

Highly Compatible Wood Thermoplastic Composites from Lignocellulosic Material Modified in Ionic Liquids: Preparation and Thermal Properties

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ABSTRACT: A study of converting chemically modified wood into thermoplastic materials was undertaken to develop a new technology platform for the effective utilization of wood-based lignocellulosic materials. Highly substituted benzoylated spruce thermomechanical pulp (TMP) and lauroylated spruce TMP were used as components for thermoplastic composites of poly(styrene) and poly(propylene). Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA) were used to characterize the interfacial morphology and thermal properties of the resultant composite filaments. The coupling of the interfacial morphology effort and that of torque analysis applied during processing indicated that the thorough modification of wood fibers by benzoylation and/or lauroylation reactions can

improve the compatibility between the wood-based lignocellulosic materials and poly(styrene) and poly(propylene). Thermal analysis showed that, with the addition of wood derivatives into poly(styrene) and poly(propylene) matrices, a slight decrease in their T_g s was observed. Furthermore, all of the prepared composites showed improved thermal stability, as revealed by TGA. The resultant thermoplastic wood composites exhibited good melting properties and were readily extruded into filaments or sheets. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2468–2476, 2009

Key words: lignocellulose; lignin; cellulose; ionic liquids; thermal analysis; differential scanning calorimetry; thermogravimetric analysis; dynamic mechanical thermal analysis; melt extrusion; polymer composites; materials

INTRODUCTION

Increasing oil prices and widespread accounts of global warming dictate the potential for environmentally sustainable, and biodegradable, commodity chemicals, and materials. Such materials should be, almost invariably, biologically-derived with the annually renewable agricultural and biomass feed stocks occupying a prominent position.^{1–3} Wood is among the most abundant lignocellulosic resources on the planet and has been considered to be a pivotal component for the production of bio-composites, otherwise referred to as “wood-thermoplastic composites” or simply “wood plastic composites” (WPCs).^{4–6} Lignocellulosic materials, including wood fibers, wood flour, etc., have been used as fillers for thermoplastics.^{7–10} Unfortunately, the large polarity difference between lignocellulosic materials and nonpolar thermoplastics, e.g., poly(ethylene), poly

(propylene), poly(styrene), etc., have prevented lignocellulosic materials from performing effectively as reinforcing agents, or even fillers within traditional thermoplastics. In most cases, techniques for increasing phase compatibility, such as coupling agents, have been used to augment interfacial bonding of the different phases, aimed at improving the processability and performance of WPCs.^{4–6} Among these technologies, due to recent advances in the potential for wood processing in ionic liquids such as 3-allyl-1-methylimidazolium chloride ([amim]Cl), chemical modification of the lignocellulosic material should be considered as an effective approach for investigating and tailoring the properties of bio-plastics, by physically blending modified natural with synthetic polymers.^{11,12}

Work in our laboratory has demonstrated that a variety of highly substituted (alkylated, benzoylated and carbanilated) wood-based lignocellulosic materials can be produced upon dissolution of wood in ionic liquids and reaction under homogeneous conditions.^{13,14} This effort showed that all wood derivatives which were synthesized showed thermal properties and characteristic of thermoplastic behavior. As such, it was anticipated that the complete

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chemical functionalization of all hydroxyl groups present in wood, to hydrophobic functionalities, would increase overall the interfacial miscibility with synthetic polymers.^{13,14} Consequently, in the present article we examine the validity of our earlier assumption by producing WPCs of poly(styrene) and poly(propylene) with completely benzoylated and lauroylated spruce wood.

MATERIALS AND METHODS

Materials, instruments and conditions

Poly(styrene), of typical number average molecular weight, $M_n = 140,000$ g/mol and isotactic poly(propylene), of typical number average molecular weight, $M_n = 67,000$ g/mol, were purchased from Aldrich chemical and used directly. *N*-butyl-*N*-methylimidazolium chloride ([bmim]Cl) was synthesized according to a standard literature procedure.^{13,14} Southern Pine Thermomechanical Pulp (TMP) was supplied by a southern US company. The wood sample was extracted in a Soxhlet extractor with acetone for 48 h and then kept in a vacuum oven for at least 48 h at 40°C prior to use. Spruce TMP solutions in [bmim]Cl were prepared according to a previous literature procedure.^{13,14} Differential scanning calorimetry (DSC) was carried out on 5–10 mg samples using a TA Instrument DSC Q100. The thermal scans were carried out at a heating rate of 20°C/min from 20°C up to 200°C under a nitrogen atmosphere. The data from the first scan was discarded since the thermograms often included unwated thermal history and volatile traces of water. After cooling, the data for a second run was recorded. Thermogravimetric analysis (TGA) measurements were carried out with a TA Instruments TGA Q 500 in the temperature range of 25–600°C, with the temperature being raised at a rate of 10°C/min. Dynamic mechanical thermal analysis were carried out with a TA instruments DMA Q 800 in tension mode. Temperature range was from 25 to 200°C at heating rate 3°C/min. The oscillation frequency was 1 Hz and the strain amplitude was 0.250%. Scanning Electron Microscopy, (SEM) was used to visualize the microstructure of the composites and evaluate their surface morphology. Sample filaments were fractured in liquid nitrogen and then were coated with gold for 15 min by using a vacuum sputter coater prior to observation. The SEM effort was carried out with a Hitachi S-3200 scanning electron microscope acceleration voltage of 142 eV.

