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Development of biodegradable composites based on wood waste flour and thermoplastic starch

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ABSTRACT: Biodegradable composites were prepared from wood flour of sawmill residues and a thermoplastic starch (Mater-Bi™ and glycerol). For the preparation of the composites flour from sawmills of 4 wood species (spruce, pine, beech and poplar), 3 particle sizes (<150 µm, 150-250 µm and 250-750 µm) and in 6 proportions (10, 20, 30, 40, 50 and 60% wt) was used. The composites were characterized by means of mechanical property measurements, scanning electron microscopy (SEM), water absorption, thermal stability and biodegradation studies. Addition of wood flour to TPS increased significantly tensile strength, modulus of elasticity, elongation and thermal stability and decreased water absorption and biodegradation rate of the composites. Almost all the properties of the composites increased with increasing wood flour content and decreasing particle size of the flour. Tensile strength increased up to 50% wt but decreased at 60% wt content of wood flour. The softwood species (spruce, pine) gave better mechanical, thermal and water absorption properties, but lower biodegradation rate than the hardwood species (beech, poplar).

Keywords: Biodegradable composites, starch; wood flour; wood residues, biodegradation.
INTRODUCTION

Most plastics based on petrochemicals are designed and manufactured to withstand environmental degradation. This fact has led to an increase in the amount of plastic wastes, which comprises a significant source of environmental pollution. Although efforts to recycle used plastics in order to reduce their volume in landfills have been improved significantly, recycling would be neither practical nor economical for certain applications, such as packaging. Besides, it is widely accepted that the use of long-lasting and strong polymers for short-lived applications (such as low strength packaging, catering, surgery or hygiene applications) is not entirely adequate and leads to unjustifiable pollution. All these reasons have increased the interest in developing of environmentally friendly biodegradable plastics.

The natural fiber-plastic composites that consist of a polymer matrix (mainly polyolefins) in combination with a cellulose or lignocellulosic fiber (e.g. wood plastic composites-WPC), are not fully biodegradable. Recent research efforts are oriented toward replacing the non-biodegradable polymer matrices with natural polymers such as starch, polylactic acid (PLA), polyhydroxyalcanoates (PHA).

One of the most promising raw material for the production of biodegradable plastics is starch, which a natural renewable polysaccharide is obtained from a great variety of crops. It is readily available and of a low cost, especially when compared to synthetic plastics. Starch is not a true thermoplastic, but in the presence of plasticizers (glycerol, water and other polyols or polysters) at high temperatures and under shear, it readily melts and flows, enabling its use as an injection, extrusion or blow-molding material, similarly to most synthetic thermoplastic polymers. However starch-based materials have some drawbacks, including limited long-term stability caused by water absorption, poor mechanical properties and bad processability.

An economical approach to improve the above properties of starch is to incorporate lignocellulosic fibers into its thermoplastic matrix. Lignocellulosic fibers are any substance that contain both lignin and cellulose. Wood, wood residues, agricultural residues (e.g., wheat straw), grasses and other plant substances fall within this category. Composites of thermoplastic starch (TPS) and lignocellulosic fibers have been studied by different researchers. Various types of lignocellulosic fillers have been tested, such as cellulose fibers, cellulose powder, micro winceyette fibers, bleached kraft and unbleached thermomechanical pulp.
sisal fibers,\textsuperscript{15-17} flax fibers,\textsuperscript{18-20} jute fibers,\textsuperscript{17, 20} cabuya fibers,\textsuperscript{17} ramie fibers\textsuperscript{18} and miscanthus fibers.\textsuperscript{21} All the above materials were compatible with starch and increased tensile strength and elastic modulus and reduced water uptake of the thermoplastic composites. The improvement of the properties was depended on the type and nature of the fiber.

In this work, the mechanical, thermal and hydroscopic behaviour as well as the biodedegradation rate of composites made of thermoplastic starch and wood flour from wood residues of four wood species were studied. More specifically, the effect of wood species, \%wt content in the composites and particle size of the wood flour on the above properties was investigated.

**EXPERIMENTAL**

**Materials**

Mater-Bi\textsuperscript{TM} (VI03S), a starch-based commercial material supplied by Novamont (Italy) was used as biodegradable thermoplastic matrix. The exact chemical composition of Mater-Bi\textsuperscript{TM} is not known but according to producer it contains starch (more than 85\% ) and a synthetic polyester. Glycerol (99+ \%), purchased by Sigma-Aldrich, was used as plastifying agent in a level of 20 wt \% to the weight of Mater-Bi\textsuperscript{TM}. The two substances were well mixed in a laboratory blend. Henceforth, the mixture of Mater-Bi\textsuperscript{TM} and glycerol will be referred as TPS (thermoplastic starch).

