Utilization of Waste Pine Cone in Manufacture of Wood / Plastic Composite

Turker Dundar, Nadir Ayrilmis, and Umit Buyuksari

Turker Dundar, Associate Prof., Ph.D., Nadir Ayrilmis, Associate Prof., Ph.D., Istanbul University, Forestry Faculty, Bahcekoy, Sariyer, 34473, Istanbul, TURKEY E-mail: <dundar@istanbul.edu.tr>, <nadiray@istanbul.edu.tr>

Umit Buyuksari, Graduate Research Assistant, Ph.D. Candidate, Istanbul University, Forestry Faculty, Bahcekoy, Sariyer, 34473, Istanbul, TURKEY E-mail: <buyuku@istanbul.edu.tr>

ABSTRACT

This study evaluated some physical and mechanical properties of polypropylene (PP) composites reinforced with various mixtures of the cone flour and the wood flour. Five wood plastic composite (WPC) types were made from the mixtures of cone flour/wood flour/PP/coupling agent, respectively. Water resistance and flexural properties of the composites were negatively affected by increasing cone flour content. We concluded that extractives in the cone flour on the mechanical properties of wood-polypropylene (PP) composites had a significant effect on the flexural properties of the composites. Based on the findings obtained from the present study, with the addition of 10% cone flour to WPC, the water resistance and flexural properties did not significantly affected as compared to WPC made from wood flour.

INTRODUCTION

The use of plant-based fiber as an additive to plastics has accelerated rapidly over the past decade, primarily due to improvements in process technology and economic factors. Further development of these applications of biorenewable fibers for use by the plastic industry could provide attractive new value-added markets for agricultural products while simultaneously displacing petrochemical-based plastic resins. The primary advantages of using lignocellulosic fibers as additives in plastics are low densities, low cost, non abrasive nature, possibility of high filling levels, high specific properties, biodegradability, availability of wide variety of fibers throughout the world, and generation of agricultural economy [Sanadi et al., 1994].

Pine tree is one of the most common species, both in Europe and North America, but it is mainly in the Mediterranean area where it obtains its highest importance of production and consumption. *Pinus pinea* L., is often called the 'Stone Pine' and sometimes the 'Umbrella Nut'. These names apparently come from the idea that this tree grows well in stony ground and also because at times it has a shape rather like an umbrella. The tree is important in Italy, Spain and Portugal, with Italy producing the bulk of the world's supply of pine nuts. Pine cones, a renewable
resource, are not used to their potential. Large quantities of cones are produced annually throughout the world, especially in pine plantations grown for the pulp and paper industry. The stone pine forests of Turkey cover 54,153 ha [Anonymous, 2001] and total cone production of the stone pine in 2006 according to Forestry Statistics of Turkish General Directorate of Forestry was 3,545,861 kg (Anonymous, 2006). They are collected, dried to facilitate seed release, and generally discarded or burned in the stove in winter. New uses for pine cones can provide additional income for forest landowners.

Maleated polypropylene (MAPP) has been extensively used in wood fiber and polymer composites. The maleic anhydride present in the MAPP provides polar interactions such as acid-base interactions and can also covalently link to the hydroxyl groups on the lignocellulosic fiber. Coupling agents played a very important role in improving compatibility and bonding strength between polar wood fibers and non-polar thermoplastics in wood fiber and polymer composites [Anonymous, 1999].

Growing demand for wood plastic composites has led to continuous efforts to find new resources as an alternative to wood. With increasing population of the world, the sustainable utilization of forest resources has been adversely influenced. One of these residuals is waste pine cone, which is produced in high quantities in the pine nut industry. The waste pine cone could play an important role in the manufacture of value-added ligno-cellulosic/plastic composites and may be the most efficient use of the pine cone. An extensive literature search did not reveal any information about the utilization of the stone pine cone as an alternative to wood in the manufacture of MDF (medium density fiberboard). From the literature, we know that physical and mechanical properties ligno-cellulosic/plastic composites can be influenced by raw material characteristics [Ashori, 2008; Ashori and Nourbakhsh, 2009; Georgopoulos et al., 2005; Liu et al., 2009; Panthapulakkal et al., 2006; Mustapa et al., 2005; Talavera et al., 2007]. The objective of this study was to determine some physical and mechanical properties of the polypropylene (PP) composites reinforced with various mixtures of the wood flour and the pine cone and to evaluate the compatibilizer performance.

