Evaluation of Micron-Sized Wood and Bark Particles as Filler in Thermoplastic Composites

David P. Harper and Thomas L. Eberhardt

Abstract

Micron-sized particles, prepared from loblolly pine (*Pinus taeda* L.) wood and bark, were evaluated for use in wood-plastic composites (WPCs). Particles were also prepared from hard (periderm) and soft (obliterated phloem) components in the bark and compared to whole wood (without bark) filler commonly used by the WPC industry. All bark fillers had different thermal degradation profiles and higher ash contents compared to whole wood and micron-sized wood particle samples. The bark particles had an increased nucleating ability on polypropylene over whole wood filler. However, a drop in modulus and decrease in interaction with matrix were observed by dynamic mechanical analysis. These characteristics of the bark particles impart significant constraints on their processing and utilization in WPCs.

Introduction

A new class of structural materials has emerged in the past decade based on a composite of thermoplastic and wood (i.e., wood-plastic composite, WPC). The thermoplastic component in the WPC provides improved resistance to moisture and biological attack over traditional wood composites by encapsulating the wood. However, the thermoplastic matrix does not chemically interact with the wood, leading to poor stress transfer and pathways for moisture uptake (Johnson and Nearn 1972). Many possible mechanisms exist for improved performance, ranging from enhanced wood distribution to covalent bonding of the wood fibers and matrix. A recent investigation showed that wood dramatically impacts the crystal morphology of an isotactic polypropylene (iPP) matrix (Harper and Wolcott 2004). However, this effect is physical and closely related to the morphology/roughness of the wood. What is unclear in the literature is how the chemical composition differences among tree parts, other than from the wood in the main stem (e.g., bark, leaves), would impact the interfacial and composite properties.

Micron-sized wood and bark particles were investigated as a means to improve the distribution of the filler in the composite. The incorporation of bark in WPCs generally results in lower strength relative to that for composite structures made with wood alone (Muszynski and McNatt 1984, Blanchet et al. 2000). However, in a study on bark-based fillers used in the preparation of plywood adhesive mixes, a bark-based filler exhibited superior performance over standard filler, furfural residue (Eberhardt and Reed 2006). To accomplish this, the outer bark of southern yellow pine (SYP) was partitioned into its hard (periderm, PE) and soft (obliterated phloem, OP) components; in SYP bark, layers of OP tissue are partitioned by layers of PE tissue (**Fig. 1**). Grinding and sieving operations afforded OP and PE fillers with inferior and superior performances, respectively. It remains to be determined if the improved performance for PE filler would carry over to other applications such as the manufacture of WPCs. In addition to improved biomass utilization through developing markets for bark, it is important to address the impact of bark contamination of wood supplies used for WPCs; the utilization of small diameter trees, with their higher proportion of bark, is becoming increasingly important. Thus, the physical and chemical properties of bark that may be problematic for the WPC industry are of particular interest.

Harper:
Assistant Professor, University of Tennessee, Tennessee Forest Products Center, Knoxville, Tennessee, USA
Eberhardt:
Research Scientist, USDA Forest Service, Southern Research Station, Pineville, Louisiana, USA

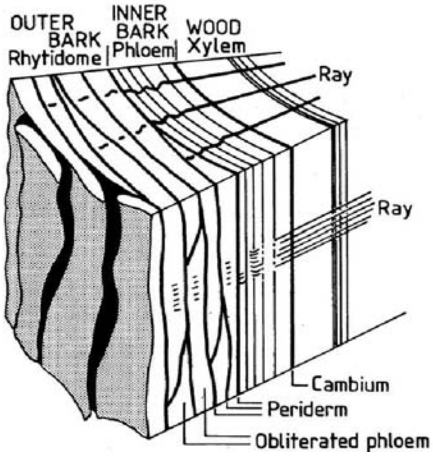

Figure 1. ~ *Anatomy of pine bark [from Fengel and Wegener (1983) with permission].*