Preparation of benzoylated spruce and lauroylated spruce^{13,14}

Preparation of benzoylated spruce

Pyridine (0.55 mL, 7.55 mmol) was added to a wood solution (6 g, containing, 4% w/w Spruce in

[bmim]Cl) followed by an incremental (over 20 mins) addition of benzoyl chloride (0.88 mL, 7.55 mmol, 2 equiv per hydroxyl group in wood^{13,14}). This solution was initially stirred at room temperature for 10 min and then kept at 70°C for 2 h. The product was isolated by triturating from the addition of the cooled solution into methanol (100 mL), followed by water (100 mL) under rapid agitation. The solid product, obtained after filtration, washing with methanol:water (1 : 1 mixture) and vacuum drying at 40°C for 18 h, was of a fluffy powdery texture (0.58 g), weight percentage gain (WPG) = 143% (theoretical WPG 164%).

Preparation of lauroylated spruce

Pyridine (0.55 mL, 7.55 mmol) was added to a wood solution (6 g, containing 4% w/w spruce in [bmim]Cl) followed by the incremental addition of lauroyl chloride (1.74 mL, 7.55 mmol, based on 2 equiv per hydroxyl group in wood). This solution was initially stirred at room temperature for 10 min and was then kept at 70°C for 2 h. The product precipitated from the solution during the reaction, presumably because of the increasing molecular weight and/or increasing hydrophobicity of the modified biopolymers. Isolation of the derivative was carried out by triturating of the cooled solution from methanol (200 mL) under rapid agitation. The solid product was obtained after filtration and washing with methanol. The product was finally vacuum dried at 40°C for 18 h being of a fluffy powdery texture (0.79 g), WPG = 229% (theoretical WPG = 283%, calculated on the basis of 15.57 mmol/g hydroxyl groups in spruce TMP).

Preparation of poly(styrene) and poly(propylene) composites with benzoylated and lauroylated spruce wood respectively

A MiniLab, counter-rotating twin-screw extruder (ThermoHaake, Rheomex CTW5) was operated at a rotation speed of 120–150 rpm. The extrusion temperature was set at 221°C for all samples. The total mass of both components introduced in the apparatus at a given experiment was kept constant at 6 g. Both components were initially manually mixed externally to the extruder and then introduced in the hopper of the extruder. After a mixing period of several minutes and once the torque curves were recorded and stabilized, the orifice of the extruder was opened and a filament was pulled and collected around a continuously rotating spool.

RESULTS AND DISCUSSION

Torque curve analyses of the extrusion processes

The analysis of the development of the torque curves, as obtained for the melted wood derivatives

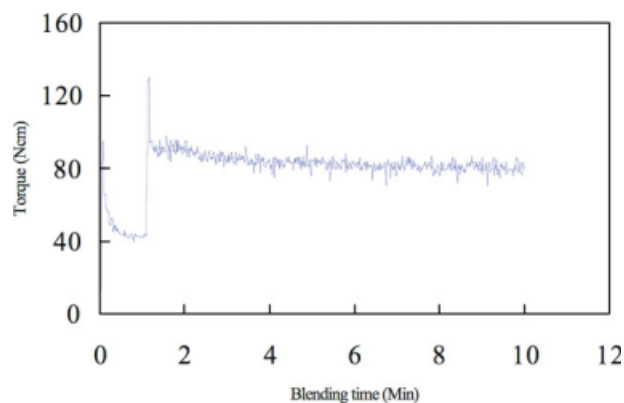


Figure 1 A typical torque versus mixing time curve for the blending of 10% w/w benzoylated spruce TMP with poly(styrene) (221°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with the two synthetic polymers, is an excellent means for monitoring the interfacial adhesion and compatibility of the two components. This information is also extremely useful in verifying and probing the effects of the chemical modification of the wood on its melt flow and melt mixing characteristics, with the synthetic polymers examined.¹⁵ A typical torque versus mixing time curve is shown in Figures 1 and 2. In all experiments, the synthetic polymer and the wood derivatives were initially mixed outside the extruder and then they were quickly added to the preheated extruder. It is apparent that the data of Figure 1 obtained for the benzoylated wood-poly(styrene) pair is significantly smoother than its control counterpart of Figure 2 obtained for the nonfunctionalized spruce TMP-poly(styrene) fibers pair.

As anticipated, Figure 1 shows that the poly(styrene) melted quickly ($T_g \sim 100^\circ\text{C}$) providing a rather smooth torque response (Fig. 1) with the torque value stabilizing at around 40 Ncm within ~ 1 min of mixing. The melting of the benzoylated TMP then

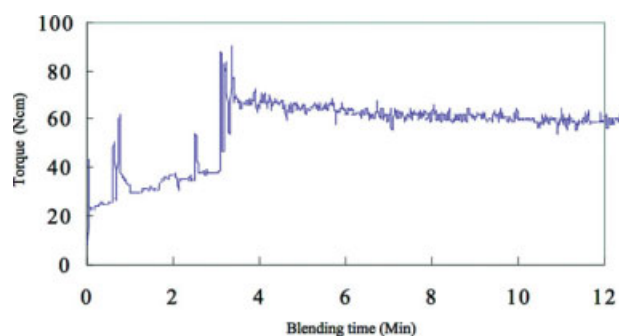


Figure 2 A typical torque versus mixing time curve for the blending of 10% w/w spruce TMP with poly(styrene). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

followed ($T_g \sim 136^\circ\text{C}$, Fig. 7) giving rise to a sharp increase in the torque, rapidly stabilizing at about 80 Ncm.

The torque curve of the nonfunctionalized TMP-poly(styrene) fibers pair was significantly different (Fig. 2). The melting of poly(styrene) provided a significantly more noisy torque curve, (without the clear plateau obtained in Fig. 1 at 40 Ncm) since the TMP fibers created a rather heterogeneous local environment. After about 3.5 min of mixing, the torque increased most likely due to the fact that the TMP fibers became coated with the melted poly(styrene). The torque value started to stabilize after about 4 min, as opposed to 1.6 min in the case of benzoylated spruce (Fig. 1).