MATERIALS AND METHODS

Materials

Fresh cones were collected from the stone pine (Pinus pinea L.) in the Fatih Forest District Sample in Belgrade Forest in Sariyer, Istanbul, Turkey. The cones were spread on plastic in the sun. After drying, the cones opened up and the nuts fell out. The pine cones without nuts were soaked in a hot water for four hours at 90°C. This treatment was believed to partially remove gum on the surface of the cones and improve the grinding process and bonding properties of the cone flour. After the treatment, the wet cones were dried in an oven at 60°C for 10 hours to moisture content of 20-30% based on the oven-dry cone weight. Following the drying, the cones were then processed by a rotary grinder without adding additional water. Finally, the cone flour passing through a U.S. 35-mesh screen and was retained by a U.S. 80-mesh screen (Fig. 1). The cone flour was then dried in a laboratory oven at 85°C for 15 hours to moisture content of 2-3%.
Wood particles (a 50:50 blend) consisting of pine (Pinus nigra Arnold var. pallasiana) and beech (Fagus orientalis Lipsky) species were obtained from a commercial particleboard plant in Turkey. The moisture content of the particles, as determined by oven-dry weight, was found to be 4-5% prior to the treatment. The wood particles were processed by a rotary grinder without adding additional water. The wood flour passing through a U.S. 35-mesh screen was retained by a U.S. 80-mesh screen and then dried in a laboratory oven at 100 °C for 15 hours to moisture content of 1-2%.

The polypropylene (PP) ($T_m = 160°C$, $\rho = 0.9$ g/cm$^3$, MFI/230°C/2.16 kg = 6.5 g/10 min) produced by Petkim Petrochemical Co., Turkey, was used as the polymeric material. Maleic anhydride-grafted PP (MAPP-OPTIM-415; the reactive modifier maleic anhydride (MAH content = 1 wt.%) was supplied by Pluss Polymers Pvt. Ltd. in India.

**WPC Composite Manufacture**

The wood flour and the waste cone flour were dried to 1–2% moisture content using an air dryer oven at 100°C for 24 h and then stored in a polyethylene bag in an environmental controller. The wood flour, the cone flour, and the PP and the MAPP granulates were processed in a 30-mm conical co-rotating twin-screw extruder (Aysa Instrument Com., Istanbul, Turkey) with a length-to-diameter (L/D) ratio of 30:1. The raw materials were fed into the main feed throat using a gravimetric feed system. The barrel temperatures of the extruder were controlled at 170°C, 180°C, 190°C and 190°C for zones 1, 2, 3 and 4, respectively, while the temperature of the extruder die was held at 200°C. The extruded strand passed through a water bath and was subsequently palletized. These pallets were stored in a sealed container and then dried for about 8 hours at 102°C before being injection molded. Temperature used for injection molded samples was 170°C to 190°C from feed zone to die zone. The WPC samples were injected at injection
The samples were conditioned at a temperature of 23 ± 2°C and relative humidity of 50 ± 5% according to ASTM D 618-08 (2008). The formulations of the composites are given in Table 1. Density values of the samples varied from 0.99- 1.03 kg/m³.

Table 1. Compositions of the Evaluated Formulations (by % Weight)

<table>
<thead>
<tr>
<th>WPC formulation code</th>
<th>Wood flour</th>
<th>Cone flour</th>
<th>Polypropylene</th>
<th>Maleic anhydride-grafted polypropylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPC1</td>
<td>40</td>
<td>-</td>
<td>57</td>
<td>3</td>
</tr>
<tr>
<td>WPC2</td>
<td>30</td>
<td>10</td>
<td>57</td>
<td>3</td>
</tr>
<tr>
<td>WPC3</td>
<td>20</td>
<td>20</td>
<td>57</td>
<td>3</td>
</tr>
<tr>
<td>WPC4</td>
<td>10</td>
<td>30</td>
<td>57</td>
<td>3</td>
</tr>
<tr>
<td>WPC5</td>
<td>-</td>
<td>40</td>
<td>57</td>
<td>3</td>
</tr>
</tbody>
</table>