Sawmill residues from different wood: spruce (\textit{Picea excelsa}), pine (\textit{Pinus sylvestris}), beech (\textit{Fagus silvatica}) and poplar (\textit{Populus sp.}) were kindly supplied by Greek sawmills. Wood residues were treated in a Willeymill and filtered through sieves, producing four different wood flour particle sizes (less than 150 µm, 150-250 µm, 250-500 µm and 500-750 µm). Prior to processing, flours were oven-dried at 75±5 °C for approximately 4 h reaching a moisture content of 3-5\%.

First, spruce and poplar flour (particle size: 150-250 µm) was used to study the effect of flour content (10 to 50 wt \% for poplar and up to 60 wt \% for spruce ) on the properties of the composites. Then a constant 50 \% wt wood flour of the four wood species was used to study the effect of wood species and particle size (less than 150 µm, 150-250 µm, 250-500 µm and 500-750 µm) of wood flour on the properties of the composites.
TPS and wood flour were well mixed in a Haake-Buchler Rheomixer. The mixing time was 5 min at a temperature of 160 °C and screw speed 50 rpm. After mixing the blends were compression molded in a hot hydraulic press to prepare the composite boards. Pressing was done at 180 °C for 10 min. The dimensions of the boards were 20 X 14 X 0.35 cm for the mechanical properties tests and 15 X 9 X 0.1 cm for water absorption and biodegradation tests.

Composites characterization

Mechanical properties
Tensile strength, Young’s modulus and elongation at break were measured on a Thümler tensile tester (Model TH 3630), according to ASTM D 638 method. The crosshead speed was 5 mm/min. Six measurements were conducted for each sample, and the results were averaged to obtain a mean value. Prior to mechanical property measurements, the samples were conditioned at 50±5% relative humidity for 48 h at ambient temperature, in a closed chamber containing a saturated H₂SO₄ solution in distilled water (ASTM E104).

Scanning Electron Microscopy (SEM)
The fractured surface of the fractured tensile testing specimens of the composites was examined using a SEM microscope (JEOL, model JSM). Prior to the analysis, the samples were coated with gold to avoid charging under the electron beam.

Water absorption
Specimens of 20 mm x 50 mm x 1 mm were dried at 103±2 °C in a vacuum oven until a constant weight was attained and then stored at 33 and 95% RH atmosphere for about a month, using saturated MgCl₂ salt solution and distilled water respectively. Four specimens were used for each RH level. The samples were removed at specific intervals and weighted until the equilibrium state was reached. The water absorption was calculated as the weight difference and is reported as percent increase of the initial weight.

Thermogravimetric analysis
Thermogravimetric analysis (TGA) measurements were performed using a Shimadzu TGA-50 thermogravimetric analyzer. Each sample was heated under a nitrogen atmosphere at a rate of 10 °C/min up to 600 °C.

Biodegradation
The biodegradation of the specimens was performed according to ISO 846. Six specimens for each variable, sized 30 x 30 x 1 mm, were placed in soil burial for 2 and 10 months (3 specimens in sterilized and 3 specimens in common soil).

RESULTS AND DISCUSSION

Mechanical properties

Effect of wood flour content

The addition of wood flour to the thermoplastic matrix (TPS) increased the tensile strength from 2 to 17.5 MPa and the modulus of elasticity from 10 to 960 MPa and decreased drastically the elongation at break of all composites (Figure 1 to Figure 3).

Figure 1 shows that the increase in the tensile strength was analogous to the % content of wood flour up to 50% wt and then decreased at 60% wt. At 50% wt the tensile strength was about 7 and 9 times higher in poplar and spruce flour, respectively. The increase of tensile strength, as a result of wood flour incorporation, can be attributed to the intrinsic adhesion of the flour-matrix interface caused by the chemical similarity of starch and lignocellulosic materials.12, 13, 18, 20 This adhesion enables good stress transfer from the polymer matrix to wood particles during stressing, causing an increase in tensile strength.25 As wood content is increased, more particles are available per unit cross-section area of the composite and hence the fracture stress increases.26 However, as wood flour load reaches 60% wt the starch matrix is less able to penetrate, disperse and wet out the wood flour resulting in a decrease in the tensile properties.19