A comparison of the final stabilized torque values for the chemically modified and unmodified pairs is also indicative of melt stability and compatibility between the polymers. The stabilized torque value for the benzoylated wood-poly(styrene) pair was about 80 Ncm as opposed to a value of about 60 Ncm, obtained for the TMP/poly(styrene) pair. This is because polymer melts between two miscible polymers are anticipated to give rise to higher torque values, in the mini extruder, as opposed to polymer melts that contain particles or fibers that create voids within the melt structure.

Overall, the melted benzoylated spruce was found to provide a melt environment that resulted in higher torque values when compared to pure poly(styrene) (Fig. 1). As such one anticipates that increasing the loading of benzoylated spruce wood within a poly(styrene) melt will increase the resulting torque values. The data in Figure 3 shows a nearly linear response of the torque versus the weight fraction of benzoylated spruce in the melt, with torque values increasing from 41 Ncm at 0% loading to 93 Ncm at 20% w/w loading, after 8 min mixing time in each case.

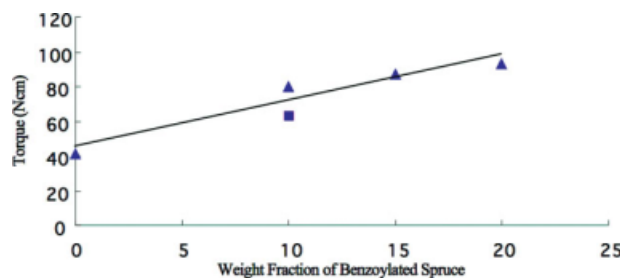


Figure 3 Effect of weight fraction of benzoylated spruce TMP on the torque observed after 8 min melt mixing; ▲ benzoylated spruce TMP-poly(styrene) composites; ■ spruce TMP-poly(styrene) composite (values recorded after 8 min of melt mixing). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

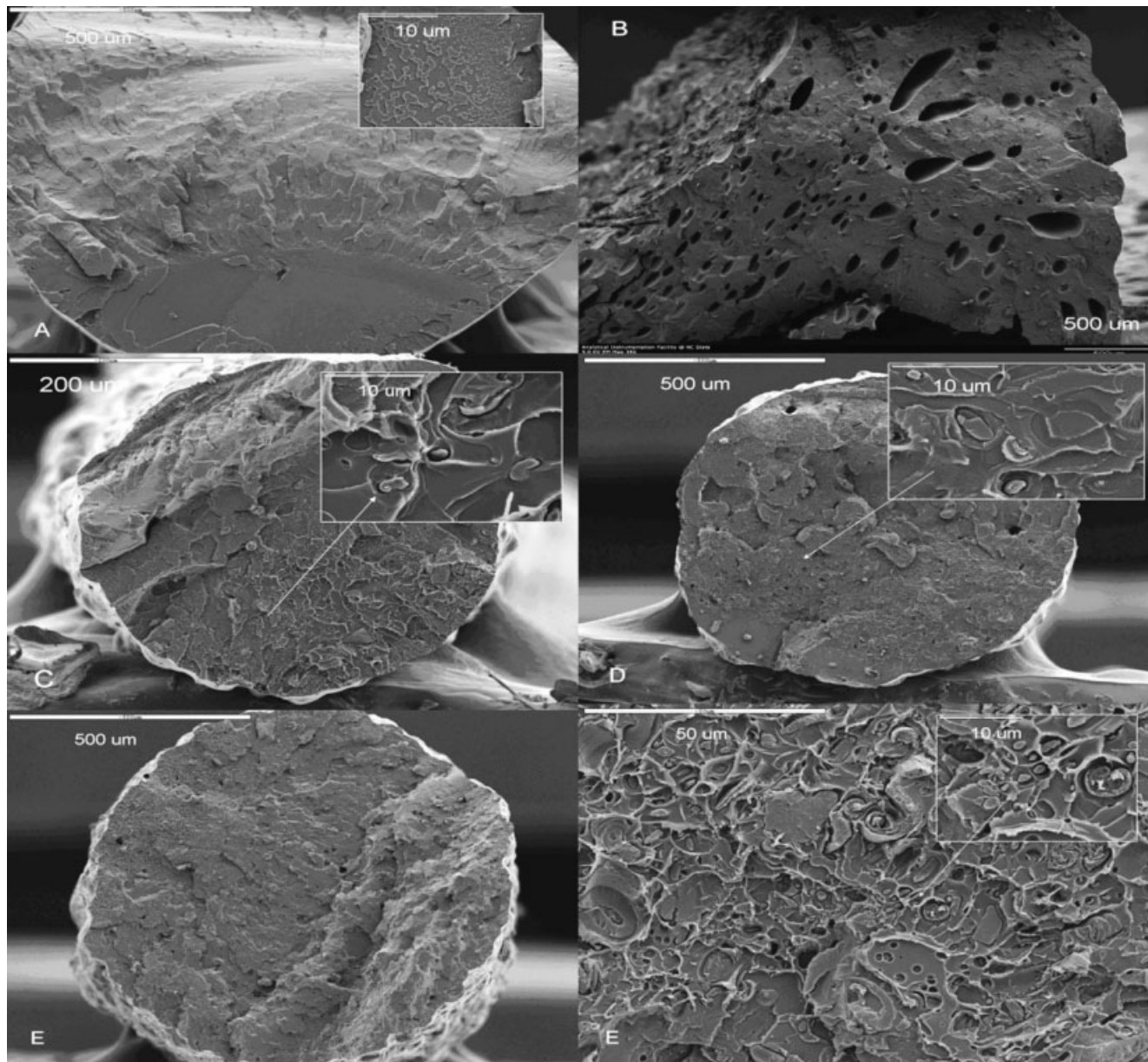


Figure 4 SEM pictures of fracture surfaces of bio-plastic filaments: A: Poly(styrene); B: 10% w/w spruce TMP-poly(styrene) composite; C: 10% w/w benzoylated spruce TMP-poly(styrene) composite; D: 15% w/w benzoylated spruce TMP-poly(styrene) composite; E: 20% w/w benzoylated spruce TMP-poly(styrene) composite.

