 PP-MAPP-Pulp	3354 (240)	32.59 (6.01)	29.32 (3.98)	1.28 (0.07)
No. 10 PP-MAPP	1688 (95)	45.03 (5.65)	30.17 (1.06)	2.38 (0.11)

* Values in parentheses refer to standard deviations; DP and LP refer to beetle-killed and live pines, respectively.

TABLE 2. Flexural properties of PP and PP composites (dry-blending)*.

Formulation	MOE (MPa)	MOR (MPa)	0.2% yield stress (MPa)	0.2% yield strain (%)
No. 1 PP	1453 (21)	43.41 (0.49)	24.95 (0.71)	2.23 (0.09)
No. 2 PP-DP	2249 (186)	23.52 (2.21)	19.61 (1.54)	1.29 (0.13)
No. 3 PP-MAPP-DP	2283 (263)	25.27 (1.41)	22.24 (1.25)	1.40 (0.14)
No. 4 PP-LP	2210 (271)	27.21 (2.97)	20.10 (1.62)	1.28 (0.08)

* Values in parentheses refer to standard deviations.

Flexural properties of PP composites

Flexural properties, including the modulus of elasticity (MOE), maximum stress at break (MOR), stress at yield σ_y (0.2% offset strain), and strain at yield, were tested according to ASTM D 790 Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials (Procedure A). The specimens were cut to dimensions $48 \times 12.5 \times 2$ or $60 \times 12.5 \times 3$ mm from round sheets with a band-saw and polished slightly in the lengthwise direction with No. 100 sandpaper. A support span of 38.1 mm (for 2-mm panels) or 50.8 mm (for 3-mm panels) was used. The specimens were deflected with a strain rate of 0.01 mm/mm/min until rupture occurred in the outer surface of the specimens or until a maximum strain of 5.0% was reached, whichever occurred first. At least 5 specimens were tested for each formulation.

Dynamic mechanical analysis (DMA)

A Perkin-Elmer Pyris Diamond dynamic mechanical analyzer was used to determine the storage modulus E' and the loss tangent $\tan\delta$. The specimens ($48 \times 10 \times 2$ mm) were placed in a dual-cantilever apparatus (10 mm between the center and each fixing clamp) and heated at a rate of 2°C min from -70° to 130°C in a nitrogen atmosphere while an oscillating stress was applied at a frequency of 1 Hz. Three specimens were tested for each formulation.

Differential scanning calorimetry (DSC)

DSC was performed on a Mettler Thermal Analysis 4000 System (DSC25) under a nitrogen atmosphere from -50° to 220°C with a heating

rate of 10°C/min . The mass of each specimen was ca. 5–7 mg. The measured properties included heat of fusion and melting peak temperature. Degree of crystallinity X_c of the PP was calculated according to the following equation: $X_c = \Delta H_m / \Delta H_0$, where ΔH_m is the measured heat of fusion and ΔH_0 the heat of fusion for the 100% crystalline PP. The value of ΔH_0 in the calculation of this study is taken as 209 J/g (Quirk and Alsamarraie 1989; Genovese and Shanks 2004). Three specimens were tested for each formulation.

Morphology of fractured surfaces

Morphology of fractured surfaces was examined using a Hitachi S-3500 scanning electron microscope. Fresh fractured surfaces were coated with gold on an ion sputter coater. The SEM microscope was operated at 5 to 10 kV and various magnification levels, depending on the need to obtain a good image.

RESULTS AND DISCUSSION

Characterization of SE fibers

The treatment with high pressure steam followed by sudden explosive release of pressure converts wood into a fibrous mass. During the reaction, the hemicelluloses are hydrolyzed and become water-soluble; the lignin softens and is depolymerized; the cellulose is also hydrolyzed to some extent, but its crystallinity index increases noticeably in the remaining fibers (Josefsson et al. 2002b; Michalowicz et al. 1991). When the pressure is released, wood cells are separated from each other producing single fibers or fiber fragments. Part of the water-soluble material is removed when the wood residue is

discharged from the reactor; however, a certain amount of these materials is still present in the SE fibers without further washing. Water-solubility measurements showed that the cold- and hot-water-soluble materials represented 5.6% and 9.1%, respectively, of the total mass of the SE fibers from beetle-killed pine. It should be noted that the SE fibers for morphology characterization, and composite preparation were not treated with such a water washing treatment.

