Use of black locust/poplar wood as filler in thermoplastic composites

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Abstract: Wood plastic composites (WPCs) were produced from different mixtures (up to 45% by weight) of poplar (Populus alba L.) and pruning branches of black locust (Robinia pseudoacacia) wood flours, polypropylene (53 wt.%), and maleic anhydride-grafted polypropylene (2 wt.%). Weight loss, flexural strength (MOR), flexural modulus (MOE), notched impact strength (IS), water absorption (WA), and thickness swelling (TS) of WPCs after 24 h of immersion in distilled water were determined before and after incubation with white-rot fungus (Trametes versicolor) for 7 weeks. The MOR and MOE increased with an increase in poplar wood in the WPC. The notched IS decreased with an increase in black locust wood and poplar wood in the WPC. The weight loss in WPCs exposed to white-rot fungus was minimal for WPCs with a high amount of black locust pruning branch flour. The MOR and MOE declined after incubation with fungus. Fungal decay had a significant influence on the notched IS. Furthermore, the results indicated that the WA and TS of white-rotted WPCs for all the WPC formulations were significantly higher than those of unrotted WPCs.

Key words: Biological durability, wood plastic composites, durable wood, technological properties, water resistance

1. Introduction
Wood plastic composites (WPCs) are increasingly used for exterior applications, which can lead to dimensional changes and fungal deterioration. WPCs have wide utilization in building construction and are used in siding and decks, windows, outdoor furniture, and other semistructural products (Mengeloğlu and Karakuş, 2008; Kord and Hosseinihashemi, 2014). However, WPCs are produced from various species of hardwoods, softwoods, and agricultural waste (up to 30%-70% by weight). Thus, WPCs have limited biological durability (Kim et al., 2008; Fabiyi and McDonald, 2010; Xu et al., 2013). Previous studies reported that wood-based panels such as particleboard and fiberboard prepared from durable species such as black locust and oak wood had a high biological durability and could be used in exterior expositions (Kamdem and Sean, 1994; Reinprecht and Zubková, 2010). WPCs for exteriors, with or without ground contact, should be adequately resistant against moisture and wood-destroying basidiomycetes. There is a commercial WPC lumber manufacturer in North America that uses western red cedar, which has biological durability, in the WPC formulation (http://www.choicedek.com/clasbul2.htm).

Currently, the most common preservative used in WPCs in North America is zinc borate due to environmental issues. Zinc borate is applied either as a powder or an emulsion/dispersion into the WPC (Laks, 1999; Badritala et al., 2013). Major problems with preservative chemicals used in WPCs include leachability and toxicity. Badritala et al. (2013) found that the flexural and tensile properties and impact strength of WPCs containing zinc borate were less than those of the untreated WPCs. They reported that these phenomena could be attributed to poor compatibility between the wood and polymer matrix due to the crystalline deposits of zinc borate and the dispersion and precipitation of zinc borate particles in the cavities of WPCs. The formation of agglomeration can cause a reduction in interfacial adhesion between the wood flour and polymer matrix (Ayrilmis et al., 2011, 2012a, 2012b; Kurt and Mengeloğlu, 2011).

Black locust (Robinia pseudoacacia L.) is an important tree species due to its excellent durability and very good physical and mechanical properties (Stringer and Olson, 1987; Barrett et al., 1990; Molnár, 1995; Adamopoulos and Voulgaridis, 2003). However, some disadvantages of black locust wood such as crooked stems and smaller stem diameter, and irregular heartwood color (from yellow to green-olive hue), were introduced by the Tequbloc project (Inco-Copernicus, 2000). The increased resistance of black locust wood against biological attack is mainly due to its chemical composition (Adamopoulos et al., 2005).
The heartwood of black locust has high amounts of condensate tannins (Reinprecht, 1992) and resorcinol (Hosseinihashemi and Kanani, 2012; Hosseinihashemi et al., 2013). Roux and Paulus (1962) determined more than 14 flavonoids in the heartwood of black locust wood. Magell et al. (1994) exactly quantified the presence of two flavonoids in black locust wood: dihydroflavonol, dihydrorobinetin (3,7,3',4',5'–pentahydroxy dihydroflavonol) and flavonol, robinetin. Dünnisch et al. (2006) described two significant accessory compounds, dihydrorobinetin and robinetin, which increase the durability of black locust wood. The noted substances are toxic against wood-destroying fungi, and for this reason heartwood of black locust is highly resistant against the decay processes (i.e. EN 350-2; European Standardization Organizations, 1994). The proportion of these substances in heartwood of black locust increases with the age of the tree, but they are not found in sapwood. Sapwood of black locust does not resist decay attack and is in the 5th durability class according to EN 350-2 (Reinprecht and Zubková, 2010).

