DECAY RESISTANCE, THERMAL DEGRADATION, TENSILE AND FLEXURAL PROPERTIES OF SISAL CARBON HYBRID COMPOSITES

Mürşit Tufan1*, Selçuk Akbaş1, Mustafa Aslan2

ABSTRACT

Sisal-carbon hybrid composites were produced from mixtures having different weight ratios of sisal, carbon fibers and recycled polypropylene. All formulations were tested and evaluated for tensile and flexural properties. In addition, the thermal stability of the sisal-carbon hybrid composites were examined via thermogravimetric analysis and decay tests were conducted to determine the degradation of the hybrid composites. Results showed that the biological durability and mechanical and thermal properties improved with the increasing weight ratios of carbon fiber in the hybrid composites. According to the mechanical tests, the optimum hybrid composite formulation was found to be 12% sisal fiber + 28% carbon fiber + 60% rPP.

Keywords: Coniophora puteana, mechanical properties, modulus of elasticity, modulus of rupture, Pinus sylvestris, thermogravimetric analysis, Trametes versicolor.

INTRODUCTION

Wood polymer composites (WPCs) are used extensively due to their outstanding properties such as enhanced strength, stiffness and creep resistance as well as their high dimensional stability. As a result, their market shares have grown dramatically (18% in North America and 14% in Europe) over the last several years. The WPCs may consist of organic fiber (wood and annual plant fiber or flours) and polymeric materials such as polyethylene, polypropylene or polyvinyl chloride (Jarukumjorn and Suppakarn 2009, Nourbakhsh and Ashori 2010, Moreno et al. 2013). When used in WPCs, organic fillers provide lower density, less abrasiveness and less energy consumption as well as being inexpensive, non-hazardous and renewable. Hence, they can be used as an excellent reinforcement for thermoplastics (Khanam et al. 2010). However, these fillers can be biodegradable over time, and their incompatibility with the hydrophobic thermoplastic matrix and poor resistance to moisture cause dimensional changes, thus restricting their potential use in WPCs (Matuana et al. 1998, Kim et al. 2008). The addition of small amounts of synthetic fibers (carbon, glass, etc.) can improve the technological properties of WPCs for industrial applications. These fibers provide material with high specific strength, resistance, rigidity, biological durability and high thermal stability. However, these fillers are costly and abrasive to the processing equipment (Caulfield et al. 2005, La Manita et al. 2005, Sharma et al. 2014). Hybrid composites are fabricated with a combination of organic and synthetic fibers to produce materials with the advantages of the desired high technological features. The incorporation of natural fibers such as sisal/jute with synthetic fibers such as glass/carbon in composites has gained increasing attention in many studies (Ramesh et al. 2013, Bajracharya et al. 2014). In this study, sisal-carbon hybrid composites were produced with different sisal-carbon rates and their mechanical and thermal properties and biological durability were investigated and compared in detail.

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Received: 08.10.2015 Accepted: 16.07.2016
MATERIALS AND METHODS

Materials

Recycled polypropylene (rPP), sisal fiber (SF) and carbon fiber (CF) were used as the thermoplastic matrix, organic and synthetic fillers, respectively. The recycled polypropylene (rPP) was obtained from Ayan Plastik Industry and Trade Co. Ltd., Samsun, Turkey. The fibers, in the form of short, recycled fibers left over from final manufacturing processes, were provided by two Turkish companies: the Esenteks Co., Ltd., for the sisal fibers and Dowaksa, Inc., for the carbon fibers (CF). The density of the SF and CF were 1.43 and 1.5 g/cm$^3$, respectively. The experimental design of the study is presented in Table 1.

Table 1. Composition of the polymer hybrid composites.

<table>
<thead>
<tr>
<th>Group ID</th>
<th>Sisal (%)</th>
<th>Carbon (%)</th>
<th>rPP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>40</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>B</td>
<td>33</td>
<td>7</td>
<td>60</td>
</tr>
<tr>
<td>C</td>
<td>26</td>
<td>14</td>
<td>60</td>
</tr>
<tr>
<td>D</td>
<td>19</td>
<td>21</td>
<td>60</td>
</tr>
<tr>
<td>E</td>
<td>12</td>
<td>28</td>
<td>60</td>
</tr>
<tr>
<td>F</td>
<td>5</td>
<td>35</td>
<td>60</td>
</tr>
</tbody>
</table>

Methods

Preparation of compression-molded polymer composites

Using a Willey mill, the air-dried sisal fibers were ground into small particles which were then screened to 60- and 80-mesh size and dried to oven-dry moisture level. The SF flour, CF and rPP granulates were processed in a co-rotating single-screw extruder (RONDOL 3212). The four barrel temperature zones of the extruder were controlled at 165-170-175-180 ºC, respectively. The extruded strand samples were collected, cooled and granulated into pellets. Finally, the pellets were compression molded in a hot press for 3 min at 175 ºC.