Materials and Methods

Preparation and Characterization of Fillers

Southern yellow pine bark from a local plywood plant was ground as described elsewhere (Eberhardt and Reed 2005, 2006) to afford OP and PE fillers, each being comprised of micron-sized particles. An ultra-centrifugal grinding mill (Retsch, Inc., Model ZM 200) equipped with a 12-tooth rotor and 0.12-mm mesh ring sieve was used to reduce the size of the PE particles obtained during prior grinding and classification operations. Whole bark (WB) and SYP wood (WO) fillers were prepared by grinding the coarse meals of each, without partitioning, directly in the ultra-centrifugal grinding mill. All SYP fillers were classified through a 200-mesh (< 75 µm) sieve before compounding into WPCs. A maple whole wood (WW) filler (60 mesh, 250 µm), prepared as commonly done by the WPC industry, was used as a control.

Thermogravimetric analysis (TGA) was performed on each filler to determine the thermal stability and temperature range needed for extrusion. Thermogravimetric analysis was performed from ambient temperature to 600ºC at a rate of 20ºC/min in a dry air environment. Percent mass loss was monitored to ensure the degradation temperature was above the melting point of the polymer used in the composite.

WPC Extrusion

Each dried filler was blended with equal parts of iPP with a melt flow index (MFI) of 35 g/10 min. A Leistritz 27 mm co-rotating extruder was initially used to compound samples in 100-g batches; however, this resulted in degraded specimens largely because of long barrel residence times caused by the large 40:1 length-to-diameter ratio. We then switched to a smaller extruder (ThermoScientific Haake Mini Lab) that allowed samples to be compounded in 10-g batches. This extruder, with two counter-rotating screws, was held at a temperature of 180ºC. These products were also extruded with iPP (MFI = 35) in a 1:1 mixture. The mixture was compounded at a screw speed of 20 rpm for 10 minutes. The die on the extruder had dimensions of approximately 4 × 1 mm.

WPC Testing

Bending analysis was performed in triplicate using a Perkin-Elmer Pyris Diamond DMA (Waltham, MA) set for synthetic oscillation at 1, 2, 4, 10, and 20 Hz. Tests were conducted on 50-mm samples throughout a temperature range of –50 to 100ºC at a rate of 3ºC/min. A dual cantilever test configuration was used on samples with 4 × 1 × 50 mm dimensions and 20 mm span.

Differential scanning calorimetry was performed on each sample in triplicate to determine the impact of the filler on the crystallization of the polymer. Specimens were heated to 200ºC for 10 min to erase previous crystallization history and then quenched to an isothermal crystallization temperature of 130ºC and held for 30 min. The specimen was then cooled to 0ºC and heated through the polymer melt to 200ºC.

Moisture sorption tests were conducted on each set of composites. A total of 10 specimens per sample with dimensions of 4 × 1 × 50 mm were submerged in a 25ºC circulating water bath and periodically weighed for 49 days.

Results and Discussion

Thermal Stability of Specimens

Micron-sized SYP bark (WB, OP, PE) and wood (WO) particles were tested for their thermal stability in an air environment along with a maple whole wood (WW) filler that is commonly used in our laboratory as a control. The thermal stabilities of the bark fillers were different whereas the thermal stabilities of the wood fillers were similar (**Fig. 2**). The wood fillers exhibited lower thermal stabilities, which were likely due to the higher polysaccharide and oxygen contents compared to bark fillers. Further, the wood fillers exhibited much lower residual ash contents. The OP and WB fillers displayed the highest moisture contents after conditioning in an ambient environment that was the same for all samples. When the OP tissue was not present, as in the PE filler, the moisture content was reduced. Similarly, the wood fillers contained less moisture. After an initial greater mass loss than the wood fillers, the bark fillers degraded at a much slower rate (**Fig. 3**). The ash content of the OP filler was the highest of all fillers (**Fig. 2**). This correlates with the hypothesis that higher mineral content may catalyze decomposition and more mass loss at lower temperatures.