Black locust wood is one of the most suitable species for production of laminated veneer lumber in terms of its durability and density (Nzokou et al., 2005; Zubková, 2009). Based on an extensive literature search, the potential use of black locust wood in production of WPC has not been extensively investigated. The aim of this work was to evaluate the technological properties and biological durability of undecayed and decayed (white-rot fungus) WPCs produced from black locust wood flour and polypropylene with a coupling agent and to compare their properties with the WPCs produced with poplar wood flour.

2. Materials and methods

2.1. Materials

Three logs (0.5 m) from poplar tree (Populus alba L.) were cut at breast height, sawed into boards 3 cm thick, and stored at 20 °C and 65% relative humidity (RH). The pruning branches from black locust (Robinia pseudoacacia L.) and poplar boards were cut into small particles and chopped using a laboratory mill (Wieser model WGLS 200/200) to obtain black locust wood flour (BWF) and poplar wood flour (PWF). The flour size was between 40 and 60 mesh. The BWF and PWF were dried in an oven at 103 ± 2 °C for 24 h to reach 0%–1% moisture content and then stored in sealed plastic bags until blending with polypropylene (PP).

Homopolymer PP was obtained from Arak Petrochemical Company in Iran. The melt flow rate of PP (trade name: P10800) was 7–10 g/10 min at 190 °C. Maleic anhydride-grafted polypropylene (MAPP; Sigma-Aldrich 427845) was used as a coupling agent. The components of each WPC formulation (PP, MAPP, BWF, and PWF) were premixed according to Table 1.

2.2. Preparation of injection molded composite specimens

The premixed components were blended in a counter rotating twin-screw extruder (Dr. Collin GmbH) at a screw speed of 60 rpm at 180 °C. The mixture was removed from the mixing bowl, cooled in water, and granulated into pellets. The pellets were dried at 85 °C for 24 h before the injection molding was done. Finally, the pellets were injection molded (Imen Machine Co., Iran) at 180–190 °C and a pressure of 10 MPa.

The specimens were conditioned at 23 °C and 50% RH for at least 40 h, according to ASTM D 618-99, prior to testing. The flexural properties (ASTM D 790-10) and notched impact strength (ASTM D 256-10) were determined according to ASTM standards.

2.3. Fungus culture

Purified turkey tail fungus (T. versicolor) was transferred to petri dishes containing malt extract agar under a sterile hood using sterile pincers. The dishes were kept at 23 °C for 1 week until the culture medium was fully covered by the fungus. The cultured fungus was transferred to petri dishes containing the culture medium that were incubated for 1 week at 23 °C.

Table 1. WPC formulations for the composition of the studied formulations.

