Effect of Extractives on the Performance Properties of Wood Flour-Polypropylene Composites

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ABSTRACT: In this study, the effects of extractives in wood flour on the physicomechanical properties of wood flour-polypropylene (PP) composites have been investigated. Three different solvents, hot-water (HW), 1% NaOH (AL), and dichloromethane (DM), were used to remove extractives in both poplar and eucalypt wood flour. The obtained results showed that mechanical properties of the composites were moderately enhanced on using extractive-free lignocellulosic materials in both the wood types. A large increase in the strength of eucalyptus flour-PP composites was observed upon the removal of extractives from eucalyptus flour. Unlike the mechanical properties, no improvement in the water absorption and thickness swelling was observed for any type of extracted-free samples. The thermal degradation behavior of the composites showed that in both cases, the degradation temperatures shifted to higher values after removing the extractives. In general, the removal of AL solubles was more effective in its improvement of the physicomechanical properties than the removal of HW and DM extractives. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1563–1567, 2012

Key words: extractives; wood; polymer; mechanical properties; thermal stability

INTRODUCTION

Composite materials based on cellulosic fibers, namely wood polymer composite (WPC), demonstrate remarkable environmental and economical advantages.[1] In the recent years, their utilization has developed rapidly, especially in Europe, the United States, and Canada. Although the use of wood flour in plastic composites has several advantages over inorganic fillers, several drawbacks (limitations) of cellulosic fillers such as low thermal stability and low compatibility greatly reduce the overall performance of WPCs.

All species of wood and other plant tissues contain small to moderate quantities of chemical substances in addition to the macromolecules of cellulose, hemicellulose, and lignin. To distinguish them from the major cell wall components, these additional materials are known as the extractive (nonstructural) components, or simply "extractives." Extractives content in most temperate and tropical wood species are 4–10 and 20% of the dry weight, respectively. Although extractives contribute merely a few percent to the entire wood composition, they have significant influence on its properties, such as mechanical strength or color and the quality of wood, which can be affected by the amount and type of these extractives.[2]

Chemically, extractives in wood consist of those components (normally of low molecular weight) that are soluble in neutral solvents, either organic solvents, or water.[3] A wide range of different substances is included under the extractive heading: flavonoids, lignans, stilbenes, tannins, inorganic salts, fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, terpenes, starch, glycosides, saponins, and essential oils. Extractives occupy certain morphological sites in the wood structure.[4] Extractives can be removed with a single solvent or a combination of solvents, such as ethanol, water, benzene, dichloromethane (DM), chloroform, or a mixture of ethanol/benzene.[3]

It is very well known that the performance, for example, the mechanical properties, of composites depends on the properties of the individual components and their interfacial compatibility. The interface between hydrophobic plastic and hydrophilic wood is typically weak and fails to transfer stress. The effective use of wood-based particles in WPCs requires a fundamental understanding of the

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structural and chemical characteristics of wood.[5] For example, a few reports have been published about the effects of wood extractives on the strength properties of the resulting WPCs.[6–8] Wood extractives are hydrophobic substances with low molecular weights. In the preparation of WPCs, wood flour is thoroughly mixed with a thermoplastic at high temperatures, for example, 170°C. At such high temperatures, wood extractives may tend to migrate to the wood flour surface, thus accumulating in the wood-plastic interphase.

The objective of this study is to investigate the effects of the wood extractives on the physicomechanical properties of wood flour-polypropylene (PP) composites. To gain a full understanding of these effects, hot water (HW), DM, and 1% alkali solution (AL) extractives, respectively, were removed from the two different wood species before the preparation of the WPCs. The physicomechanical properties of WPCs produced with extractive-free wood were determined and compared to the properties of WPCs with untreated (unextracted) wood.

EXPERIMENTAL

Materials

The polymer matrix, PP, was supplied by Bandar Imam Petrochemical Company, Iran, in the form of homopolymer pellets with a density of 0.90 g/cm^3 and a MFI of 7–10 g/10 min.

The cellulosic materials used in the composite were eucalypt (*Eucalyptus camaldulensis*) and poplar (*Populus deltoides*) from local sources. Wood pieces were ground with a Thomas–Wiley miller to pass through a 60-mesh screen and then were dried and stored in sealed plastic bags prior to compounding. To simplify the experiments, no other materials/additives, such as coupling agents, were used.

Extractives determination

The extractives of the above-mentioned samples were determined gravimetrically following the appropriate Tappi Test Methods.[3] The screened samples were extracted with DM (T 204 cm-97), hot 1% AL solubility (T 212 om-98) and HW solubility (T 207 cm-99), individually. In addition, cellulose (T 203 cm-99) and Klason lignin (T 222 om-02) were determined. Three replicates were done for each experiment.