Anatomical and ultrastructural changes were observed with SEM. Figure 1a provides an overview of the SE fibers (<16 mesh) and reveals their heterogeneous nature in shape and size. The individual components could be single fibers, cell fragments, or fiber bundles. Although the size distribution is difficult to analyze quan-

titatively, it is possible to get qualitative information about the composition of the SE fibers from the SEM images. The average sizes of tracheids in loblolly pine are 35 μm –45 μm in diameter and 3.42 mm–5.24 mm in length (Panshin and De Zeeuw 1980). Most of the SE wood components seem much smaller than single anatomic units in the natural wood structure, suggesting that the main components of this fibrous material are cell fragments. Single fibers can be obtained by softening the lignin and splitting cells from inter-lamella but they are not frequently observed, which implies their proportion is much less important than that of cell fragments. This observation may reflect a fact that the rupture of chips was more likely to occur by exploding cells from their lumens than by sepa-

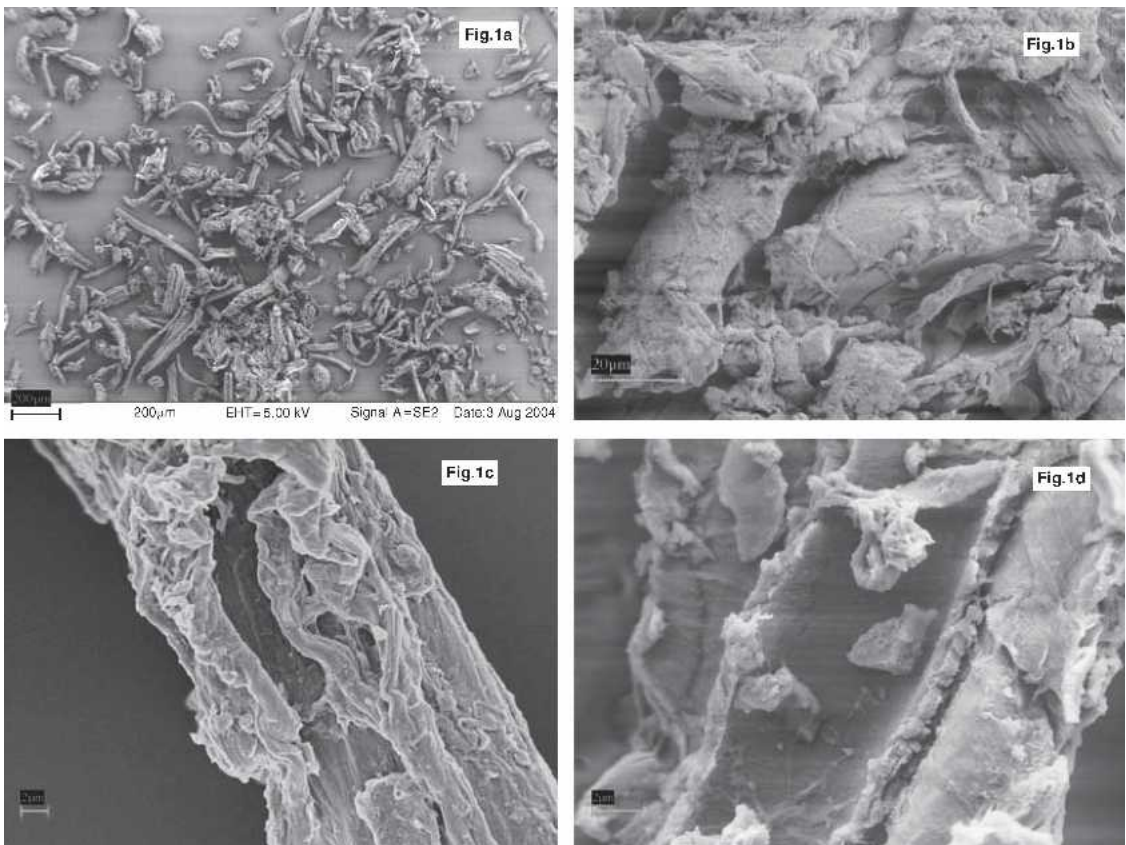


FIG. 1. SEM micrographs of the SE fibers. 1a: Overview of the SE fibers; 1b: An aggregate of fiber fragments glued by lignin; 1c: Outside surface of a fiber fragment covered by lignin; 1d: Inside surface of a fiber fragment with lignin droplets.

rating cells from their inter-lamella. On the other hand, separated cell fragments and single fibers may be aggregated by the adhesion of lignin, resulting in aggregates that look like large particles (Figs. 1a and 1b). However, this adhesion should be much weaker than in natural wood and could be easily destroyed in the compounding or blending process.