Determination of Water Resistance

The thickness swelling (TS) and water absorption (WA) tests were carried out according to ASTM D 570 – 05 (2005) specifications. The test samples were in the form of a disk 50.8 mm in diameter and 3.2 mm in thickness. The ten samples were taken from each of the five formulation. The conditioned samples were placed in a container of distilled water maintained at a temperature of 23 ±1°C. The weights and thicknesses of the samples were measured at different time intervals during the long period of immersion. At the end of 2-, 24-, 48-, and 72-h of submersion, the samples were removed from the water one at a time, all surface water were wiped off with a dry cloth, and weighed to the nearest 0.001 g and measured to the nearest 0.001 mm immediately. The values of the WA as percentages were calculated with Eq. (1):

\[
WA(t) = \frac{W(t) - W_0}{W_0} \times 100
\]  

(1)

where \( WA_0 \) is the water absorption (%) at time \( t \), \( W_0 \) is the initial weight, and \( W(t) \) is the weight of the sample at a given immersion time \( t \).

The values of the TS as percentages were calculated with Eq. (2):

\[
TS(t) = \frac{T(t) - T_0}{T_0} \times 100
\]  

(2)

where \( TS_0 \) is the thickness swelling (%) at time \( t \), \( T_0 \) is the initial thickness of the sample, and \( T(t) \) is the thickness at time \( t \). Density of the samples was measured on the TS samples.

Determination of Flexural Properties

The flexural properties, modulus of rupture (MOR) and modulus of elasticity (MOE), were measured in three-point bend tests using a standard Material Testing System (Zwick Z010 with
2.5 kN load cell) at a crosshead speed of 2.8 mm/min in accordance with ASTM D 790-03 (2003). The MOR and MOE of the samples with dimensions of 127 mm x 12.7 mm x 3.2 (thickness) mm were determined at ambient conditions of 23 ± 2°C and 50 ± 5% relative humidity according to ASTM D 618-08. Five replicate samples were tested for each formulation.

RESULTS AND DISCUSSION

Water Resistance

Table 2 displays the TS and WA values of the samples. The WPC samples showed no significant differences in density. The TS and WA values significantly decreased with increasing cone flour content. Statistical analysis found some significant differences among the WPC means for the TS and WA values. Significant differences were determined individually for these tests by Duncan’s multiple-comparison tests. The results of Duncan’s multiple range test are shown by letters in Table 2. The lowest TS value was 0.30% for the samples containing 40% wood flour (WPC1), while the highest TS value was found as 0.53% for the samples containing 40% cone flour (WPC5) after 2-h of submersion in water. The similar trends were also observed for 24-, 48-, and 72-hr of submersions. (Table 2). The WA values of the composites were higher than the TS values. Hardboard (density ≥ 800 kg/m³) standard ANSI/AHA A135.4 (American Hardboard Association, 1995) was used here for comparison of the TS and the WA values since there was no established minimum property for wood plastic composite. The TS and WA values of all composite types did not exceed the hardboard (3.2 mm thickness) minimum property requirements of 20% (TS) and 25% (WA) according to ANSI/AHA A135.4 [(American Hardboard Association, 1995) Standard, respectively. The TS and WA values of the samples were also much less than those of particleboard, oriented strandboard, and medium density fiberboard because the matrix polymers are hydrophobic (Anonymous 1999). In a previous study, average TS and WA values of MDF panels after 24-h of submersion were found as 15.9% and 6.7%, respectively (Anonymous 1999). With the increase in the pine cone content in the composite, more water was absorbed. The TS and WA curves for all formulations are presented in Fig. 2. On the other hand, plastics are water repellent and have much lower water sorption capability than wood.

The moisture absorption in composites is mainly due to the presence of lumens, fine pores and hydrogen bonding sites in the wood flour, the gaps and flaws at the interfaces, and the micro cracks in the matrix formed during the compounding process (Stokke and Gardner, 2003). Water absorption by cellulose and hemicelluloses depends on the number of free hydroxyl groups thus the amorphous regions are accessible by water. Polar hydroxyl groups on the lignocellulosic material are contributed predominantly by holocellulose (cellulose and hemicellulose) and lignin (Aydin, 2004). Although amount of holocellulose which has a large of polar hydroxyl groups in the cone flour is lower than its wood flour, composites containing the cone flour showed higher TS and WA. This was attributed to the polar hydroxyl groups were mainly responsible for hydrogen bonds with polar adhesives polymers. The lower TS and WA values of the composites containing higher amounts of the cone flour can be related to lower amounts of cellulose and lignin materials in the cell walls of the cone flour (Gonultas, 2008).
Table 2. Results of the Water Resistance of the Composites