Morphology study of the fractured surfaces of resultant composite filaments

Examination of the fractured surfaces of the composites by SEM gave a direct indication about how modifications affect the morphology of the composite and interaction between the synthetic polymeric matrix and wood derivatives. A series of comparative SEM pictures of the cross section fractured surfaces of benzoylated wood and poly(styrene) composites are given in Figure 4. We find that pure poly(styrene) shows a very homogenous morphology fractured surface [Fig. 4(A)]. With the addition

of unmodified 10% spruce TMP, the fibers homogeneity is reduced, and a relatively strong fiber pullout is observed. Both findings indicate that there is a poor adhesion between the two phases [Fig. 4(B)], which is possible due to the poor dispersion of hydrophilic spruce TMP in nonpolar poly(styrene). Another possible reason is the absorbed water by spruce TMP was evaporated during the blending process leaving cavities in the composites. From the magnification of Figure 4(C–E), representing the benzoylated spruce TMP/poly(styrene) blends, we can conclude that, although there are very small residual fiber-like regions observable in the composite

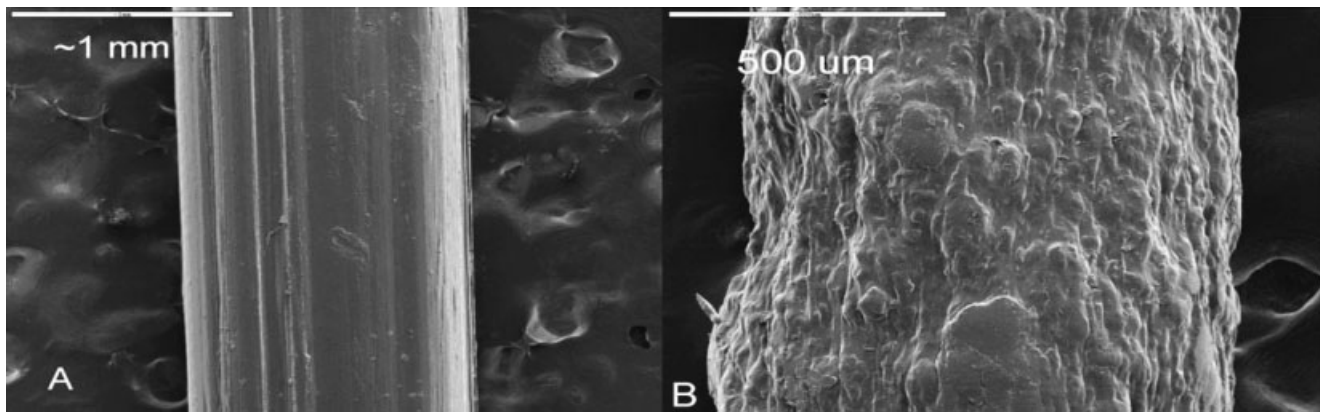


Figure 5 Surface morphology of A: poly(styrene); B: 20% w/w benzoylated spruce TMP-poly(styrene) composite.

fractures, the increased interface miscibility was observed by dispersion of these fibrous structures evenly through the fracture surface. Logic suggests that this is most likely due to the reduced hydrophobicity and more specifically increased Van der Waals interaction between the aromatic functionalities both in benzoylated spruce and poly(styrene).¹⁶

We also can conjecture that the fiber-like structure observable in the fractures is due to the larger sized wood fibers in the spruce TMP, as previous studies from our laboratories¹⁷ have indicated that, although TMP will effectively dissolve in certain ionic liquids, high polydispersity would suggest that some fragments may not dissolve completely during our

