Development of Biodegradable Composites Based on Wood Waste Flour and Thermoplastic Starch

E. Agnantopoulou,[1] V. Tserki,[2] S. Marras,[2] J. Philippou,[1] C. Panayiotou[2]

[1]*Faculty of Forestry & Natural Environment, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece*
[2]*Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece*

Received 24 March 2009; accepted 3 August 2011
DOI 10.1002/app.35420
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Biodegradable composites were prepared from wood flour of sawmill residues and a thermoplastic starch (Mater-Bi^{TM} and glycerol). For the preparation of the composites flour from sawmills of four wood species (spruce, pine, beech and poplar), three particle sizes (<150, 150–250, and 250–750 μm) and in six proportions (10, 20, 30, 40, 50, and 60% wt) was used. The composites were characterized by means of mechanical property measurements, scanning electron microscopy, water absorption, thermal stability and biodegradation studies. Addition of wood flour to thermoplastic starch 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). © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: biodegradable composites; starch; wood flour; wood residues; biodegradation

INTRODUCTION

Most plastics based on petrochemicals are designed and manufactured to withstand environmental degradation.[1] This fact has led to an increase in the amount of plastic wastes, which comprises a significant source of environmental pollution.[2] Although efforts to recycle used plastics to reduce their volume in landfills have been improved significantly, recycling would be neither practical nor economical for certain applications, such as packaging.[3] 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.[4] 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 lignocellusic fiber (e.g., wood plastic composites).[1–3] are not fully biodegradable. Recent research efforts are oriented towards replacing the nonbiodegradable polymer matrices with natural polymers such as starch, polylactic acid, polyhydroxyalcanoates.[2–5]

One of the most promising raw material for the production of biodegradable plastics is starch, which is a natural renewable polysaccharide 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 polyesters) 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.[6] However starch-based materials have some drawbacks, including limited long-term stability caused by water absorption, poor mechanical properties and bad processability.[7]

An economical approach to improve the above properties of starch is to incorporate lignocellulosic fibers into its thermoplastic matrix.[5] 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.[8] Composites of thermoplastic starch (TPS) and lignocellulosic fibers have been studied by different researchers. Various types of lignocellulosic fillers have been tested, such

Correspondence to: J. Philippou (jfilippo@for.auth.gr).
Contract grant sponsor: Ministry of National Education, Religious Affairs of Greece-Programme PYTHAGORAS II (EPEAEK)

as cellulose fibers,[9–12] cellulose powder,[7] micro winceyette fibers,[12] bleached kraft and unbleached thermomechanical pulp,[13,14] semichemical pulp,[11] sisal fibers,[15–17] flax fibers,[18–20] jute fibers,[17,20] cabuya fibers,[17] ramie fibers,[18] and miscanthus fibers.[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 TPS 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™ (VI03S), a starch-based commercial material supplied by Novamont (Italy) was used as biodegradable thermoplastic matrix. The exact chemical composition of Mater-Bi™ 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™. The two substances were well mixed in a laboratory blend. Henceforth, the mixture of Mater-Bi™ and glycerol will be referred as TPS.

Sawmill residues from different wood: spruce (*Picea excelsa*), pine (*Pinus sylvestris*), beech (*Fagus silvatica*), and poplar (*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 (<150, 150–250, 250–500, and 500–750 μm). Before processing, flours were oven-dried at 75°C ± 5°C for ~ 4 hour reaching a moisture content of 3–5%.

First, spruce and poplar flour (particle size: 150–250 μm) were used to study the effect of flour content (10–50 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 (<150, 150–250, 250–500, 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 mim. The dimensions of the boards were 20 × 14 × 0.35 cm for the mechanical properties tests and 15 × 9 × 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. Before mechanical property measurements, the samples were conditioned at 50% ± 5% relative humidity for 48 hour at ambient temperature, in a closed chamber containing a saturated H_2SO_4 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 scanning electron microscopy (SEM) microscope (JEOL, model JSM). Before the analysis, the samples were coated with gold to avoid charging under the electron beam.

Water absorption

Specimens of 20 mm × 50 mm × 1 mm were dried at 103°C ± 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 $MgCl_2$ 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 × 30 × 1 mm, were placed in soil

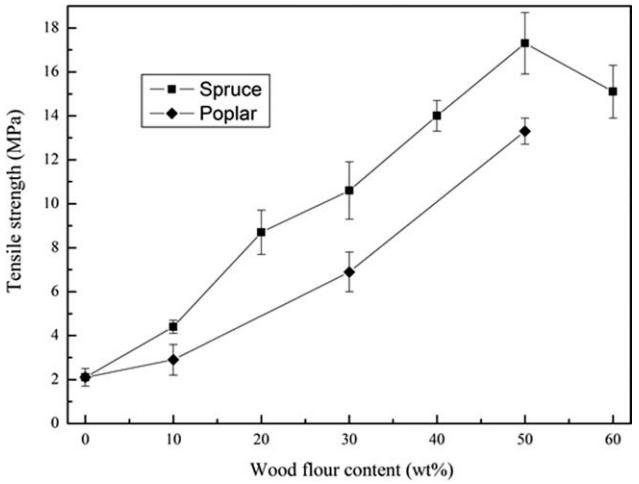

Figure 1 Effect of wood flour content on tensile strength.

burial for 2 and 10 months (three specimens in sterilized and three 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 (Figs. 1–3).