Figure 2 shows that increasing of wood flour content also increases the modulus of elasticity of the composites up to 50% wt. At 50% content the modulus of elasticity was about 42 and 47 times higher in poplar and spruce flour, respectively. This improvement was expected as starch is a plastic material. Wood has a high modulus of elasticity and its incorporation in the composites reinforces the plastic matrix of TPS and increases the modulus of elasticity of the composites.25

Figure 3 shows a decrease in the elongation at break of the composites as the content of wood flour increases. This decrease is very high at the 10% level of wood flour and then the rate of change decreases as the content of wood increases. This effect could be attributed to the fact that TPS as a plastic material under stress has the tendency to flow (enlarge its dimensions) and the incorporation of lignocellulosic materials in the plastic matrix reduces this tendency and leads to the creation of hard
and brittle materials. This is shown better from the type of stress-stain curves of thermoplastic starch and the composites with various amounts of spruce flour (Figure 4).

Figure 5 shows SEM micrographs of the fracture surface of TPS and TPS/spruce flour composites and reveal the distribution of the wood particles in the matrix and the state of wood flour/matrix interface. Pure TPS shows an even smooth flawless fracture surface (Figure 5a). This topography changes and becomes more and more rough and rigid as the % content of wood flour in the matrix increases (Figures 5a, 5b and 5c). The flour particles are well dispersed and the starch matrix evidently promotes a good wetting and interface of them. In the fractures of the three TPS/flour composites wood breakage was seen indicating a strong interfacial adhesion. This was better seen in the high percentages of wood flour. Based on this, the differences in the fracture surface topography seen in the SEM micrographs could also explain the higher mechanical properties of the composites containing higher percentage of wood flour.

Effect of wood species

Table I shows the effect of wood species on mechanical properties of the composites made up of 50 wt% wood flour. The softwoods tend to show better behaviour than hardwoods. Spruce appears to give better properties than pine, pine than beech and beech than poplar. This species effect appears to be analogous to the specific axial and bending strength properties (strength/density) of each species. However, the difference between the species was statistically significant (t-test, 95%) only between spruce and poplar (see also Figures 1 to Figure 3) and pine and poplar.

Effect of particle size

Table II shows the effect of particle size of wood flour on the mechanical properties. Increasing the particle size from 150 µm to 750 µm appears to decrease the tensile strength of the composites, but had no obvious effect on the modulus of elasticity and the elongation at the break point. Apparently smaller particles are better dispersed in the thermoplastic starch, have more surface area contact with the polymer matrix and allow for an increased interfacial adhesion. Reduction of tensile strength with increasing flour particle size from 40- in 20 - mesh was also found in composites with polypropylene as polymer matrix.
Water absorption

Figure 6 and Figure 7 shows that incorporation of spruce wood flour in the TPS matrix reduced the water absorption of the TPS when exposed to relative humidity of 33% or 95% for various periods of time. The reduction in moisture absorption increased with the increase of wood flour content. Figure 6 shows that when the composites were exposed to 33% RH (a rather dry condition) the composites absorbed small amount of water after 30 days of exposure (about 2.5 to 6% depending on the %wt of wood flour) but continue to absorb at almost the same rate even after this time. Measuring the water absorption until the composites have reached their equilibrium moisture content (at 33% RH) could have given a better inside in the behaviour of the composites. However, the low moisture absorption observed for 30 days could suggest that the composites are very stable at dry conditions and they could be used safely for interior uses. Figure 7 shows that when the composites were exposed in relative humidity >95% (a wet condition) the composites absorbed a rather high amount of water (about 35 to 55% depending on the % of wood flour) and reached their maximum absorption after 1 or 2 days of conditioning. Beyond this time period, more of the composites showed a slight weight loss. This weight loss was more profound in pure TPS specimens. Also, it was observed in all cases that water absorption resulted in analogous swelling of the specimens.

The reduction of water absorption when wood flour is added to the composites is attributed mainly to the fact that wood, because of its lignin content and its crystallinity, is less hydroscopic than thermoplastic starch and glycerol. Water absorption will depend on the percentage of each of the above components in the composites. This is also evident of previous work in this area. An additional explanation could be that the components interact during the manufacture of the composites and less hydroxyls on their surfaces are available to absorb water. The weight loss observed when the composites where conditioned for long times after their saturation could probably be attributed to leaching of components of Mater-Bi™ used in this study or/and of glycerol. The exact cause of this observation should be investigated. However the results shown in Figures 6 and 7 suggest that these materials should not be used for prolong times in wet conditions.