It is reported that surface fibrillation of cell fragments could occur by SE treatment, resulting in raised fibrils and microfibrils on the fiber surface (Donaldson et al. 1988; Kallavus and Gravitis 1995). This is, however, not evident on the micrographs of this study, where the surface of most fibers appears smooth rather than rough. It is possible that the fibrils and microfibrils produced by SE treatment adhere back to the fiber surface and are covered by lignin (Fig. 1c) during the subsequent air drying (Kallavus and Gravitis 1995). Softening and redistribution of the lignin are common phenomena occurring under SE treatment. It is observed (Figs. 1c and 1d) that the lignin has a tendency to deposit as droplets on both the outer and inner surfaces of cell fragments.

Water-solubility analysis and SEM observations reveal some unique features that distinguish the SE fibers from the ground flour, i.e. removal of hemicelluloses, fragmentation of anatomical units, and redistribution of lignin. All these changes from the natural structure of wood affect the topochemistry and surface energy of SE fibers and hence the nature of the interactions between the SE fibers and the PP matrix (Anglès et al. 1999).

Flexural properties of PP composites

Stress-strain behavior.—The stress-strain curves of the PP composites with SE fibers are quite different from that of neat PP (Fig. 2). All the samples show an initial straight-line portion on the stress-strain curve; however, the slope of this portion is much steeper for the composites than for neat PP, indicating the composites have a higher MOE. In addition, the composites show a yield point and a break point, while PP exhibits a ductile behavior that does not break at strains

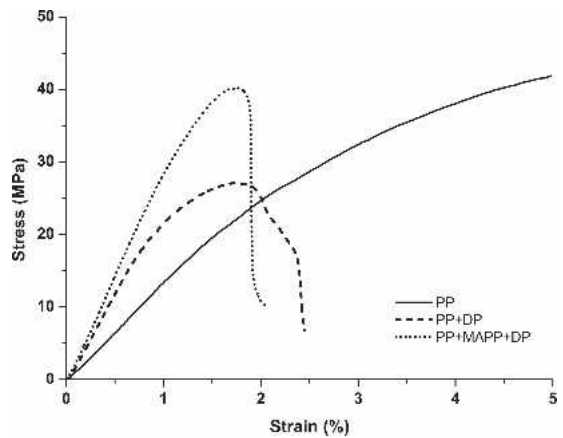


FIG. 2. Typical stress-strain curves of PP and PP/SE fiber composites.

of up to 5% (applicable limit of flexural test). Obviously, the increase in MOE of the composites comes from the inclusion of SE fibers, and this is accentuated by the incorporation of MAPP.

Influence of SE fibers without MAPP.—Table 1 presents the flexural modulus and strength for different composite formulations. MOR is a value most often quoted to characterize the strength of materials because it is easy to determine and provides a measure of the maximum load that a material can withstand without sudden failure. It is useful for the purposes of specifications and for quality control of a product, but cannot be used directly as a design property. For this reason and considering the difficulty of determining the MOR for neat PP in flexural tests, both the MOR and the yield strength σ_y (0.2% offset) are included here as strength characteristics for PP composites and neat PP.

The MOE is 2651 MPa for the PP-DP composite (No. 2), nearly twice that of neat PP (1367 MPa, No. 1). This indicates clearly, within the elastic limit, that the SE fibers from dead pine do play a role in reinforcing and stiffening the PP matrix and are able to effectively transfer stress even without compatibilizer. On the other hand, the strength (MOR and σ_y) of PP composites experiences a decrease by loading SE fibers if no compatibilizer is incorporated.

The σ_y of neat PP is 24.76 MPa and its MOR

is estimated to be 44.41 MPa (44.41 is the stress value at 5% strain; the actual value of MOR for neat PP cannot be determined by the flexural test because the samples do not break at 5% strain). With 50% DP SE fibers (No. 2), the MOR of the composite (27.86 MPa) is reduced by at least 37%, whereas the σ_y (22.93 MPa) is only slightly reduced. These reductions imply the interfacial adhesion is no longer strong enough to effectively transfer stress from the matrix beyond the elastic limit of the composite without using the MAPP as a compatibilizer.

Yield strain can be considered as a criterion for the rigidity of a material, under which any deformation is recoverable. PP panels have a yield strain of 2.38% while the composites with 50% DP SE fibers yield at much lower strain, i.e. 1.28%, indicating the composite is more rigid or less flexible compared with neat PP.