Preparation of composites

The amount of fiber was fixed at 30 wt %; this amount is selected, because it is typical of many industrial formulations and represents excellent balance between performance and cost. The wood flour and PP were premixed before being fed into the corotating (Collin) extruder. The screw speed was between 70 and 80 rpm. The extruded strand was passed through a water bath and palletized. The resulting granules were subsequently injection molded at 190°C to produce standard ASTM specimens.

Mechanical testing

All the specimens were tested following ASTM standard D 638 for tensile properties, ASTM D 790 for flexural properties, and D 256 for notched Izod impact strength. Tensile and bending tests were conducted using an Instron Universal Testing Machine (model 1186) at speeds of 1.5 and 2 mm/min, respectively. A pendulum impact tester (Zwick 1446) was used for the notched Izod impact test. Each value obtained represented the average of four samples.

Physical testing

Physical properties, namely, thickness swelling, and water absorption were tested in accordance with ASTM D 570. Before testing, the weight and dimensions, that is, length, width, and thickness of each specimen were measured. Conditioned samples of each type of composite were soaked in distilled water at room temperature for 2 h. Samples were removed from the water, patted dry, and then measured again. Each value obtained represented the average of four samples.

Thermal characterization

Thermogravimetric analysis was conducted with a Polymer Laboratories Thermogravimetric Analyzer. This method measures the change in weight as a function of temperature with a resolution of 0.1 mg under nitrogen atmosphere. The samples of $\sim$ 4 mg of each composite were analyzed and heated from 20 to 600°C at a rate of 20°C/min in a platinum sample pan.

RESULTS AND DISCUSSION

Extractives content

Extractives in woody materials come in three main categories—those that are soluble in organic solvents (such as "DM" mixtures), those that are soluble in water, and those that are soluble in aqueous AL. As it can be seen from Table I, ED solubles in eucalypt are only a little higher than those in poplar fibers, but AL and HW solubles in eucalypt are significantly higher. Eucalypt contains more polar extractives, which is indicated by a higher amount of HW

TABLE I
Chemical Compositions of Woody Materials

Chemicals (%)	Species	
	Poplar	Eucalypt
Cellulose	53.2	50.3
Lignin	21.3	26.3
DM[a] solubles	1.9	3.8
1% NaOH solubles	12.5	17.7
Hot water solubles	3.6	5.7

[a] Dichloromethane.

than DM extractives. The DM procedure removes a part of extraneous components, such as waxes, fats, resins, and some gums. The composition and amount of the extractives depend on factors such as wood species, wood age, and the location of the wood in the tree.[7]

Tensile properties

The tensile properties of composites containing extracted and unextracted wood are presented in Figure 1(a). It is evident that steady and moderate increase in tensile strength occurred upon filling the polymer matrix with extracted wood when compared with untreated ones. Tensile modulus exhibited a similar trend as that of tensile strength and showed a maximum improvement of 2862 MPa for alkaline treated eucalypt sample, which is 15% higher than that of the control sample. The possible reason proposed for this kind of behavior may be the improved interfacial adhesion between the matrix and wood flour. In addition, various parameters influence the mechanical properties of fiber reinforced composites including the fiber aspect ratio, fiber-matrix adhesion, stress transfer at the interface, and mixing temperatures.

The higher tensile properties of WPCs with extracted samples, found in this study, are in good agreement with that reported by Saputra et al.[8] They claimed that such extraction improved mechanical properties because of an improvement in interfacial shear strength between the PP matrix and the extracted wood filler.

Flexural properties

The effects of extractives on the flexural strength and flexural modulus for poplar/PP and eucalypt/PP composites are given in Figure 1(b). It is seen that like tensile properties, the extractive-free samples showed higher flexural properties compared to the unextracted composites. Both flexural strength and modulus showed a significant increase with decreasing extractives materials. Composite made with AL treated eucalypt wood flour reached the maximum values for flexural strength (37.7 MPa) and flexural modulus (2941 MPa). It is notable that the total extractives present in eucalypt are much more than poplar (Table I). The explanation is similar to that of the tensile properties, which is believed to be due to better interfacial bonding between the fiber and matrix by removing the extractives. HW procedure removes a part of extraneous components, such as inorganic compounds, tannins, gums, sugars, starches, and fatty derivates.[3] They can diffuse to the surface, thus blocking cells and reducing contact of the matrix with the hydroxyl groups (—OH) of cellulosic material.[9] This, in turn, could reduce adhesion at the interface, which causes inferior interfacial bonding strength when compared with the extracted (extractive-free) samples.