Figure 8 shows that species of wood had a considerable effect on the water absorption at 95% relative humidity. Softwood species (spruce and pine) due to
higher amount of lignin in their composition are less hydrophilic than hardwoods (beech and poplar), which have higher content of hemicelluloses.\textsuperscript{30}

Figure 9 shows that particle size of wood flour also influences the water absorption of the composites. Increasing the particle size from 150 $\mu$m to 750 $\mu$m results in increased water absorption. Small particles apparently mix better with the starch matrix and due to their higher surface area could develop better interfacial adhesion bonds and make the composite stronger (see Figures 1, 2) and more resistant to water uptake and swelling.

**Thermal stability**

Figure 10 presents thermogravimetric results of the composites made up of TPS and spruce wood flour in contents from 10 to 60 wt%. The mass loss curves show that increasing addition of wood flour appear to increase slightly the thermal stability of TPS composites, giving the most thermally stable material when wood flour is in its higher content (60 wt%). Analogous results have been found also by other researchers and they are attributed mainly to the higher thermal resistance of wood.$^5,11,12$

Figure 11 shows that thermal resistance of the composites appears to be influenced by wood species. Spruce and pine gave slightly more resistant products than beech and poplar. This effect could be attributed to the chemical composition of these species, as in general softwoods (because of their higher lignin and lower hemicelluloses content) are more thermally resistant than hardwoods.$^{31}$

**Biodegradation**

Table III gives the results of the biodegradation tests (weight loss after burial for 2 and 10 months in the soil) of TPS and the composites. It emerges that TPS degrades faster than composites with wood flour. The incorporation of wood flour reduced the biodegradation rate of the composites. This rate appeared to be slightly higher when the wood content increased from 30\% to 50\%.

Wood species appeared to influence the rate of biodegradation. The degradation rate was higher in beech than in the other species (spruce, pine and polar). Pine had the lower rate of biodegradation. These differences are hard to explain according to the chemical constitution of the species, as some fungi decompose faster the cellulose or hemicelluloses than lignin, while other fungi decompose faster lignin than polysaccharides.$^{27,32}$ The resistance of various species varies also according to their
content in toxic extractives and their density. However, it could be mentioned that beech is a highly susceptible species, followed by poplar and spruce, while pine is the most resistant of the above-mentioned species.27

The size of the particles of wood flour also appeared to affect the rate of biodegradation of the composites. Composites made up with wood flour of big particles (500-750 µm) showed higher rate of degradation than composites of smaller particles, but the composites of 150-250 µm showed lower rate than <150 µm). However, the difference between the two small sizes was not statistical different (t-test 95%)

To reach more sound conclusions on the biodegradibility of the wood/starch composites further studies and longer times of exposures of the composites and of their individual components to various environments and various fungi are needed.

CONCLUSIONS
Summarizing the results of the present study, it can be concluded that wood flour from sawmill residues represent a good material in mixtures with thermoplastic starch to manufacture low cost biodegradable composites intended for interior uses. Incorporation of wood flour in the starch matrix increased tensile strength, modulus of elasticity and thermal stability and decreased elongation at the break point, water absorption and rate of biodegradation of the composites. This effect increased with increasing the content of wood flour in the composites from 10 wt% up to 50 wt%.

Wood species had a profound effect on the properties of the composites. Spruce and pine gave better mechanical properties, thermal stability, water absorption, but lower rate of decomposition than beech and poplar. Beech composites were very susceptible to biodegradation.

Also the particle size of the wood flour had a considerable effect on the properties of the composites. Decreasing the particle size from 750µm down to 150 µm appears to increase the tensile strength, water absorption, thermal stability and resistance to degradation of the composites, but had no obvious effect on the modulus of elasticity and the elongation at the break point.
ACKNOWLEDGMENTS