Influence of MAPP.—With 2.5% MAPP replacing a comparable portion of the PP, the MOR of the PP composite (No. 3) is increased by 32%, from 27.86 to 36.88 MPa, and the σ_y by 45%, from 22.93 to 33.29 MPa, which is even higher than that of neat PP (24.76 MPa). In the case of PP composites with ground wood flour or fibers, the improvements in strength may be ascribed to 1) the compatibilization effect of MAPP, which is accomplished by reducing the total wood fiber surface free energy, improving the polymer matrix impregnation, improving fiber dispersion, and enhancing the interfacial adhesion through mechanical interlocking (Kazayawoko et al. 1999), and 2) the formation of ester bonds between the hydroxyl groups of cellulose and the anhydride carbonyl groups of MAPP (Felix and Gatenholm 1991). These mechanisms need to be confirmed by further studies in the case of PP composites with SE fibers.

Because the SE fibers have some lignin redistributed on their surface, the interactions of MAPP with the lignin are also likely to contribute to the improvement in flexural strength. Table 1 shows that mixing lignin with PP (No. 6) results in a material with remarkably reduced flexural strength compared to that of PP, while the incorporation of MAPP imparts much better

strength to the PP-MAPP-lignin composite (No. 7). A similar result was obtained by Toriz et al. (2002), who ascribed the improvement to the possible formation of ester linkages between lignin and MAPP. No evidence of esterification was observed between lignin and MAPP by other authors (Kazayawoko et al. 1998).

The stiffness of the PP composites is also increased by incorporating MAPP. The MOE increases from 2651 MPa (No. 2, no MAPP) to 3008 MPa (No. 3, 2.5% MAPP), i.e. by 13%. This improvement is much less pronounced compared with that of the MOR and σ_y . The reason for this is that the MOE is defined as the strain approaches zero (Kardos 1985) and measured within a range of small strains. At an infinitesimal strain, even the poorest interface in which only the friction force exists between the fiber and the matrix may effectively bear the shear stress; and better interfacial adhesion may not necessarily be reflected by a higher MOE as long as the friction forces are not exceeded by the applied external stresses.

No significant improvement in the yield strain is observed when MAPP is added. The yield strain of composites with 2.5% MAPP is 1.55%, slightly greater than that of the composites without MAPP (1.28%) but still much lower than that of neat PP (2.39%, No. 1) and PP-MAPP blend (2.38%, No. 10).

Dead pine vs. other materials.—Loblolly pine is a species of slight or non-decay resistance (Simpson and TenWolde. 1999). Because the trees cut for this project had stood on the stump for more than two years, deterioration inevitably occurred in the logs that reduced the strength of wood to some extent. In order to examine the effect of the decay and evaluate the reinforcement potential of the two principal chemical components (cellulose and lignin) of SE fibers, a series of composites were prepared under the same conditions with reference materials, namely, SE fibers from live loblolly pine (LP), bleached pulp and kraft lignin. Flexural properties of these composites are also presented in Table 1.

It is shown (Table 1) that all the fillers except the lignin improve the MOE of PP composites.

The addition of 2.5% MAPP produces further improvement in the MOE, and even the composite of PP-MAPP-lignin (No. 7) exhibits a higher MOE than the neat PP and PP-MAPP blend (No. 10). This suggests that the interaction of MAPP and the remaining lignin on the surface of SE fibers may contribute to the interfacial adhesion and hence improve the stiffness of PP composites, although the lignin itself cannot be used as a reinforcing material for PP.

Bleached pulp fibers are essentially composed of cellulose. The pulp composites (No. 8 and No. 9) display the greatest MOE among all the composites, probably owing to the high cellulose content and aspect ratio of the pulp fibers. However, their flexural strength (MOR and σ_y) seems inferior to those of PP-DP composites (No. 2 and No. 3), due to the poor dispersion of pulp fibers. The latter tended to agglomerate together instead of being well separated during the preparation of composites. This finding reveals that, at high strains (yielding and rupture), the dispersion of a reinforcing material is crucial in determining the flexural strength of PP composites. The better dispersion of SE fibers in PP matrix was observed from the fractured surfaces of their composites and could be considered as a processing advantage compared with pulp fibers.

It is worthy noting from Table 1 that the flexural properties of the composites with DP SE fibers (No. 2 and No. 3) are extremely close to those with LP SE fibers (No. 4 and No. 5). No significant difference has been found between these two types of composites in their MOE, MOR, σ_y and yield strain, indicating the reinforcement of DP fibers is as effective as that of LP fibers. This similarity in reinforcing efficiency suggests that the SE treatment could reduce the amount of decay in DP fibers to such an extent that the presence of remaining decay would not be significantly detrimental to the flexural properties of PP composites. By minimizing the effect of decay, the SE treatment provided a unique processing advantage in transforming the beetle-killed, partially decayed wood into a reinforcing material for PP composites.