<table>
<thead>
<tr>
<th>WPC code</th>
<th>Black locust wood flour (wt.%)</th>
<th>Poplar wood flour (wt.%)</th>
<th>PP (wt.%)</th>
<th>MAPP (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B45%PP53%</td>
<td>45</td>
<td>0</td>
<td>53</td>
<td>2</td>
</tr>
<tr>
<td>B30%P15%PP53%</td>
<td>30</td>
<td>15</td>
<td>53</td>
<td>2</td>
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<tr>
<td>B22.5%P22.5%PP53%</td>
<td>22.5</td>
<td>22.5</td>
<td>53</td>
<td>2</td>
</tr>
<tr>
<td>B15%P30%PP53%</td>
<td>15</td>
<td>30</td>
<td>53</td>
<td>2</td>
</tr>
<tr>
<td>P45%PP53%</td>
<td>0</td>
<td>45</td>
<td>53</td>
<td>2</td>
</tr>
</tbody>
</table>

2.4. Contamination of WPC specimens with the purified fungus
The composite specimens were placed in the petri dishes. The dishes containing the fungus and the composite specimens were stored in an incubator for 7 weeks at 23 °C and 75% RH.

2.5. Weight loss
Dry weights of the specimens were measured after 24 h at 103 ± 2 °C. Weight losses were calculated using the following formula (1):

\[
\text{Weight loss (\%)} = \left( \frac{M_b - M_a}{M_b} \right) \times 100, \quad (1)
\]
where \(M_b\) and \(M_a\) denote the oven-dried weights prior to and after incubation with fungus, respectively.

2.6. Determination of water resistance and mechanical properties
Water absorption and thickness swelling of the WPCs was determined according to the ASTM D 570 standard. The water absorption and thickness swelling of the WPC specimens was determined after 24 h of immersion in distilled water at room temperature. Four specimens of each WPC group were conditioned at 50% RH at 23 °C in a chamber. The conditioned specimens were weighed with a precision of 0.001 g, and then they were placed in distilled water. After the weight measurements, the thickness of the same specimens was measured to the nearest 0.001 mm immediately. At the end of the immersion period (24 h), the specimens were removed from the distilled water, the surface water was wiped using blotting paper, and wet mass and thickness were measured.

Three-point flexural modulus and strength were tested according to the ASTM D 790 specification of 1990. The notched Izod impact tests were carried out according to ASTM D 256 (1991). Four specimens were used for each type of WPC.

2.7. Statistical analysis
Statistical analysis was conducted using SPSS in conjunction with analysis of variance (ANOVA). Significant differences (\(P < 0.05\)) among the average values of the WPC groups were determined using Duncan's multiple range tests.

3. Results and discussion
3.1. Weight loss
The influence of the BWF and PWF contents on the weight loss of WPCs exposed to the white-rot fungus is shown in Figure 1. The weight loss in the WPC specimens decreased with increasing BWF content. The lowest weight loss, with a value of 0.12%, was found in the specimens containing 22.5 wt.% BWF and 22.5 wt.% PWF. The weight loss of the specimens with BWF was significantly lower than weight loss in other specimens. This result was consistent with previous studies (Kamdem and Sean, 2001).

Figure 1. The averages and standard deviations for the weight loss measurements of the WPCs. Bars with different letters indicate that the results of WPC groups are significantly different from each other.
Hosseinihashemi et al. investigated the weight loss of phenolic-bonded particleboards. They reported that the incorporation of 20 to 40 wt.% black locust wood enhanced internal bond strength, linear expansion, and decay resistance of particleboards with a minimum reduction in flexural strength and modulus. The WPCs produced with black locust wood flour were more durable against white-rot fungus *Trametes versicolor* (average weight loss: 0.18%) than WPCs produced with PWF (average weight loss: 0.20%–0.44%). Consequently, the presence of the BWF made the WPC less accessible for the fungus through a reduction of nutrients and gain in toxic material.

The SEM micrographs showing the fracture surfaces of the WPCs produced with various amounts of BWF and PWF are presented in Figure 2. The extent of degradation increased with increasing PWF. These results were consistent with the observed losses of the mass. Structural decomposition of WPCs produced with PWF was considerable after 7 weeks of exposure.