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REFERENCES

5. Curvelo, AAS.; De Carvalho, AJF.; Agnelli, JAM. Carbohydr Polym 2001, 45, 183.
7. Di Franco, CR.; Cyras, VP.; Busalmen, JP.; Ruseckaite, R.A.; Vázquez, A. Polym Degrad Stab 2004, 86, 95.
10. Avérous, L.; Fringant, C.; Moro, L. Polymer 2001b, 42, 6565.
13. De Carvalho, AJF.; Curvelo, AAS.; Agnelli, JAM. Int J Polym Mater 2002, 51, 647.
14. De Carvalho, AJF.; Zambon, MD.; Curvelo, AAS.; Gandini, A. Polym Degrad Stab 2003, 79, 133.
15. Alvarez, VA.; Ruseckaite, RA.; Vázquez, A. Polym Degrad Stab 2006, 91, 3156.
17. Torres, FG.; Arroyo, OH.; Gómez, C. J Thermoplastic Compos Mater 2007, 20, 207.
### TABLE I

Average tensile properties of composites of flour* of various wood species and their standard deviations (in brackets)

<table>
<thead>
<tr>
<th></th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS-Spruce (50wt%)</td>
<td>17.3(±1.4)</td>
<td>954(±24)</td>
<td>2(±0--)</td>
</tr>
<tr>
<td>TPS-Pine (50wt%)</td>
<td>15.5(±0.6)</td>
<td>935(±30)</td>
<td>2(±0)</td>
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<tr>
<td>TPS-Beech (50wt%)</td>
<td>14.6(±1.4)</td>
<td>887(±89)</td>
<td>2(±0)</td>
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<tr>
<td>TPS-Poplar (50wt%)</td>
<td>13.3(±0.6)</td>
<td>854(±71)</td>
<td>2(±0)</td>
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* particle size 150-250 µm
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<tr>
<th></th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS-Spruce (&lt;150 µm)</td>
<td>18.1±0.6</td>
<td>998±52</td>
<td>2±0</td>
</tr>
<tr>
<td>TPS-Spruce (150-250µm)</td>
<td>17.3±1.4</td>
<td>954±24</td>
<td>2±0</td>
</tr>
<tr>
<td>TPS- Spruce (250-500µm)</td>
<td>15.3±0.8</td>
<td>992±11</td>
<td>2±0</td>
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<tr>
<td>TPS- Spruce (500-750µm)</td>
<td>14.1±1.6</td>
<td>1042±73</td>
<td>2±0</td>
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* 50% wt of wood flour
### TABLE III

Average weight loss for TPS and composites after 2 and 10 months burial in the soil

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<tr>
<th>Composite type</th>
<th>Weight loss (%)</th>
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<tr>
<td></td>
<td>2 months</td>
<td>10 months</td>
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<tr>
<td>TPS</td>
<td>7.02</td>
<td>45.21</td>
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<tr>
<td>TPS-Spruce (30 wt%)</td>
<td>5.58</td>
<td>36.40</td>
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<tr>
<td>TPS-Spruce (50 wt%)</td>
<td>5.52</td>
<td>32.01</td>
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<tr>
<td>TPS-Pine (50 wt%)</td>
<td>1.68</td>
<td>30.07</td>
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<tr>
<td>TPS-Beech (50 wt%)</td>
<td>5.85</td>
<td>44.23</td>
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<tr>
<td>TPS-Poplar (50 wt%)</td>
<td>2.64</td>
<td>32.03</td>
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<tr>
<td>TPS-Spruce (&lt;150µm)</td>
<td>5.48</td>
<td>28.82</td>
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<tr>
<td>TPS-Spruce (500-750µ)</td>
<td>7.11</td>
<td>37.41</td>
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1 particle size 150-250µm  
2 wood flour content 50%
Effect of wood flour content on tensile strength

59x41mm (300 x 300 DPI)
Effect of wood flour content on Young’s modulus

59x41mm (300 x 300 DPI)
Effect of wood flour content on elongation at break

59x41mm (300 x 300 DPI)
Stress-Stain curves of TPS and composites with spruce flour
59x41mm (300 x 300 DPI)
SEM micrograph at 700X magnification of fragile fractured surface of TPS composites with different flour contents a) 0% flour content, b) 20% flour content, c) 30% flour content, d) 50% flour content.

254x190mm (72 x 72 DPI)
Effect of wood flour content in absorption (RH 33%)
59x41mm (300 x 300 DPI)
Effect of wood flour content in absorption (RH 95%)
59x41mm (300 x 300 DPI)
Effect of wood species in absorption (RH 95 %)

59x41mm (300 x 300 DPI)
Effect of particle size in absorption (RH 95%)

59x41mm (300 x 300 DPI)
Effect of wood flour content in thermal stability of composites

59x41mm (300 x 300 DPI)
Effect of wood species in thermal stability of composites
59x41mm (300 x 300 DPI)