Influence of mixing processes.—Table 2 shows the flexural properties of the composites

obtained by dry-blending process. The impacts of DP SE fibers on these properties are similar as in the case of compounding process. However, the values of these properties appear consistently lower than those of the composites prepared by compounding process and the difference is more pronounced when MAPP is added (Table 1). For instance, the compounding PP-DP composite (No. 2) has a MOE of 2651 MPa, i.e. 18% higher than that of the dry-blending one (2249 MPa); when MAPP is incorporated, the MOE increases to 3008 MPa by compounding while no appreciable improvement is obtained by dry-blending. The advantages of compounding process over dry-blending can be illustrated more evidently by comparing the yield strength. The σ_y of compounding PP-DP composite with MAPP (No. 3) is 33.29 MPa, which exceeds that of neat PP (ca. 24 MPa), while that of dry-blending composite is 22.24 MPa, which remains slightly inferior to that of neat PP.

The greater flexural modulus and strength exhibited by the compounded composites indicate that compounding leads to more efficient reinforcement by DP fibers due to shear mixing of MAPP with the other components and a more uniform dispersion. In the compounding process, the interactions of PP, SE fibers, and MAPP (when present), occurred first in the compounder and then in the mold so that the fibers had more chances to interact with MAPP, to form physical liaisons and/or covalent bonds with the PP and to disperse more evenly in the PP matrix. In dry blending, the interactions could only take place in the consolidation step and the movement of the fibers was restricted in the mold. Nevertheless, considering the advantages of the dry-blending process, i.e. requiring fewer operations, consuming less energy, and resulting in less damage to wood fibers, it is still interesting to take this process as an alternative for preparing PP composites.

Dynamic mechanical analysis (DMA)

Figures 3a and 3b show respectively the temperature dependence of the $\tan\delta$ and the storage modulus (E') in the range of -50° to 130°C for

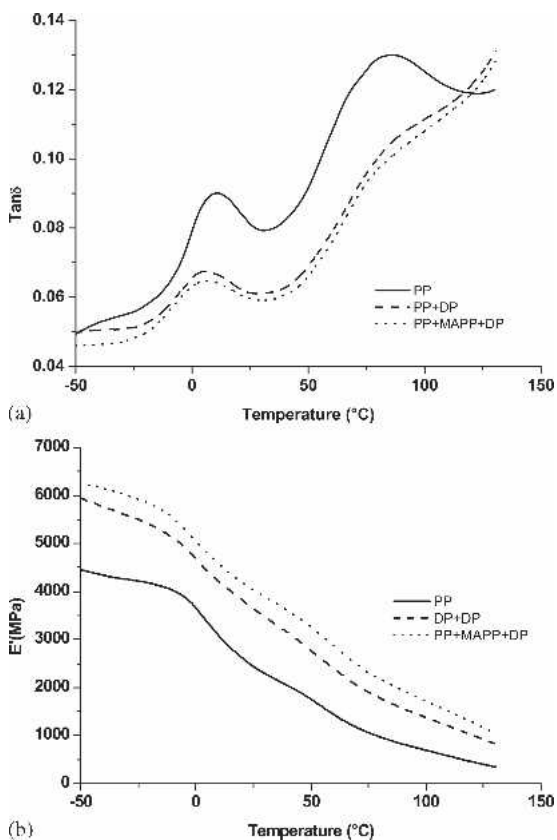


FIG. 3a. $Tan\delta$ of PP and PP/SE fiber composites vs. temperature. FIG. 3b. Storage modulus E' of PP and PP/SE fiber composites vs. temperature at 1 Hz.

PP and PP-DP composites. Neat PP displays two rubbery transitions in the vicinity of 10°C and 90°C. The low temperature one corresponds to the β -transition that is often referred to as the glass transition and is believed to be associated exclusively with the molecular relaxations of the amorphous phase. The high temperature α -transition peak is related to the relaxation of bound amorphous phase surrounding the crystals and only occurs when a crystalline phase is present (Boyd 1985). The E' decreases with the temperature and this depression accelerates in the β -transition while it decelerates in the α -transition. At higher temperature, E' of the composites drops to the level of neat PP.

The composites exhibit a distinct β -transition peak with reduced magnitude. However, the α -transition manifests as an inclined shoulder,

probably due to the damping contribution of the SE fibers which becomes more important at higher temperatures. The location of the β -transition (T_g) is shifted to lower temperatures by the SE fiber loading (Table 3). This effect may be suitably explained by the role of SE fibers that acts as nucleating agent for PP and accelerates the crystallization kinetics. That crystallization speed-up caused an amorphous phase more inhomogeneous, which contained molecular segments with higher mobility and resulted in a lower T_g (Nuñez et al. 2002).