Izod impact strength and elongation

Figure 1(c) presents the results of notched Izod impact strength measurements with or without extractives. The eucalypt fiber appeared to improve impact strength in comparison with the poplar flour. However, the improvement for extractive-free samples was not significant. With respect to the chemical properties (Table I), this was expected, because eucalypt should be more resistant to crack propagation in the matrix. Generally, the presence of wood flour in the PP matrix provides points of stress concentration, thus providing sites for crack initiation. Hamzeh et al.[10] reported that extractives play a major role in determining the crack initiation process by lowering the interaction between the lignocellulosic materials and the coupling agent.

Our analysis showed that, extracted wood-PP affected the elongation at break. Figure 2(c) shows the effects of different extractive types on the composites elongation at break. It is clearly seen that by removing alkaline solubles, there is moderate improvement in the elongation at break. This could be explained by the good dispersion of this particle type. Some lipophilic extractives might help disperse the particles during WPC preparation. There is no significant difference between the two cellulosic materials. Composites filled with unextracted wood flour show brittle behavior.

Water absorption and thickness swelling

Figure 1(d) shows the values of the water absorption for the composites, which vary depending upon the extractive types. The PP matrix does not absorb any moisture, indicating that moisture is absorbed by the wood component in the composites.[9] The hygroscopic properties of wood can be affected by the extractives. Nzokou and Kamdem[11] believe that extracted wood generally absorbs more water and swells more than unextracted wood, which is due to

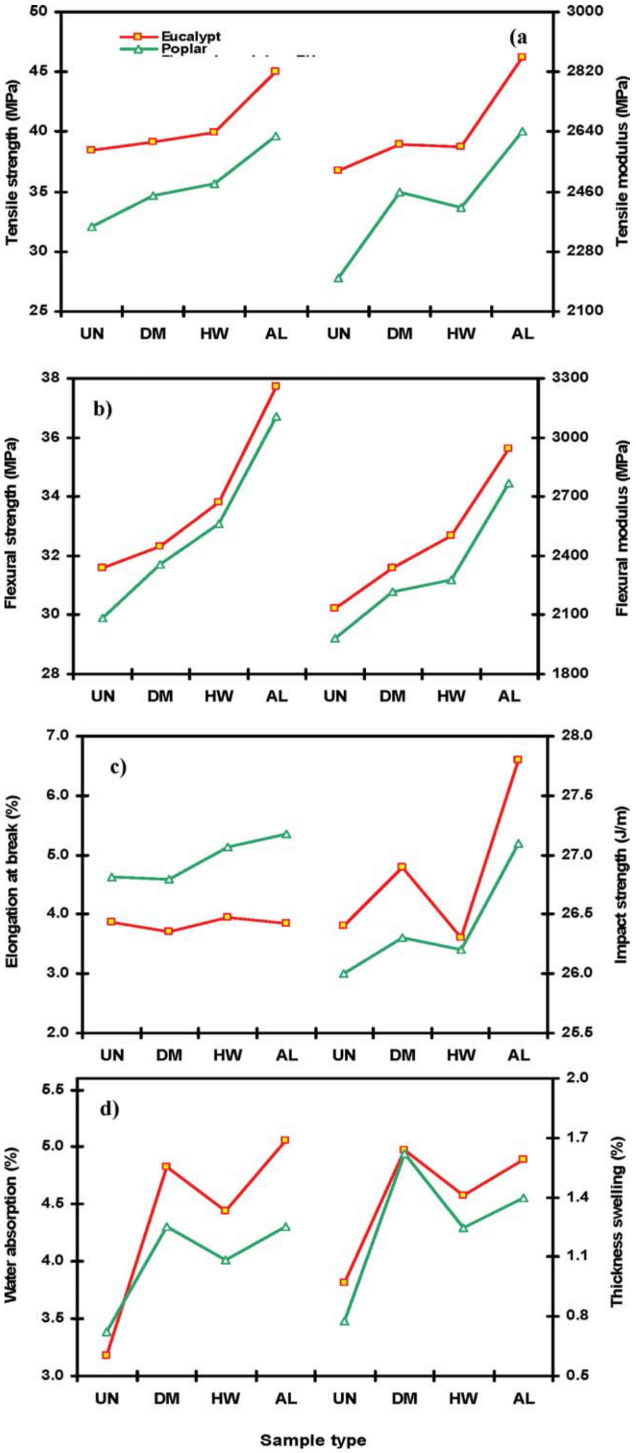

Figure 1 Comparison of physicomechanical properties of the composites with treated and untreated wood. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the increased availability of moisture sites previously occupied by extractives and increased diffusion coefficient. Wood contains numerous free hydroxyl groups present in the cellulosic cell wall materials, which are responsible for interaction with water molecules by hydrogen bonding. The absorption of water by different fiber-based composites is largely dependent on the availability of free hydroxyl groups on the surface of the wood flour. On unextracted samples, some of these hydroxyl groups are blocked, as a result of which the absorption of water gets restricted.[6] Figure 1(d) clearly shows that the water absorption of unextracted composites is less than extractive-free samples. As mentioned earlier, extractives may have acted similar to wax, which is normally used to control water absorption. It could result in a significant decrease in the degree of moisture absorption of the composite. Because the lumens of wood flour were filled with extractives, the penetration of water by the capillary action into the deeper parts of composite was prevented. This may suggest that the water absorption has occurred in the surface layer.