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 seven and nine 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.[22] As wood content is increased, more particles are available per unit cross-section area of the composite and hence the fracture stress increases.[23] 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.[22]

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.[22] This is shown better from the type of stress-stain curves of TPS and the composites with various amounts of spruce flour (Fig. 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

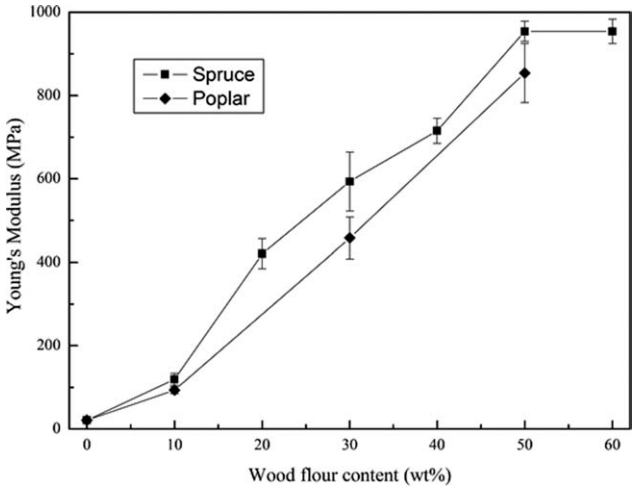

Figure 2 Effect of wood flour content on Young's modulus.

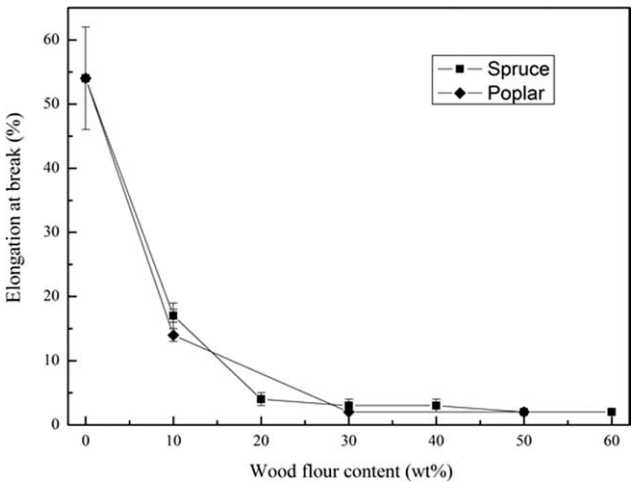

Figure 3 Effect of wood flour content on elongation at break.

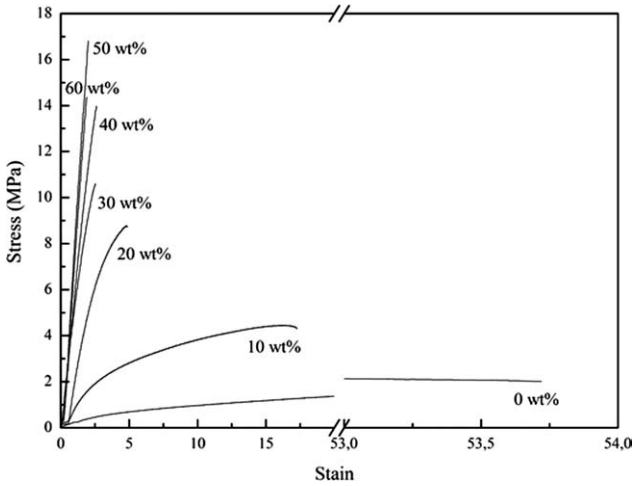

Figure 4 Stress-Stain curves of TPS and composites with spruce flour.

matrix and the state of wood flour/matrix interface. Pure TPS shows an even smooth flawless fracture surface [Fig. 5(a)]. This topography changes and becomes more and more rough and rigid as the % content of wood flour in the matrix increases [Fig. 5(b–d)]. 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.[24–26] However, the difference between the species was statistically significant (t-test, 95%) only between spruce and poplar (see also Figs. 1–3) 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