The magnitude of the $tan\delta$ peak decreases as the SE fibers is incorporated (Table 3), primarily because the PP volume fraction is reduced. The increase of the crystallinity around the fiber fragments and therefore less amount of amorphous phase in the PP matrix is another possible reason for this decrease in the magnitude of $tan\delta$. The addition of MAPP results in further depression in $tan\delta$, indicating that the interfacial adhesion has been enhanced as the magnitude of $tan\delta$ is inversely proportional to the interfacial adhesion strength when the volume fraction of the filler is constant (Murayama 1978).

The α -transition peak for the composites manifests as an inclined shoulder from which the peak temperature is not able to be determined. Nevertheless, the reduced magnitude reveals clearly the amount of the bound amorphous phase surrounding the crystals is also lowered in the composites than in the neat PP.

Differential scanning calorimetry (DSC)

Typical DSC curves (normalized to unit mass of PP or PP-MAPP, i.e. 1 mg) of PP, MAPP, PP-MAPP blend, and PP-DP composites are shown in Fig. 4. The apparent melting temperature, heat of fusion, and degree of crystallinity are presented in Table 4. It should be noted these curves and data are all obtained from the first fusion and hence reflect the melting behavior of PP with its structure formed *in situ* by compression molding. Subsequent scan (e.g. second fusion after cooling from melt) in the DSC may generate results that differ more or less from

TABLE 3. $\tan\delta$ of PP and PP composites*.

Formulation	T_g ($^{\circ}\text{C}$)	$\tan\delta$ at T_g
No. 1 PP	10.8 (0.8)	0.0856 (0.0036)
No. 2 PP-DP	7.1 (1.5)	0.0672 (0.0046)
No. 3 PP-MAPP-DP	7.4 (1.6)	0.0652 (0.0026)

* Values in parentheses refer to standard deviations.

those of the first run, because the PP undergoes different crystallization history.

All the samples display a peak associated with the melting of PP or PP-MAPP blend. The apparent melting temperature of neat PP is about 164°C . This temperature is slightly shifted upwards, ca. $1\text{--}2^{\circ}\text{C}$, by incorporation of SE fibers and/or MAPP (Table 4). The heat of fusion and hence the overall crystallinity increase in a similar manner. Both the observations signify that more energy is needed to transform the PP in the composites from a semi-crystalline solid to a molten liquid, reflecting that the interactions among the filler, MAPP and PP have restricted the mobility of PP molecules around the filler to some extent.

Cellulose (Qiu et al. 2003), lignin (Canetti et al. 2004), wood fibers and MAPP (Yin et al. 1999) are all able to act as a nucleating agent for the crystallization of PP and hence increase generally the crystallinity of PP. Table 4 reveals that the SE fibers also play such a role in enhancing the crystalline structure of PP. The heat of fusion (ΔH_m) of neat PP is 94.83 J/g , corresponding to a degree of crystallinity X_c of 45.4% . Inclusion of SE fibers results in an increase in the ΔH_m and raises the X_c to 51.3% , which is further increased to 55.2% by the addition of MAPP.

MAPP has a lower X_c than PP. However, the PP-MAPP blend exhibits a crystallinity greater than either PP or MAPP. Crystallization conditions are probably the main causes responsible for this phenomenon, because the MAPP sample (No. 11) was in powder form and tested as received while the blend sample underwent consolidation in which the MAPP might act as a nucleating agent for PP.

Apart from the overall crystallinity, an examination of the shape of the melting peaks is also helpful to get some insight into the crystalline structure of PP. It is known that several crystal-

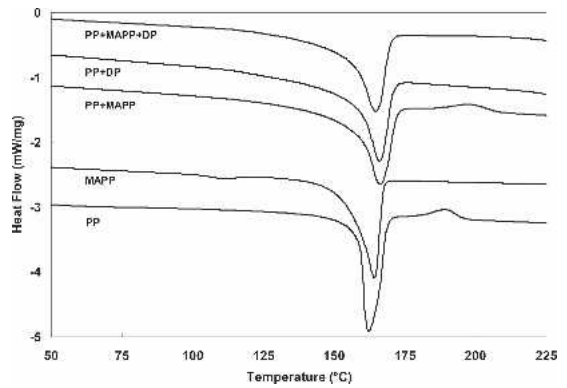


FIG. 4. DSC curves for PP, PP-MAPP blend, and PP composites.

line modifications can coexist within a given PP sample and cause multiple melting behaviors, depending on the crystallization conditions and the presence of certain heterogeneities (Amash and Zugenmaier 2000; Genovese and Shanks 2004). In the presence of lingocellulosic fibers, both α -monoclinic and β -hexagonal crystalline phases can be formed in the matrix PP (Mi et al. 1997). The relative amount of β -form crystal, though always small, increases considerably by mixing with lingocellulosic fibers and in some scenarios, a transcrystalline layer (TCL) may be created around the fibers which was observed to melt before the bulk crystallinity (Harper 2003).