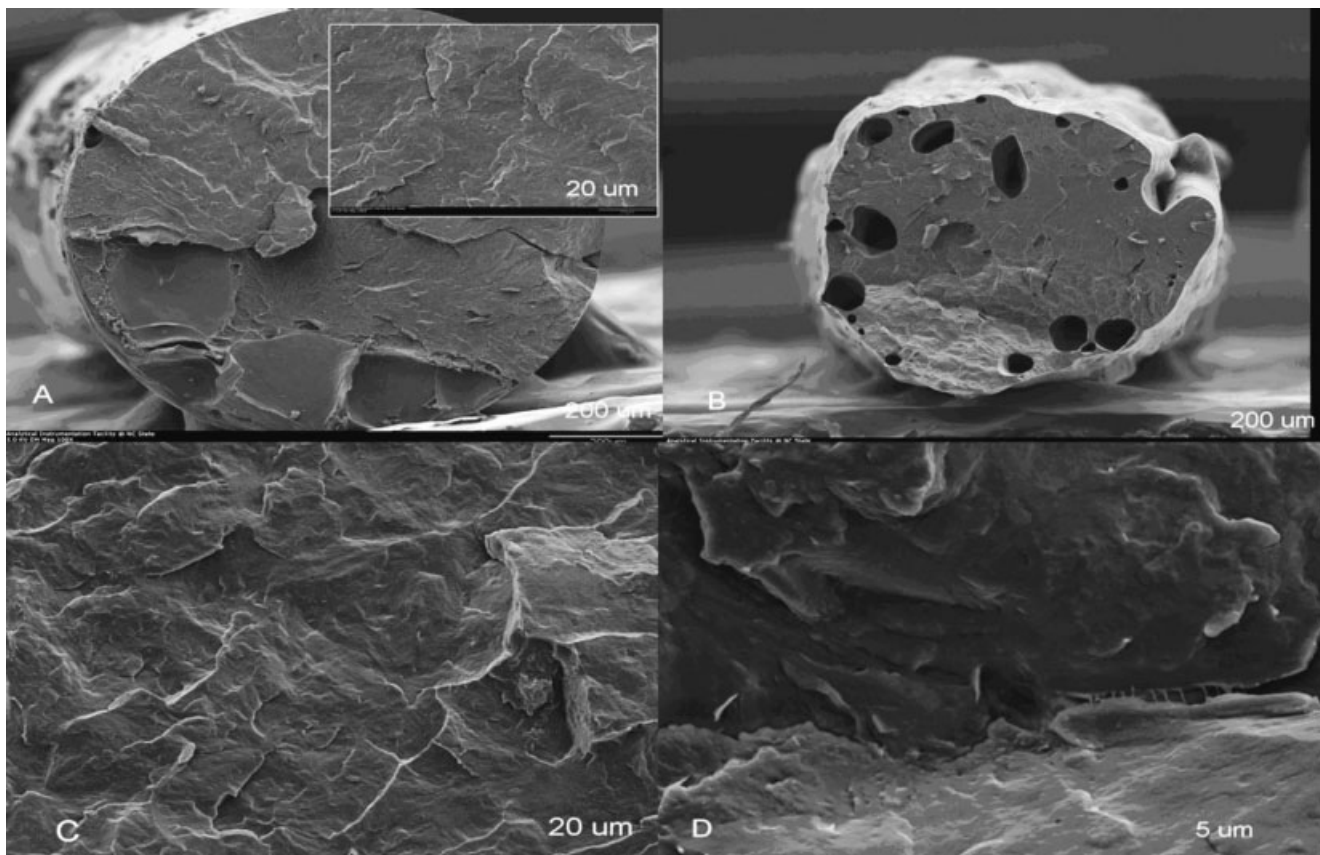


Figure 6 SEM pictures of cross-sectional fractured surfaces of bio-plastic filaments: A: Poly(propylene); B: 10% w/w spruce TMP-poly(propylene) composite; C: 5% w/w lauroylated spruce TMP-poly(propylene) composite; D: 15% w/w lauroylated spruce TMP-poly(propylene) composite.

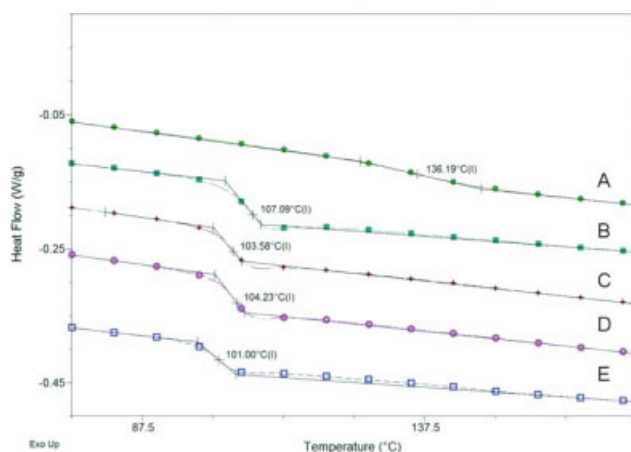


Figure 7 DSC analysis of A: benzoylated spruce TMP; B: Poly(styrene); C: 10% w/w fraction of benzoylated spruce TMP-poly(styrene) composite; D: 15% w/w fraction of benzoylated spruce TMP-poly(styrene) composite; E: 20% w/w fraction of benzoylated spruce TMP-poly(styrene) composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

modification process, which results in the observed heterogeneous structure in the composites. It is unclear as yet whether this will provide more or less desirable physical properties for particular material uses, in comparison to a completely homogeneous sample and this is subject to further investigation, in the anticipated light of continually improving procedures for dissolution of the technically useful TMP substrate.

This heterogeneous structure is also evident from SEM pictures of filament's surface (Fig. 5). We can find that with incorporation of benzoylated spruce, a smooth surface of poly(styrene) was converted into a rough one. The symmetrical roughness of the filament suggests that the benzoylated wood in the poly(styrene) matrix is well dispersed.

Similar phenomenon has been found in the composites of lauroylated spruce TMP and poly(propylene) (Fig. 6). With the addition of spruce TMP to the poly(propylene), SEM images of cross-sectional surface fractures show that a homogenous morphology of poly(propylene) was converted to a foamed one. However, with the addition of lauroylated spruce TMP, all the composites with different % composition of wood derivative showed improved miscibility between the components in the composites [Fig. 6(C,D)].