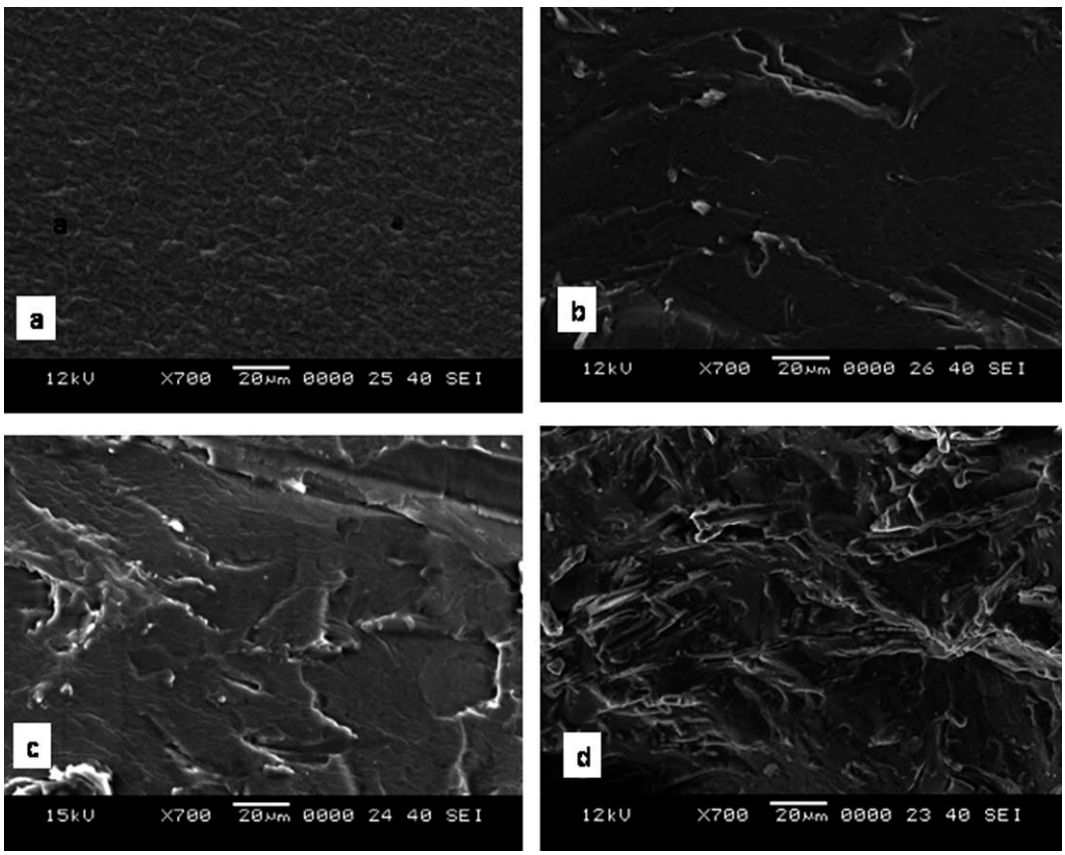

Figure 5 SEM micrograph at 700× magnification of fragile fractured surface of TPS composites with different flour contents (a) 0% flour content, (b) 20% flour content, (c) 30% flour content, (d) 50% flour content.

TABLE I
Average Tensile Properties of Composites of Flour of Various Wood Species and Their Standard Deviations (in Brackets)[a]

	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
TPS-spruce (50 wt %)	17.3 (±1.4)	954 (±24)	2 (±0)
TPS-pine (50 wt %)	15.5 (±0.6)	935 (±30)	2 (±0)
TPS-beech (50 wt %)	14.6 (±1.4)	887 (±89)	2 (±0)
TPS-poplar (50 wt %)	13.3 (±0.6)	854 (±71)	2 (±0)

[a] Particle size 150–250 μm.

particle size from 150 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 TPS, 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- to 20-mesh was also found in composites with polypropylene as polymer matrix.[27]

Water absorption

Figures 6 and 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 insight into the behaviour of the composites. However, the low moisture absorption observed for 30 days could suggest that the composites are very

TABLE II
Average Tensile Properties of Composites of Various Particle Sizes and Their Standard Deviations (in Brackets)[a]

	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
TPS-spruce (<150 μm)	18.1 (±0.6)	998 (±52)	2 (±0)
TPS-spruce (150–250 μm)	17.3 (±1.4)	954 (±24)	2 (±0)
TPS-spruce (250–500 μm)	15.3 (±0.8)	992 (±11)	2 (±0)
TPS-spruce (500–750 μm)	14.1 (±1.6)	1042 (±73)	2 (±0)

[a] 50% wt of wood flour.