Each melting peak in Fig. 4 may be the superposition of two or more peaks associated with different forms of crystals so that its appearance depends on the relative amount of these crystals. From Fig. 4 and Table 4 (onset and endset temperatures), it is found that the peak of PP is narrower than that of the PP-DP composites (No. 2 and No. 3) and the PP-MAPP blend (No. 10). This may imply that the relative amount of β -form crystal in the composites and the blend is increased by the nucleating effect of DP fibers and MAPP. Because the β -form crystal has a melting temperature $5\text{--}6^{\circ}\text{C}$ lower than the α -form crystal (Harper 2003), the overlapping of the two peaks would generate a single broader peak as shown in Fig. 4. However, the higher peak temperature for the composite samples indicates that the PP structure in the composites is still α -form dominant.

TABLE 4. Melting temperature, heat of fusion, and crystallinity for neat PP, PP-MAPP blend and PP-DP composites*.

Formulation	Heat of fusion (J/g)	Crystallinity index (%)	Peak temperature (°C)	Onset (°C)	Endset (°C)
No. 1 PP	94.83 (6.47)	45.4	163.8 (2.1)	158.4	170.6
No. 2 PP-DP	107.24 (10.86)	51.3	165.5 (0.8)	155.8	171.0
No. 3 PP-MAPP-DP	115.38 (6.37)	55.2	164.6 (0.6)	155.7	170.3
No. 10 PP-MAPP	104.07 (1.48)	49.8	165.6 (0.2)	158.7	171.0
No. 11 MAPP (powder)	86.61 (0.73)	41.4	163.8 (0.3)	155.5	167.4

* Values calculated based on the weight of PP or PP-MAPP; values in parentheses refer to standard deviations.

Morphology of the fractured surfaces of PP-DP composites

Complementary information about the interface can be obtained by examining the fracture modes of PP-DP composites (Fig. 5a to Fig. 5d). For the composite without MAPP, fibers or fiber

fragments are pulled out with surfaces clear of PP material (Fig. 5a), indicating that the interfacial failure is a main mechanism causing the rupture. Although the presence of SE fibers alters the structure of PP as demonstrated by the DMA and DSC, (i.e. increase of crystallinity of the PP around the fibers), the extent of the in-