Evaluation of Extruded Composites

The dynamic mechanical response of composites can vary depending upon morphological and chemical differences present in the composite. The storage modulus is highly dependent on the filler, density, crystallinity of the matrix, and the presence of any voids that may be in the composite. The underlying assumption in our analysis is

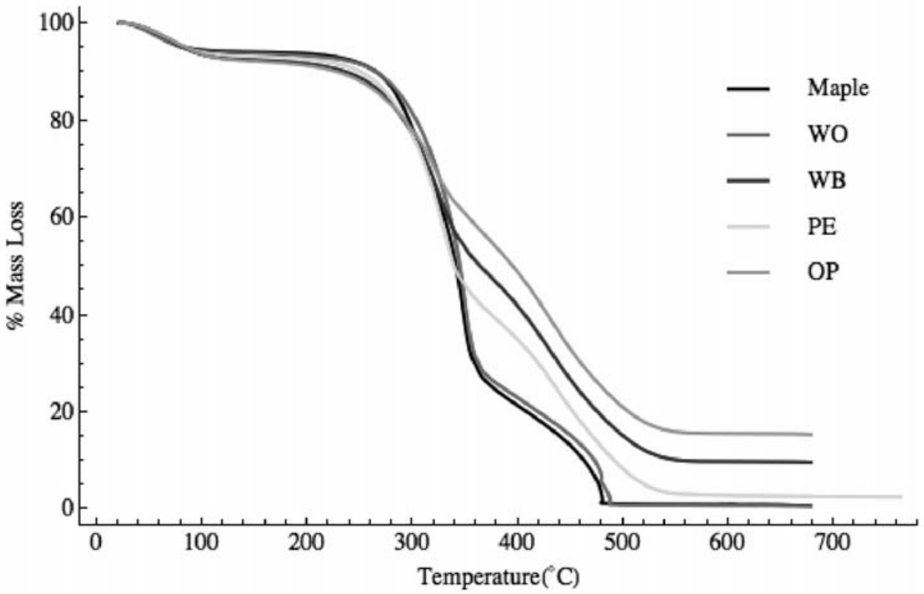

Figure 2. ~ *Mass loss of fractionated woody samples in a dry air environment.*

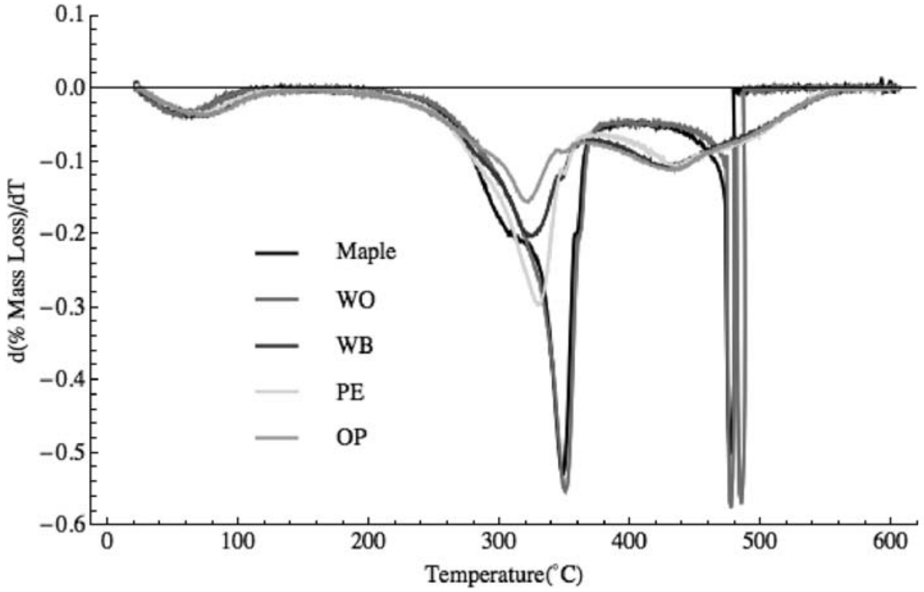

Figure 3. ~ *Derivative of mass loss data for fractionated woody samples in a dry air environment.*

that each of the composites contains the same weight percent of filler. The density of the extruded composite gives us some indication that these composites are comparable.