<table>
<thead>
<tr>
<th>WPC Code</th>
<th>WPC Density (g/cm³)</th>
<th>Water Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Thickness Swelling (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-h</td>
</tr>
<tr>
<td>WPC1</td>
<td>0.99 (0.03)</td>
<td>0.30 (0.08) A</td>
</tr>
<tr>
<td>WPC2</td>
<td>1.03 (0.01)</td>
<td>0.34 (0.11) A</td>
</tr>
<tr>
<td>WPC3</td>
<td>1.01 (0.02)</td>
<td>0.43 (0.13) B</td>
</tr>
<tr>
<td>WPC4</td>
<td>1.03 (0.04)</td>
<td>0.50 (0.16) C</td>
</tr>
<tr>
<td>WPC5</td>
<td>1.02 (0.01)</td>
<td>0.53 (0.14) C</td>
</tr>
</tbody>
</table>

Groups with same letters in column indicate that there was no statistical difference (p < 0.01) between the samples according to the Duncan’s multiply range test. Values in parentheses are standard deviations.
Figure 2. Thickness Swelling (A) and Water Absorption (B) Curves for all Formulations.

The moisture absorption in composites is mainly due to the presence of lumens, fine pores and hydrogen bonding sites in the wood flour, the gaps and flaws at the interfaces, and the micro
cracks in the matrix formed during the compounding process (Stokke and Gardner, 2003). Water absorption by cellulose and hemicelluloses depends on the number of free hydroxyl groups thus the amorphous regions are accessible by water. Polar hydroxyl groups on the lignocellulosic material are contributed predominantly by holocellulose (cellulose and hemicellulose) and lignin (Aydin, 2004). Although amount of holocellulose which has a large of polar hydroxyl groups in the cone flour is lower than its wood flour, composites containing the cone flour showed higher TS and WA. This was attributed to the polar hydroxyl groups were mainly responsible for hydrogen bonds with polar adhesives polymers. The lower TS and WA values of the composites containing higher amounts of the cone flour can be related to lower amounts of cellulose and lignin materials in the cell walls of the cone flour [Gonultas, 2008].

Generally, it is necessary to use compatibilizers or coupling agents to improve the filler/fiber bonding and in turn to enhance the water resistance. The compatibilizing agents have a positive effect on water absorption. The strong interfacial bonding between the filler and polymer matrix caused by the compatibilizing agents (the MAPP chemically bonds with the OH groups in the lignocellulosic filler) limits the water absorption of the composites. A larger amount of the pine cone influences the MAPP performance in such a way that it cannot cause good bonding between polypropylene and the filler. The cone flour has less cellulose, more lignin, and more extractives than wood flour. With the addition of MAPP (3 wt%) the compatibility between the lignocellulosic and the PP is improved because the anhydride moieties in MAPP entered into an esterification reaction with the surface hydroxyl groups of wood flour [Matuana et al., 2001].

**Flexural Properties**

The WPC samples showed no significant differences in density while they had significant differences (p< 0.01) in the MOR and MOE. Significant differences between groups were also determined individually for TS and WA tests by Duncan’s multiple-comparison tests as displayed in Table 3. The MOR and MOE significantly decreased with increasing cone flour content from 10 to 40% in the composite. For example, the average MOR and MOE values of the composites containing 40% wood flour (composite code: WPC1) was 48.1 N/mm² and 5005.2 N/mm² as compared to composites containing 40% cone flour (composite code: 5) which is about 41.9 N/mm² and 4355.3 N/mm², respectively. In a previous study, MOR and MOE values were found as 72.4 N/mm² and 3220 N/mm² for WPCs made from 57% PP and 40% hardwood fiber, and 3% coupling agent, respectively [Anonymous, 1999].

**Table 3. Results of the Flexural Properties of the Composites**

<table>
<thead>
<tr>
<th>Composite Code</th>
<th>Composite Density (g/cm³)</th>
<th>Flexural Properties</th>
<th>Modulus of Rupture (N/mm²)</th>
<th>Modulus of Elasticity (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPC1</td>
<td>0.99 (0.03)</td>
<td></td>
<td>48.1 (2.17) A*</td>
<td>5005.2 (109.4) A</td>
</tr>
<tr>
<td>WPC2</td>
<td>1.03 (0.01)</td>
<td>46.8 (1.57) AB</td>
<td>4967.7 (91.2) A</td>
<td></td>
</tr>
<tr>
<td>WPC3</td>
<td>1.01 (0.02)</td>
<td>45.3 (13.5) B</td>
<td>4660.1 (59.6) B</td>
<td></td>
</tr>
<tr>
<td>WPC4</td>
<td>1.03 (0.04)</td>
<td>43.1 (1.61) C</td>
<td>4415.0 (82.8) C</td>
<td></td>
</tr>
<tr>
<td>WPFC5</td>
<td>1.02 (0.01)</td>
<td>41.9 (1.32) C</td>
<td>4355.3 (68.5) C</td>
<td></td>
</tr>
</tbody>
</table>
Groups with same letters in column indicate that there was no statistical difference ($p < 0.01$) between the samples according to the Duncan’s multiply range test. Values in parentheses are standard deviations.