The thickness swelling of the WPC samples showed a similar pattern to the water uptake data [Fig. 1(d)]. It is obvious that extractive-free samples cause slightly higher values of thickness swelling, compared to the control composites. However, there is no significant difference in thickness swelling between the two species (poplar and eucalypt), and

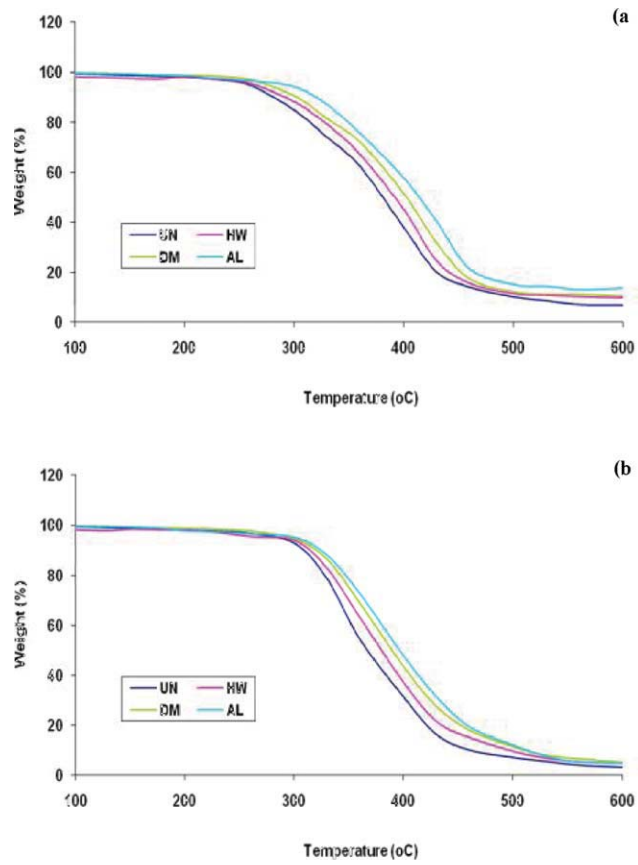

Figure 2 Thermal decomposition curves of eucalypt (a) and poplar (b) composites with treated and untreated wood. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

various extractive types, as can be seen from Figure 1(d). Kim et al.[6] reported that the thickness swelling of WPCs made with extracted wood is also higher than unextracted wood.

Thermal degradation behavior

As mentioned earlier, the major chemical components of wood are cellulose, hemicelluloses, lignin, and extractives, and they degrade at different temperatures. Wood materials are known to present different degradation profiles depending on the wood composition. Cellulose is highly crystalline, which makes it thermally stable. Hemicelluloses and lignin, on the other hand, are amorphous and start to degrade before cellulose. Hemicelluloses are the least thermally stable wood components, due to the presence of acetyl groups. Lignin degrades partly over a wide temperature range, starting at relatively low temperatures.[2]

Figure 2 shows significant differences in the degradation characteristics of the WPCs containing wood with and without extractives. The removal of wood extractives improved the thermal stability of WPCs. The removal of both DM and HW extractives showed less improvement in the thermal stability of WPCs than the removal of AL extractives. This could be explained by the elimination of a larger quantity of material in AL extraction; low-molecular weight carbohydrates consisting mainly of hemicelluloses and degraded cellulose. A distinct improvement of the thermal stability was achieved when both types of extractives were removed.

CONCLUSIONS

Based on the results of this study the following conclusions can be drawn.

1. The two investigated wood species were clearly distinguishable by differences in their chemical compositions.
2. Results showed that tensile and flexural properties of the composites were moderately enhanced on using extractive-free lignocellulosic materials in both the wood types.
3. The largest improvement in the mechanical properties of WPCs was achieved when alkaline solubles were removed.
4. The WPCs with extracted wood flour absorbed water more than those made with unextracted wood. The difference in water uptake between extracted and unextracted composites is due to blocking of the free hydroxyl groups by extractives.
5. Significant differences were observed in the thermal stability between extracted wood-PP and unextracted wood-PP composites with the exception of the DM extracted poplar, which was not significantly different from the control sample. The removal of DM and HW extractives showed less improvement in the thermal stability of WPCs than the removal of AL extractives.

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