### 3.2. Mechanical properties

The results of Duncan’s multiple range tests indicated that the blend of BWF and PWF significantly affected the flexural strength of the WPCs. The increase in PWF improved the flexural strength to fewer degrees than it did the flexural modulus. In general, the optimum results for flexural and tensile properties were found in WPCs produced with 30% BWF/15% PWF and 22.5% BWF/22.5% PWF, respectively. There was a significant difference in the flexural modulus between the WPCs produced with BWF and PWF. The significant differences (P < 0.05) among some of the WPC groups for the flexural properties are shown in Figures 3 and 4. The different letter designations in Figures 3 and 4 mean that there were significant differences in the mechanical properties of the WPC groups according to Duncan’s multiple range test.

The flexural strength and flexural modulus of WPCs produced with PWF or mixtures of PWF and BWF were higher than those of WPCs produced with 45% BWF (Figures 3 and 4). This was probably due to an increase in the amount of extractives in the BWF, which decreased interfacial compatibility between the wood and polymer matrix. Extractives in BWF increase the polarity of the wood, which decreases the compatibility of the blend of the thermoplastic composite (Fan et al., 2010). This incompatibility produces poor interfacial adhesion between the polymer matrix and wood filler, which results in a reduction in mechanical properties because stress cannot be transferred properly from the matrix to the filler. Wood flour with lower polarity is more compatible with thermoplastics, resulting in better dispersion of wood flour in the polymer matrix (Hosseinihashemi and Kanani, 2012). Fungal decay had a significant influence on the flexural strength and modulus of the WPCs. A similar result was observed for the decayed BWF- and PWF-filled thermoplastic composites exposed to white-rot fungus.

![SEM micrographs](image-url)
**Figure 3.** The averages and standard deviations for flexural strength measurements of the WPCs. Results with different letters are significantly different (Ud: undecayed, D: decayed).

**Figure 4.** The averages and standard deviations for flexural modulus measurements of the WPCs. Results with different letters are significantly different.
The flexural properties of the decayed WPCs were lower than those of the undecayed WPCs, but the decrements were not significant. The decrement in the mechanical properties of the decayed WPCs was mainly due to the degradation of wood components by white-rot fungus (Figures 3 and 4).

The results of Duncan’s multiple range tests indicated that different mixtures of the BWF and PWF had a significant effect on the notched impact strength of the WPCs. There were no significant differences in the impact strength values of the WPCs produced with 45% BWF and 45% PWF. As shown in Figure 5, the WPCs produced with 45% BWF showed lower impact strength than other WPC specimens. The impact resistance of the WPCs produced with a mixture of 22.5% BWF and 22.5% PWF increased by 22% over the WPCs produced with 45% BWF. Furthermore, the WPCs produced with 45% BWF had slightly lower impact resistance than the WPCs produced with 45% PWF. Fungal decay decreased the impact strength of the WPCs, but there was no significant effect of fungal decay on the impact strength of WPCs produced with BWF or PWF.

3.3. Water absorption
Water absorption and thickness swelling of the WPCs are summarized in Table 2. Water absorption and thickness swelling of the undecayed WPCs were considerably lower than those of the decayed WPCs. For example, the water absorption of the decayed WPCs produced with a mixture of 22.5% BWF and 22.5% PWF was 2.43%, while it was 1.22% for the undecayed WPC. Results of Duncan’s multiple range tests for thickness swelling and water absorption are shown by letters in Table 2. The water absorption values were significantly lower than the thickness swelling values. As the amount of BWF increased in the composition, the water absorption of the undecayed and decayed WPC specimens increased. There was no significant difference in the water absorption between the WPC produced with black locust (45 wt.%) and poplar (45 wt.%) WPC, while a significant difference was not observed for the undecayed WPCs. There was no significant difference in the water absorption values between undecayed and decayed WPC specimens produced with BWF (45 wt.%) or PWF (45 wt.%). Similar results were observed for thickness swelling. However, some significant differences in the thickness swelling and water absorption were observed for WPCs produced with different mixtures of BWF and PWF. The results of thickness swelling and water absorption showed that the compatibility (interfacial bonding) between the polymer matrix and BWF was lower than that of PWF. As the amount of BWF increased in the composition, compatibility in the interfacial area between the wood flour and polymer matrix decreased. This was confirmed by the results of flexural properties and impact strength. The extractives that increase the polarity of wood in the

![Figure 5. The average and standard deviation for impact strength measurements of the WPCs. Results with different letters are significantly different.](image)
BWF are higher than those in PWF (Csanády et al., 2015). This could decrease the compatibility between the wood and polymer matrix, which can result in lower mechanical properties.