Thermal analysis of thermoplastic composites

DSC is extensively used to investigate miscibility in polymer blends. A single compositionally dependent glass transition temperature (T_g) is an indication of full miscibility at a dimensional scale between 5 and 15 nm.¹⁸ Figure 7 shows DSC analyses of the various

% w/w fractions of benzoylated Spruce TMP-poly(styrene) composites. The pure poly(styrene) and benzoylated Spruce exhibit T_g values at 107°C and one slight T_g at 136°C, respectively. All of the composites appeared to exhibit miscible blend behavior. The observed T_g values decrease with increasing wood derivatives content. Several theoretical and empirical equations (Fox, Gordon-Taylor, Kwei) have been proposed for the prediction of T_g in miscible polymer blends, based on the composition of the blend, the T_g values of the individual components and the nature of the interactions between these components.^{19–24}

The equations are shown as follows:

$$\text{Fox: } 1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

$$\text{Gordon-Taylor: } T_g = (W_1T_{g1} + W_2kT_{g2}) / (W_1 + kW_2) \quad k = 0.37 \pm 0.04$$

$$\text{Kwei: } T_g = (W_1T_{g1} + kW_2T_{g2}) / (W_1 + kW_2) + QW_1W_2 \quad q = -147 \pm 10, k = 1$$

where W_1 and W_2 denote weight composition of the components, T_{g1} and T_{g2} represent the individual component glass transition temperatures, k and q are the fitting constant, respectively. The calculated and experimental T_g 's of benzoylated spruce TMP-poly(styrene) composites with different mixing ratios are shown in Figure 8. The differences between experimental and calculated T_g 's became larger when the fraction of benzoylated spruce increases in the composites. Both of the calculated T_g 's of the composites, based on the empirical equations by Fox and Gordon-Taylor appear between the individual T_g 's of the two components. Obviously, the observed T_g 's of the various composites are not in accordance with the calculated values from the Fox and Gordon-

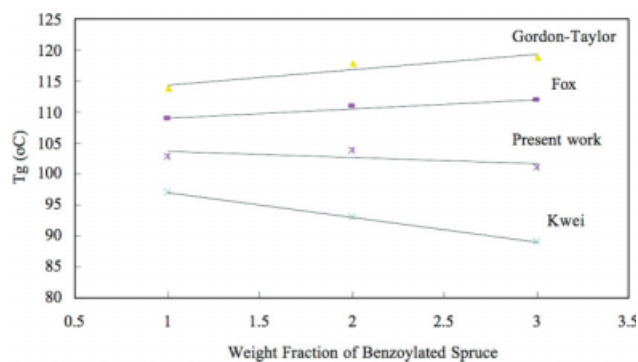


Figure 8 The calculated and experimentally obtained T_g values of benzoylated spruce TMP-poly(styrene) at different mixing ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

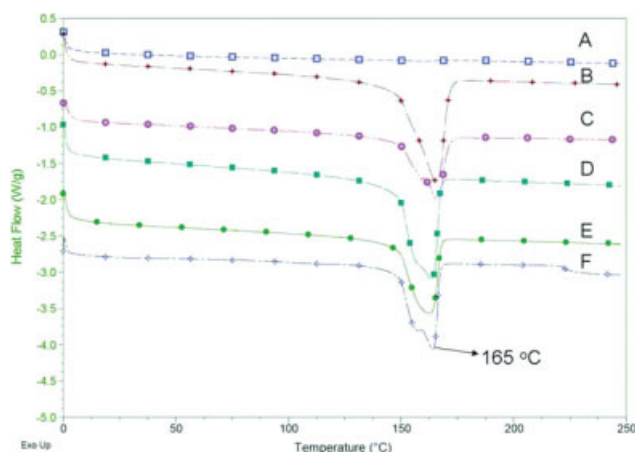


Figure 9 DSC analysis of A: Lauroylated spruce TMP; B: Poly(propylene); C: 5% w/w fraction of lauroylated spruce TMP-poly(propylene) composite; D: 10% w/w fraction of lauroylated spruce TMP-poly(propylene) composite; E: 15% w/w fraction of lauroylated spruce TMP-poly(propylene) composite; F: 10% w/w fraction of spruce TMP-poly(propylene) composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Taylor equations. In our case, the Kwei equation is more suitable for the prediction of T_g of the benzoylated Spruce TMP-poly(styrene), in which extensive crosslinking and strong intramacromolecular interaction between the lignocellulose components presumably still exist, after functionalization. Similar phenomena have been reported in the literature that decreased T_g values of the composites below those of the individual components of the composites.²⁵ The strong interfacial action between the components was held responsible for the decreased in the

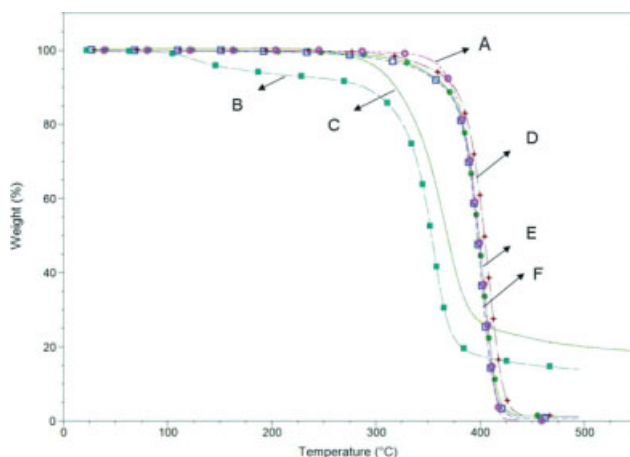


Figure 10 TGA of A: Poly(styrene); B: Spruce TMP; C: benzoylated spruce TMP; D: 20% w/w benzoylated spruce TMP-poly(styrene) composite; E: 10% w/w benzoylated spruce TMP-poly(styrene) composite; F: 15% w/w benzoylated spruce TMP-poly(styrene) composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