Mechanical properties

The property evaluations of the manufactured hybrid composites were conducted in a climate-controlled testing laboratory at 23 ºC and 65% RH. Flexural and tensile properties were determined using specimens with the dimensions of 150 mm (length) × 13 mm (width) × 5 mm (thickness). The modulus of rupture (MOR) and modulus of elasticity (MOE) were measured in a three-point bending test in accordance with ASTM D 790 (2004). Dog-bone shaped (type III) samples were used for the tensile tests, which were carried out according to ASTM D 638 (2004). The specimens were tested with a crosshead speed of 2 mm/min and all tests were performed on a Zwick 10kN Universal Testing Machine (Zwick Inc., Germany). Seven test samples for each group were tested in order to get average values of tensile and flexural properties.

Thermogravimetry and differential scanning calorimetry

The thermal behavior of the rPP and hybrid composites was examined using the PelkinElmer STA 6000 thermal analyzer. The test samples, each weighting 3-5 mg, were heated in an aluminum crucible from room temperature to 600 ºC with the heating rate of 10 ºC/min and kept at this temperature for 2 min to monitor thermal history. The thermal decomposition temperature of each sample was examined under nitrogen with a 30 mL/min flow rate.
## Decay tests

Hybrid composites and Scots pine (*Pinus sylvestris* L.) solid wood specimens were carried out according to European standard EN 113. Six pieces of samples with size 20 (length) x 20 (width) x 5 (thick) mm were prepared each fungus. The specimens were dried at 103±2 °C for 24 h and weighed to the nearest 0.01 g to determine the initial weight (\(M_1\)). One white rot fungi, *Trametes versicolor* L.Pilat (Mad-697) and one brown rot fungi, *Coniophora puteana* (Schumach.: Fr.) P. Karst (Mad-15) were used for the decay tests. All test fungi were grown on a malt extract agar medium (concentration 48g/L). The solution was autoclaved at 120 °C for 20 min and poured into petri dishes. After cooling of the medium, a mycelium plug was transferred to the center of each petri dish. The dishes were incubated at 24 ± 2 °C and 75% RH until the fungal mycelium reached the edges of the dishes. Six specimens of each formulation were sterilized in an autoclave for 30 min at 121 °C and placed in the pre-inoculated petri dishes. At the end of the exposure time (16 weeks), the surfaces of the specimens were cleaned. The specimens were then dried at 103 ± 2 °C for 24 hours (\(M_2\)) for the calculation of the mass loss. The percent mass loss (ML) was calculated as follows, \(\text{ML(%) = \left(\frac{M_1-M_2}{M_1}\right) \times 100}\).

A set of Scots pine (*Pinus sylvestris*) specimens were also tested as control against both fungi used in this experiment.

## RESULTS AND DISCUSSION

### Mechanical properties

The effects of filler type and rate on flexural and tensile properties are shown in Table 2. All the hybrid composites had higher flexural and tensile properties than the SF composites (group ID A). Statistical analysis showed that filler type and rate significantly affected the flexural and tensile properties. Flexural and tensile strength values increased sharply with the rate of CF addition up to 28% (Group ID E). Flexural and tensile strength values also increased in the composites where the CF rate was 35%; however, this increase was not statistically significant. A similar trend was observed with the tensile modulus values.

The flexural modulus values were improved in the hybrid composites with the addition of CF content; however, the increase was not significant with the CF ratio of more than 21% (Group ID D).

It is recognized that the addition of synthetic fibers in hybrid composites causes substantial changes in the mechanical properties (Abu *et al.* 2005, Indicula *et al.* 2005, Haneefa *et al.* 2008, Khanam *et al.* 2010). As shown in Table 2, it is clear that the flexural and tensile properties in the hybrid composites were enhanced with the increase the CF content.
Table 2. Mechanical properties of hybrid composites.

<table>
<thead>
<tr>
<th>Group ID</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30.33 a (3.46)</td>
<td>2.55 a (0.14)</td>
<td>15.24 a (0.68)</td>
<td>3.05 a (0.08)</td>
</tr>
<tr>
<td>B</td>
<td>31.39 ab (1.01)</td>
<td>2.76 a (0.30)</td>
<td>15.60 a (0.79)</td>
<td>3.10 a (0.33)</td>
</tr>
<tr>
<td>C</td>
<td>33.92 b (0.47)</td>
<td>3.17 b (0.21)</td>
<td>17.07 a (1.05)</td>
<td>3.31 ab (0.23)</td>
</tr>
<tr>
<td>D</td>
<td>36.92 c (2.61)</td>
<td>3.81 c (0.36)</td>
<td>17.25 ab (0.37)</td>
<td>3.66 b (0.34)</td>
</tr>
<tr>
<td>E</td>
<td>43.59 d (1.24)</td>
<td>4.03 c (0.46)</td>
<td>20.85 c (0.40)</td>
<td>3.86 c (0.58)</td>
</tr>
<tr>
<td>F</td>
<td>45.33 d (2.14)</td>
<td>4.06 c (0.33)</td>
<td>22.40 c (2.49)</td>
<td>4.12 c (0.31)</td>
</tr>
</tbody>
</table>

Note:
- The value in parenthesis is the standard deviation.
- Each value is the average of seven samples tested.
- Groups with same letters in column indicate that there is no statistical difference (p < 0.05).