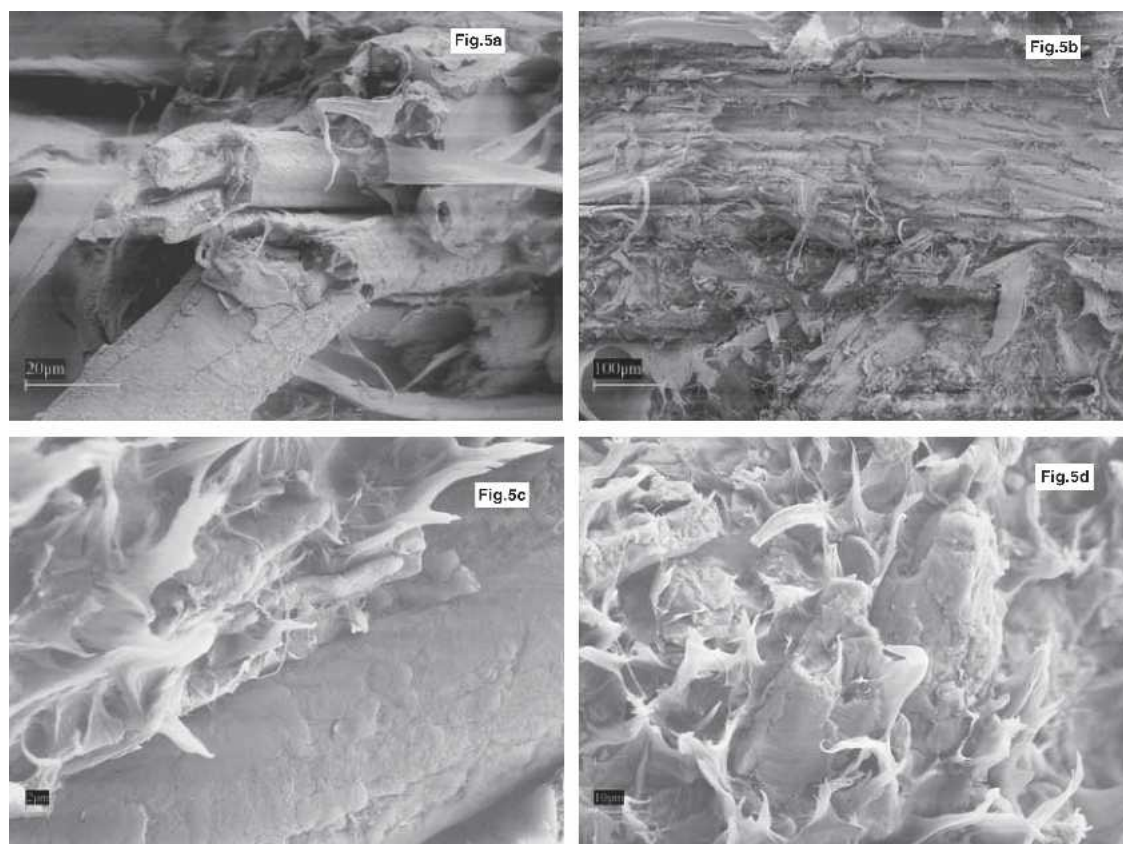


Fig. 5. SEM micrographs of the fractured surface of PP composites. 5a: Without MAPP—fiber pull-out with surface clear of PP; 5b: Without MAPP—fiber splitting in the transverse direction; 5c: With MAPP – rough fractured surface with necking regions in the matrix and a gap between the matrix and the fiber; 5d: With MAPP – Necking regions in the matrix and fiber breakage in the longitudinal direction.

teractions between these two individual components does not seem sufficient to produce a strong interphase capable of bearing stress at larger strain (at break). Fiber splitting may also be involved in the fracture of the composites, but this occurs more likely in the transverse direction when the fiber orientation is perpendicular to the applied stress (Fig. 5b).

The fracture of the PP-DP composite with MAPP is characterized by a rougher surface with many necking regions in the matrix and by fiber breakage in the longitudinal direction (Figs. 5c and 5d). These observations imply the interfacial adhesion can be stronger when MAPP is added such that the matrix cracking and fiber breakage become dominant in causing the fracture. However, gaps between the PP matrix and some SE fibers can still be observed (Figs. 5c), indicating the existence of some weak interphase regions in the compression-molded samples that need to be improved in subsequent studies.

CONCLUSIONS

Beetle-killed loblolly pine trees were transformed to a fibrous mass by steam explosion with a severity factor of 4.8 followed by a sieve step to remove oversize particles (>16 mesh). The sieved SE fibers (<16 mesh) contained 5%–10% water-soluble materials and were mainly composed of fiber fragments. Single fibers could be produced in the SE treatment, but their proportion was very limited. During the SE treatment, the lignin softened and tended to deposit as droplets on both the outer and inner surfaces of cell fragments.

Composites were obtained by first compounding the PP and SE fibers with or without the MAPP as a compatibilizer, and then by compression-molding the mixtures. The MOE of the composites increased greatly even without MAPP, as compared with that of neat PP. The stress at yield σ_y was decreased slightly, but the MOR reduced appreciably by inclusion of 50% SE fibers if no compatibilizer was used. Addition of a small amount (2.5%) of MAPP improved significantly the flexural modulus and strength of the PP/SE fiber composites, espe-

cially the yield strength σ_y , which was eventually superior to that of neat PP. Composites were also prepared using dry-blended PP/SE fiber mixtures; their mechanical properties, however, appeared inferior to those of the composites produced from compounded mixtures.

In addition to the benefit of lower energy consumption compared to mechanical grinding, the SE treatment could reduce the amount of decay in beetle-killed pine to such an extent that the remaining decay in the SE fibers is not significantly detrimental to the flexural properties of PP composites. These advantages suggest that SE processing can be promoted as a technique with great potential of commercial application to utilize beetle-killed, partially decayed wood in wood plastic composites.

DMA and DSC measurements revealed that the SE fibers increased the crystallinity of PP, probably by forming more crystalline fractions around the fibers or fiber fragments. The addition of MAPP resulted in a reduction in the damping and an increase in the heat of fusion of the PP in the composites, suggesting that a stronger interface between the matrix and the SE fibers was developed by this additive. SEM observations also demonstrated the better interfacial adhesion produced by the MAPP, which improved the stress transfer efficiency from the matrix to the SE fibers and prevented fiber pull-out from occurring.

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