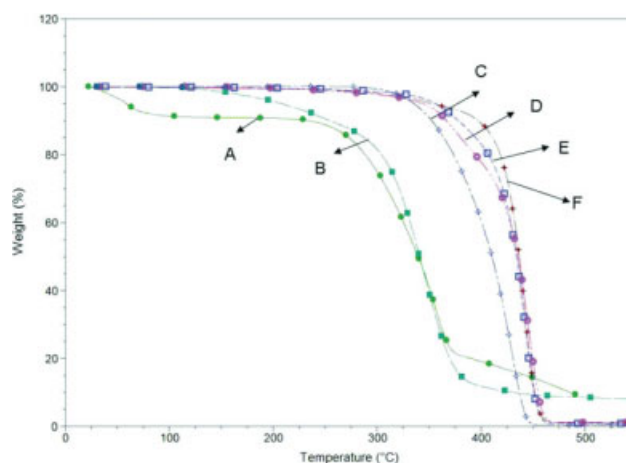


Figure 11 TGA of A: Spruce TMP; B: Lauroylated spruce TMP; C: Poly(propylene); D: 20% w/w lauroylated spruce TMP-poly(propylene) composite; E: 5% w/w lauroylated spruce TMP-poly(propylene) composite; F: 10% w/w lauroylated spruce TMP-poly(propylene) composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

degree of crystallinity of the polymer, which resulted in subsequent decreased phase transition temperature.²⁵

A series of DSC analyses for lauroylated spruce, poly(propylene) and their composites was also obtained (Fig. 9). Apparently there was no obvious thermal transfer for lauroylated spruce and a large melt peak for poly(propylene) was observed at 165 °C.

The TGA data of Figure 10, shows that there was a small weight loss from wood, around 100 °C, which was due to the evaporation of water from spruce TMP (Fig. 10). After the chemical modification, the benzoylated spruce showed a hydrophobic

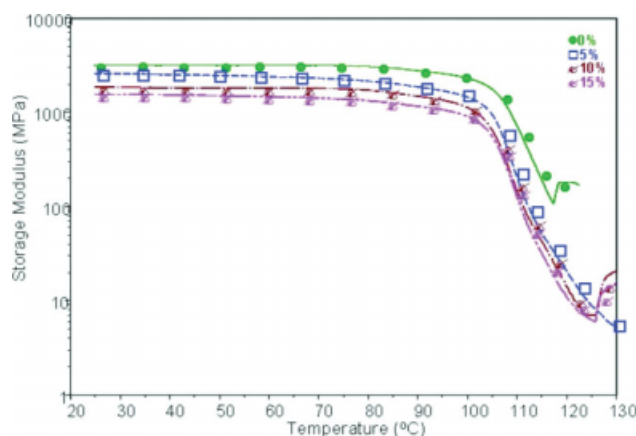


Figure 12 DMA curves of poly(styrene); 5%, 10%, 15%, and 20% w/w fraction of benzoylated spruce TMP-poly(styrene) composite: Storage modulus. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

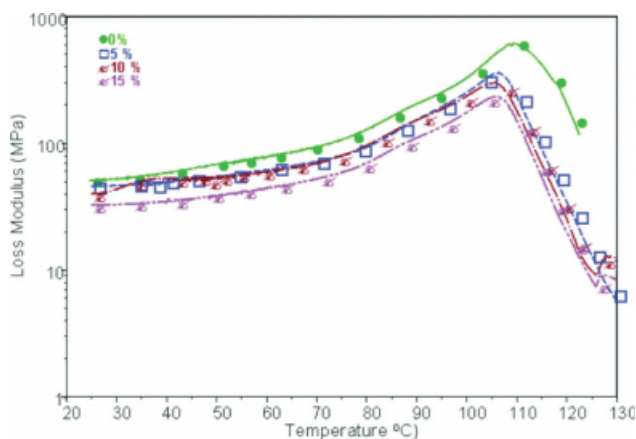


Figure 13 DMA curves of poly(styrene); 5%, 10%, 15%, and 20% w/w fraction of benzoylated spruce TMP-poly(styrene) composite: Loss modulus. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

characteristic demonstrated by absence of weight loss around 100°C. Poly(styrene) has higher thermal stability than benzoylated spruce, and started to degrade at 380°C. Therefore, all three composites have a slightly higher thermal stability than wood and benzoylated wood. All three composites were almost completely decomposed at about 420°C, which means that they have a similar thermal stability and similar thermal degradation pattern (Fig. 10). This also suggests that no adverse chemical reactions occur from the interaction of the two feedstocks. A similar observation of a transformation of hydrophilicity to hydrophobicity was observed upon lauroylation of spruce TMP from the exclusion of absorbed water in Figure 11. We also found that all

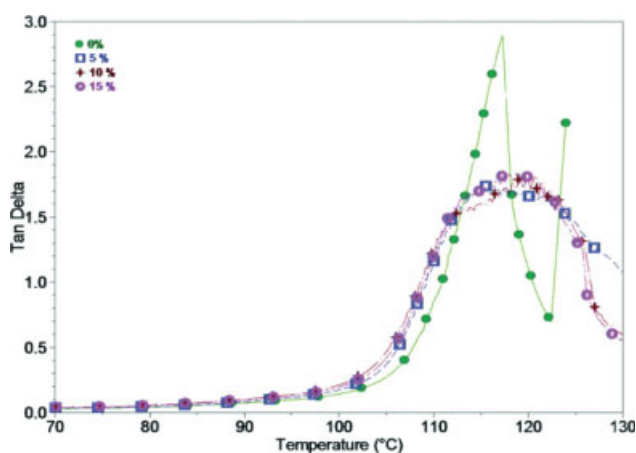


Figure 14 DMA curves of poly(styrene); 5%, 10%, 15%, and 20% w/w fraction of benzoylated spruce TMP-poly(styrene) composite: tan δ as a function of temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
DMA and DSC Transitions of Poly(styrene); 5%, 10%, 15%, and 20% w/w Fraction of Benzoylated Spruce TMP-Poly(styrene) Composite

Sample	T_g (DSC)	T_g (E') (DMTA)	T_g (E'') (DMTA)	T_g (Tan δ) (DMTA)
Poly(styrene)	107	105	109	117
5%	— ^a	103	106	116
10%	104	103	106	120
15%	104	103	106	119
20%	101	— ^b	— ^b	— ^b

^a Data not measured.