It was found that effect of wood was notable in material properties of the composites. Wood is a lignocellulosic material made up of three major constituents (cellulose: 42–44%, hemicelluloses: 27–28%, and lignin: 24–28%) with some minor constituents (extractives: 3–4%) [Walker, 2004]. The major portion of wood is crystalline cellulose. The aligned fibril structure of the cellulose along with strong hydrogen bond has high stiffness thus addition of the wood flour can increase the stiffness of the thermoplastic based composites. The flexural strength of the composite containing the wood flour was significantly higher than that in composites containing the cone flour. This could be explained by a strong interfacial adhesion between the PP and the wood flour due to their higher cellulose content, since cellulose is the main component providing the wood’s strength and structural stability. Lignin as an amorphous polymer does not greatly contribute to the mechanical properties of wood flour but plays an important role in binding the cellulose fibrils that allows efficient stress transfer to the cellulose molecules. According to Bledzki et al. [1998] and Bledzki and Gassan [1999], an increase in the composite’s strength can be ascribed to higher cellulose and lignin contents, as well as better dispersion and adhesion to the matrix. The better interfacial adhesion between wood flour and PP, due to the high cellulose content, increases the toughness or ductility [Marcovich and Villar, 2003]. Moreover, the ratio of lignin and cellulose can also play a role - the higher it is, the better the interfacial adhesion that can be achieved since lignin acts as a natural adhesive within the cellulose [Shebani et al., 2009]. Hence, wood filler increases the stiffness of the polymer without excessively increasing the density [Adhikary et al., 2008]. The addition of the coupling agent improves the compatibility between the lignocellulosic material and the PP through esterification and thus reduced the WA and improved the dimensional stability and mechanical properties [Matuana et al., 2001].

Extractives have a significant effect on adhesive bonding performance of wood. They negatively affect bonding performance between wood fibers or particles. In a previous study, extractives in wood flour on the mechanical properties of wood-polypropylene (PP) composites had a significant effect on the flexural properties of the composites [Saputra et al., 2004]. Significant differences were also observed in stiffness between extracted Douglas fir wood-PP and unextracted wood-PP composites. Based on the results of flexural strength, it can be stated that the extractives in the pine cone had a similar effect on the bond strength between cone flour and PP. The pine cone contains lower holocellulose which has a large number of polar hydroxyl groups and higher extractives than in wood. Amounts of holocellulose (hemicelluloses and cellulose) and lignin in the stone pine cone were found as 67.6% and 37.2% based on the weight of extracted wood, respectively [Gonultas, 2008]. Contents of extraction substances in the cone have a big role, as they determine bond quality. The stone pine cone contains significant amounts of ethanol/toluene extractives (29.2%) as compared to contents of such substances, 5.1% for sapwood and 22.6% for heartwood, in its wood. Reduction in the flexural properties and water resistance of the WPC composites containing the cone flour can be attributed to higher contents of the extractives in the pine cone than in the wood.
CONCLUSIONS

The pine cone has been demonstrated capable of serving as new reinforcing filler in the manufacturing of thermoplastic polymer composites. The flexural properties and water resistance of the composites were negatively affected by increasing cone flour content. We concluded that extractives in the cone flour on the mechanical properties of wood-polypropylene (PP) composites had a significant effect on the flexural properties of the composites. Based on the findings obtained from the present study, with the addition of 10% cone flour to WPC, the water resistance and flexural properties did not significantly affect as compared to WPC made from wood flour.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the material support of Turkish General Directorate of Forestry, Forest District Sample in Belgrade Forest in Sariyer, Istanbul, Turkey. Further acknowledgement goes to Research Fund of Istanbul University for the laboratory equipment used in the panel manufacture and testing of the panels.

REFERENCES