The storage modulus for the maple WW composites is much higher across the whole evaluated temperature range than for the other composites (**Fig. 4**). The maple WW filler is likely to have much higher cellulose content than that of the bark fillers and results in a higher overall modulus. The higher tan δ peak at the T_g for PP in the PE composite reveals a decrease in interaction between the filler and matrix (Harper et al. 2004) (**Fig. 5**). At this point there is no real indication as to why there is disparity in these values. Nevertheless, the high T_g observed in the WB and PE composites may be an indication that there is some interaction of the bark extractives with the matrix. The T_g is dependent only on the amorphous fraction of the PP matrix. Lubricants and adhesion promoters can have a profound influence on the location of PP's Tg (Harper and Wolcott 2004).

Water sorption values can also be an indicator of interaction between matrix and filler (Mishra and Verma 2006) (**Fig 6**). This result would be in agreement with the DMA results where the lower mechanical dampening corresponds to the lowest moisture sorption for maple WW composite samples. Also, an increase in moisture sorption can be a good indicator of an increase in surface area of the milled particle.

Calorimetry of the composites offers some insight into probable explanations for the differences in the DMA response. Isothermal crystallization of the PP matrix takes far less time with the PE filler than the WB or maple WW fillers (**Fig. 7**). The PP crystallite growth rate is most likely unchanged by the filler as has been previously observed (Harper and Wolcott 2004). Thus, differences are caused by variation in the ability of the