3.4. Conclusions
The technological properties and biological durability of WPCs prepared from black locust pruning branches and poplar wood were investigated in this work. The decay resistance of the WPCs against the white-rot fungus *Trametes versicolor* improved with increasing amounts of black locust wood in the wood mixture. At the same wood flour content, flexural properties and notched impact bending strength of WPCs produced with BWF were higher than those in WPCs produced with PWF, while water resistance decreased. As expected, the mechanical properties and water resistance of decayed WPCs were lower than those of the undecayed WPCs, but the decrement was not significant. Based on the findings obtained from the present study, it is suggested that BWF can be efficiently used to increase biological durability of WPCs against wood-destroying basidiomycetes, particularly in WPCs exposed to ground contact.

Table 2. The averages and standard deviations for water absorption and thickness swelling of the WPCs.

<table>
<thead>
<tr>
<th>Test type</th>
<th>WPC codes</th>
<th>Immersion time (24 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water absorption (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B45%PP53%-undecayed</td>
<td>1.42 ± 0.010 b</td>
<td></td>
</tr>
<tr>
<td>B30%P15%PP53%-undecayed</td>
<td>1.71 ± 0.015 c</td>
<td></td>
</tr>
<tr>
<td>B22.5%P22.5%PP53%-undecayed</td>
<td>1.22 ± 0.035 a</td>
<td></td>
</tr>
<tr>
<td>B15%P30%PP53%-undecayed</td>
<td>1.44 ± 0.286 b</td>
<td></td>
</tr>
<tr>
<td>P45%PP53%-undecayed</td>
<td>1.30 ± 0.085 abc</td>
<td></td>
</tr>
<tr>
<td>B45%PP53%-decayed</td>
<td>2.81 ± 0.072 c</td>
<td></td>
</tr>
<tr>
<td>B30%P15%PP53%-decayed</td>
<td>2.97 ± 0.026 ef</td>
<td></td>
</tr>
<tr>
<td>B22.5%P22.5%PP53%-decayed</td>
<td>2.43 ± 0.119 d</td>
<td></td>
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<tr>
<td>B15%P30%PP53%-decayed</td>
<td>3.04 ± 0.020 f</td>
<td></td>
</tr>
<tr>
<td>P45%PP53%-decayed</td>
<td>2.24 ± 0.119 d</td>
<td></td>
</tr>
<tr>
<td>Thickness swelling (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B45%PP53%-undecayed</td>
<td>2.18 ± 0.015 c</td>
<td></td>
</tr>
<tr>
<td>B30%P15%PP53%-undecayed</td>
<td>1.33 ± 0.015 c</td>
<td></td>
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<tr>
<td>B22.5%P22.5%PP53%-undecayed</td>
<td>1.72 ± 0.015 b</td>
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<td>B15%P30%PP53%-undecayed</td>
<td>3.11 ± 0.015 c</td>
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<td>P45%PP53%-undecayed</td>
<td>2.17 ± 0.100 c</td>
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<td>3.20 ± 0.106 c</td>
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<td>B30%P15%PP53%-decayed</td>
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<td>B22.5%P22.5%PP53%-decayed</td>
<td>2.74 ± 0.198 d</td>
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<tr>
<td>B15%P30%PP53%-decayed</td>
<td>3.81 ± 0.015 f</td>
<td></td>
</tr>
<tr>
<td>P45%PP53%-decayed</td>
<td>3.17 ± 0.042 f</td>
<td></td>
</tr>
</tbody>
</table>

*Same letters indicate that there is no statistical difference (P < 0.05) between the WPC types according to Duncan’s multiple range test.

References