^b Results could not be measured. (Sample broke during the DMTA measurement).

of the composites showed slightly higher thermal stability than all of the individual components. The exact reason for this is not clear up to now.

Figure 12–14 have presented storage modulus E' , loss modulus E'' and tan δ as a function of temperature. The measurement was performed from 25 to 200°C but the data is cut from 130°C because of noisy data after glass transition temperature. In the case of the E' , as can be seen that the modulus value decreases when the amount of benzoylated spruce increases. Similar behavior can be seen in the E'' curves also. This indicates that the spruce works as a softener for the poly(styrene). In storage can be seen step like transition around 100°C, in loss modulus can be seen maxima around 110°C and in tan delta can be seen maxima around 115°C. These transitions correspond as glass transition for the composite materials.

In Table I, comparison of glass transition temperatures obtained from DSC measurements and DMTA measurements has been presented. In DMTA the glass transition temperature can be determined as onset temperature of storage modulus E' , as a maxima of loss modulus E'' or as a peak maxima of tan δ . The value can differ greatly from the value observed with DSC. In DMTA measurements, when T_g is determined from E' or E'' , similar decrease in T_g can be observed than in the case of DSC. Although the T_g values determined from the maxima of tan δ differ from this trend. DMTA data was not obtained for poly(propylene) composites because of the fragility of the samples.

CONCLUSIONS

Highly substituted benzoylated and lauroylated spruce lignocellulosic materials have been used as a filler for thermoplastic composites. The resultant thermoplastic wood composites exhibited good melting properties and processability and were readily

extruded into filaments or sheets. Morphology studies have shown that effective modification of wood by benzylation and lauroylation reactions can improve the compatibility between the wood-based lignocellulosic materials and poly(styrene) or poly(propylene). SEM has highlighted that the woody fibrous material remains dispersed throughout the composite materials. This dispersion has been attributed to the increased hydrophobicity of the lignocellulose material, allowing for efficient blending with the traditional synthetic polymers, maintaining mechanical strength and improving thermal stability in the process.

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References

1. Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Rederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* 2006, 311, 484.
2. Mohanty, A. K.; Misra, M.; Hinrichsen, G. *Macromol Mater Eng* 2000, 276/277, 1.
3. Mohanty, A. K.; Misra, M.; Drzal, L. T. *J Polym Environ* 2002, 10, 19.
4. Rowell, R. M. *Handbook of Wood Chemistry and Wood Composites*; CRC Press, 2005; pp 365–380.
5. Lee, S.; Shupe, T. F.; Groom, L. H.; Hse, C. Y. *Wood Fiber Sci* 2007, 39, 424.
6. Dominkovics, Z.; Danyadi, L.; Pukanszky, B. *Compos A* 2007, 38, 1893.
7. Fernandes, E. G.; Pietrini, M.; Chiellini, E. *Biomacromolecules* 2004, 5, 1200.
8. Singh, S.; Mohanty, A. K. *Compos Sci Technol* 2007, 67, 1753.
9. Marcovich, N. E.; Aranguren, M. I.; Reboredo, M. M. *Polymer* 2001, 42, 815.
10. Maldas, D.; Kokta, B. V.; Raj, R. G.; Daneault, C. *Polymer* 1988, 29, 1255.
11. Rowell, R. M. *Handbook of Wood Chemistry and Wood Composites*; CRC Press, 2005; pp 215–380.
12. Rowell, R. M. In *ACS Symposium Series No. 954 Materials, Chemicals and Energy from Forest Biomass*; Argyropoulos, D. S., Ed.; ACS Books: Washington, 2006; Chapter 5, pp 76–92 (ISBN: 978-0-8412-3981-4).
13. Xie, H. B.; King, A.; Kilpelainen, I.; Granstrom, M.; Argyropoulos, D. S. *Biomacromolecules* 2007, 8, 3740.
14. Argyropoulos, D. S.; Xie, H. B. U.S. Pat. 12/026,998, World Pat. PCT/US2008/053151 (2008).
15. David, N. S. H.; Ren, S. J. *Reinforced Plast Compos* 2003, 22, 957.
16. Hon, D. N. S.; Chao, W. Y. *J Appl Polym Sci* 1993, 50, 7.
17. Kilpelainen, I.; Xie, H. B.; King, A.; Granstrom, M.; Argyropoulos, D. S. *J Agric Food Chem* 2007, 55, 9142.
18. Paul, D. R.; Bucknall, C. B. *Polymer Blends*; Wiley: New York, 2000.
19. Gordon, M.; Taylor, J. S. *Non-Cryst Copolym* 1952, 2, 493.
20. Lu, X.; Weiss, R. A. *Macromolecules* 1992, 25, 3242.
21. Kwei, T. K. *J Polym Sci Polym Lett* 1984, 22, 307.
22. Kwei, T. K.; Pearce, E. M.; Pennacchia, J. R.; Charton, M. *Macromolecules* 1987, 20, 1174.
23. Couchman, P. R. *Macromolecules* 1983, 16, 1924.
24. Couchman, P. R.; Karasz, F. E. *Macromolecules* 1978, 11, 117.
25. Liang, X. H.; Guo, Y. Q.; Gu, L. Z. *Macromolecules* 1995, 28, 6551.