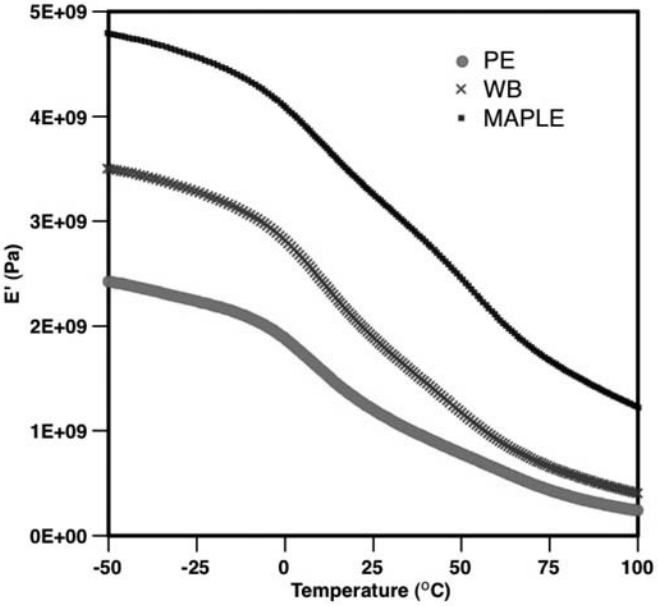

Figure 4. ~ *Storage modulus of extruded composites.*

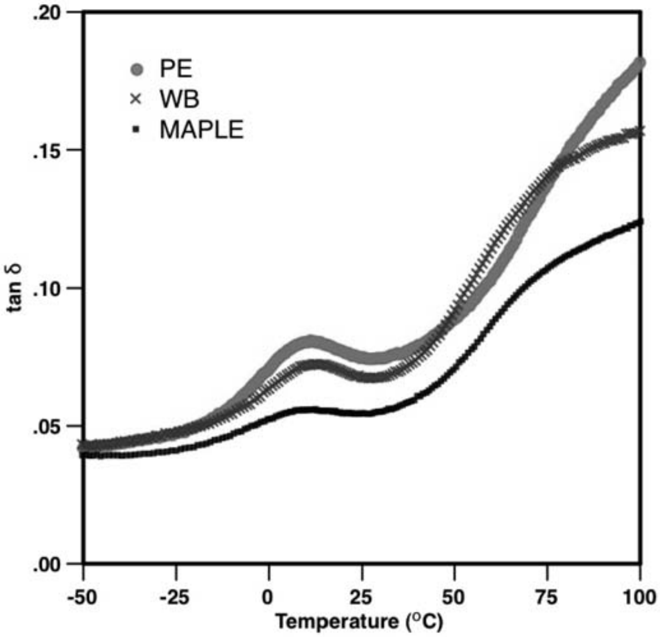

Figure 5. ~ *Loss tangent of extruded composites.*

filler to nucleate crystal growth. The two most important parameters impacting the amount of nucleation are the differences in surface energy and surface area. Given the fillers used, both factors are likely causes for differences. An increase in polymer nucleation is observed for filler that can more readily disperse in the matrix and is less likely to agglomerate. There is, therefore, more surface area for the PP to nucleate on in the PE samples. A more detailed analysis of each of the tissue's surface energy needs to be conducted to determine this with certainty. There is likely a large amount of variability in the amount of filler actually captured in the DSC pan, which

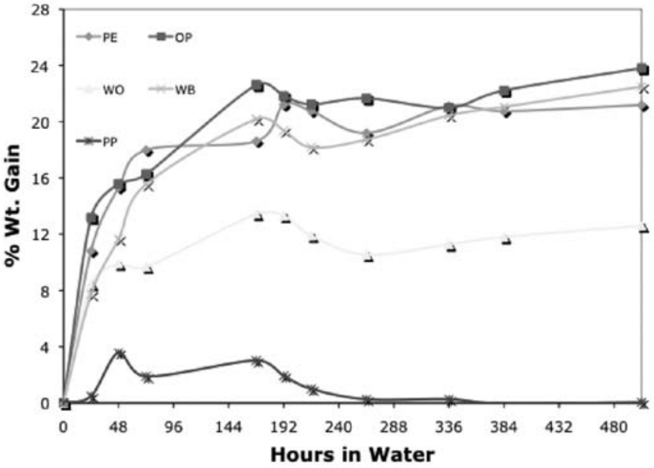

Figure 6. ~ *Water sorption for extruded composites.*

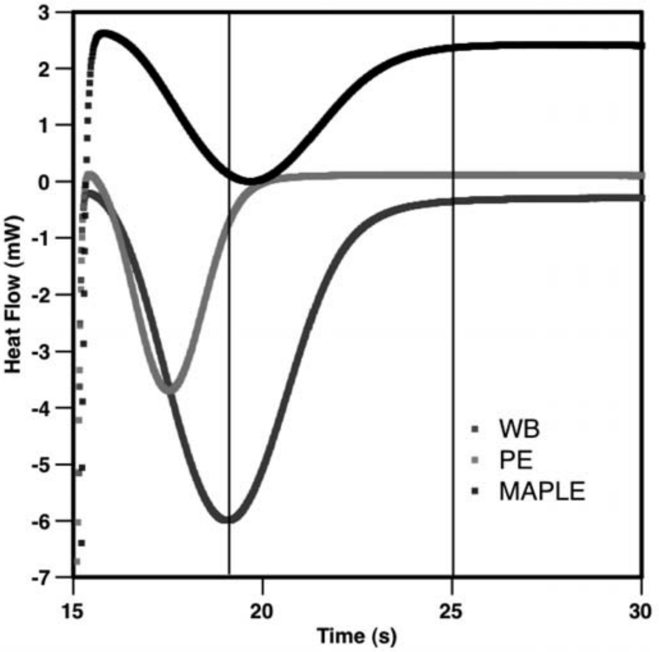

Figure 7. ~ *DSC isothermal crystallization curves for composites at 130°C.*

can contribute to uncertainty in the results. However, the melt data of the composites is consistent with the crystallization data (**Fig. 8**). The maple WW composite takes longer to crystallize and displays a higher degree of order (perfection) in its structure by having a higher melt temperature. The higher amount of hydroxyl groups in the wood fillers contributes to hydrogen bonding and clustering of wood particles. The WB and PE follow respectively in melt temperature.