Thermogravimetric analysis

The thermal behavior of the rPP and hybrid composites was evaluated using thermogravimetric analysis (TGA). The results of the TGA thermographs of the samples are shown in Figure 1, where two main decomposition peak areas can be seen. The first decomposition peak starts at around 200-220 ºC. Lignocellulosic fibers are known to have low thermal stability, and the degradation temperatures of hemicelluloses, lignin and cellulose start at 180, 200 and 210 ºC, respectively (Jarukumjorn and Suppakarn 2009, Tufan et al. 2015). With the increased CF content, the decomposition value of the hybrid composites was enhanced. The second peak area gives the highest decomposition temperatures as 440-460 ºC. It is known that PP degrades around this temperature. In addition, after the final decomposition temperature, the residual mass amount in the hybrid composites increased with the increase in the CF rate (Mallick 2008, Paiva et al. 2009).

Figure 1. TGA results of rPP and hybrid composites.
Decay resistance, thermal degradation .: Tufan et al.

Table 3 shows the mean mass loss rate of the hybrid composites and Scots pine control after exposure to white-rot (*Trametes versicolor*) and brown-rot (*Coniophora puteana*) fungi for 16 weeks. In general, the mass loss rate was very limited in the hybrid composites, while that of the control samples (Scots pine) was found to be very high. The highest mass loss rate was found in the control samples; at 29.35% for white rot and 40.99% for brown rot. These results demonstrated that the decay activity was acceptable for test conditions. Moreover, this rate did not exceed 6.37% and 4.44% for white and brown rot fungi, respectively, in any of the hybrid composites. The mass loss rate decreased in all hybrid composites with the addition of CF. The smallest mass losses found for white rot and brown rot were 0.14% and 0.78%, respectively (GroupID F). This rate increased to 2.50% and 3.78% (GroupID A) with the increase of the sisal fiber ratio in the composites. Previous literature has indicated that wood or natural fiber polymer composites are not fully protected against fungal attack. Composites with higher wood flour or fiber content in particular exhibit increasing mass loss. Due to less encapsulation, increasing the rate of wood flour or natural fiber in polymer composites causes poor moisture resistance and this leads to greater decay susceptibility (Morris and Cooper 1998, Verhey and Laks 2002, Clemson and Ibach 2004). Similar results were observed in the current study. The SF ratio negatively affected the fungal resistance of the hybrid composites. It is accepted that CF is more durable against moisture and fungi degradation than SF. Studies have reported that water absorption decreases in hybrid composites using CF (Thwe and Liao 2003, Samal et al. 2009). Therefore, in this study, increasing the CF rate resulted in hybrid composites which were more resistant to fungi.

<table>
<thead>
<tr>
<th>Group ID</th>
<th><em>Trametes versicolor</em> (%)</th>
<th><em>Coniophora puteana</em> (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.44 b (0.43)</td>
<td>6.37 f (0.85)</td>
</tr>
<tr>
<td>B</td>
<td>2.50 a (0.34)</td>
<td>3.78 e (0.58)</td>
</tr>
<tr>
<td>C</td>
<td>1.68 a (0.40)</td>
<td>2.90 cde (0.47)</td>
</tr>
<tr>
<td>D</td>
<td>0.63 a (0.47)</td>
<td>1.68 abc (0.56)</td>
</tr>
<tr>
<td>E</td>
<td>0.85 a (0.23)</td>
<td>1.92 bcd (0.54)</td>
</tr>
<tr>
<td>F</td>
<td>0.14 a (0.17)</td>
<td>0.78 ab (0.38)</td>
</tr>
<tr>
<td>Scots pine</td>
<td>29.35 c (6.98)</td>
<td>40.99 g (4.20)</td>
</tr>
</tbody>
</table>

Note:
- The value in parenthesis is the standard deviation.
- Each value is the average of six samples tested.
- Groups with same letters in column indicate that there is no statistical difference (p < 0.05).
CONCLUSIONS

Based on the results of this study, the following facts were observed.

The flexural and tensile properties of the hybrid composites were increased with the addition of CF. The optimum ratio of CF in the produced composites was determined as 28%; however, no significant improvement in mechanical properties was seen with CF ratios higher than 28%.

From the results it can be concluded that the hybrid composites exhibited better biological performance than the SF composites.

The addition of CF improved the thermal stability of the hybrid composites. The thermal decomposition values of the hybrid composites were enhanced with increased CF content.

ACKNOWLEDGEMENTS

This study was supported by BAP (Directory of Scientific Research Projects of Artvin Çoruh University) under grant number 2014.F11.02.03.

REFERENCES