Conclusions and Recommendations

The high extractive and mineral content of the fractionated bark tissues made extrusion processing difficult. The extractives may be interacting with the PP matrix and causing change in the rheology, but this needs further

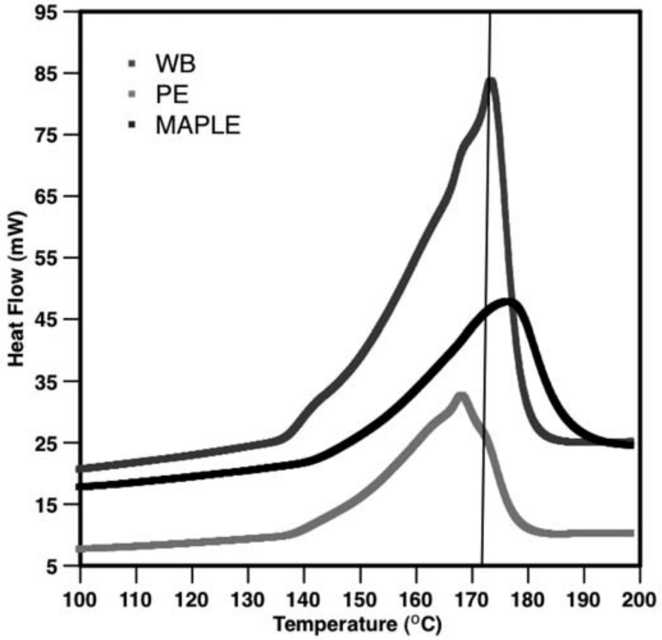

Figure 8. ~ *DSC melt curves for composites isothermally crystallized at 130ºC.*

confirmation. This initial study does indicate that there is a difference in the surface chemistry and morphology of the particles that result in real differences in the mechanical, thermal, and moisture performance when compared to whole wood. At present, there is an indication that these materials disperse better in a polymer matrix than wood flour, but this does not result in any mechanical benefit. There is an added benefit of being a nucleation agent, and some UV stability may be gained with the bark addition. However, this warrants further investigation.

Acknowledgments

SYP wood and bark fillers were prepared by Karen Reed, USDA Forest Service, Southern Research Station, Pineville, LA. Moisture and thermal analysis was performed by Tim Stortz at The University of Tennessee.

Literature Cited

Blanchet, P., A. Cloutier, and B. Riedl. 2000. Particleboard made from hammer milled black spruce bark residues. Wood Sci. Technol. 34(1):11–19.

Eberhardt, T.L., and K.G. Reed. 2005. Grinding and classification of pine bark for use as a plywood adhesive filler. *In* Proc. 13th International Symposium on Wood, Fibre, and Pulping Chemistry, Rotorua, New Zealand. pp 109–113.

Eberhardt, T.L., and K.G. Reed. 2006. Strategies for improving the performance of plywood adhesive mix fillers from southern yellow pine bark. Forest Prod. J. 56(10):64–68.

Fengel, D., and D. Wegener. 1983. Wood: Chemistry, Ultrastructure, Reactions. Walter de Gruyter, Berlin. 613 pp.

Harper, D.P., and M.P. Wolcott. 2004. Interactions between coupling agents and lubricants in wood-polypropylene composites. J. Compos. A. 35:385–394.

Harper, D.P., M.P. Laborie, and M.P. Wolcott. 2004. Molecular relaxations in wood-polypropylene composites. *In* 32nd Annual Conference on Thermal Analysis and Applications, Williamsburg, VA.

Johnson, J.A., and W.T. Nearn. 1972. Reinforcement of polymeric systems with douglas-fir bark fibers. *In* B.A. Jayne (ed.) Theory and Design of Wood and Fiber Composite Materials. Syracuse Univ. Press.

Mishra, S., and J. Verma. 2006. Effect of compatibilizers on water absorption kinetics of polypropylene/wood flour foamed composites. J. Appl. Polym. Sci. 101(4):2530–2537.

Muszynski, Z., and J.D. McNatt. 1984. Investigations on the use of spruce bark in the manufacture of particleboard in Poland. Forest Prod. J. 34(1):28–35.