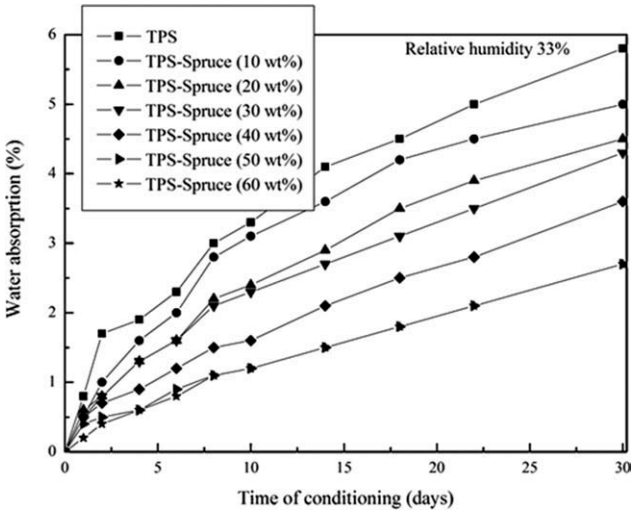

Figure 6 Effect of wood flour content in absorption (RH 33%).

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 TPS and glycerol.[12] Water absorption will depend on the percentage of each of the above components in the

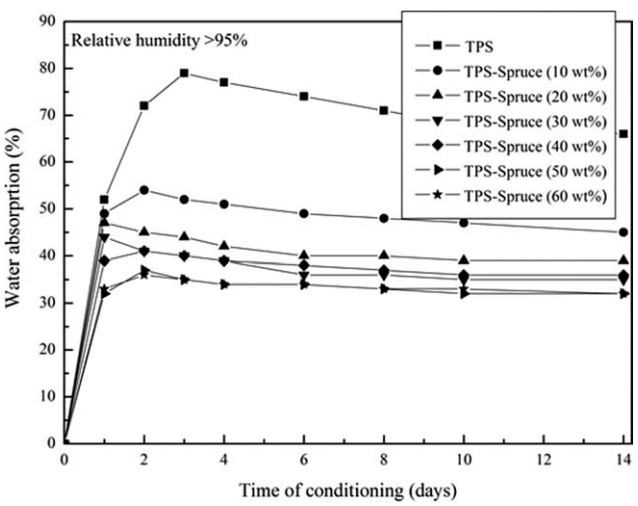

Figure 7 Effect of wood flour content in absorption (RH >95%).

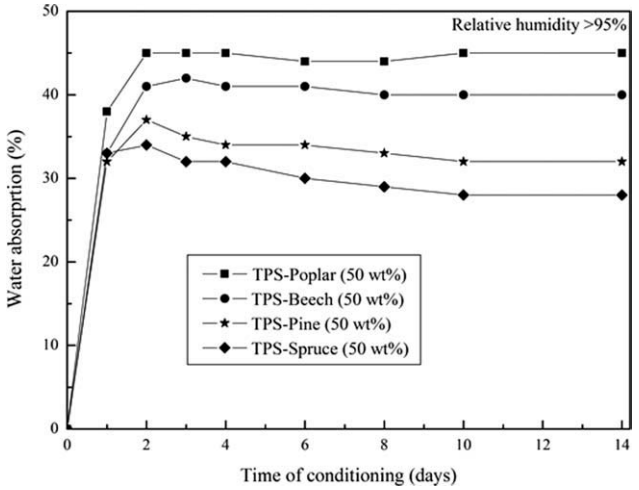

Figure 8 Effect of wood species in absorption (RH >95%).

composites. This is also evident of previous work in this area.[12,13,16,28] 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^{TM} 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. This effect could be attributed mainly to the differences in hygroscopicity of the various wood constituents (cellulose, hemicelluloses and lignin) and their % in the composition of various species. Hemicelluloses are the most and lignin the least

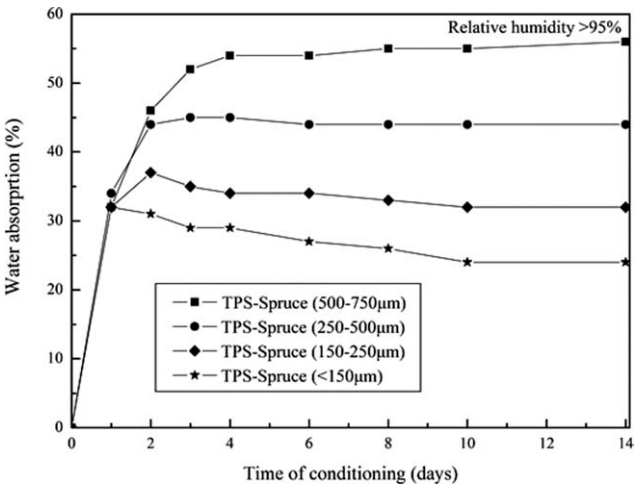

Figure 9 Effect of particle size in absorption (RH >95%).

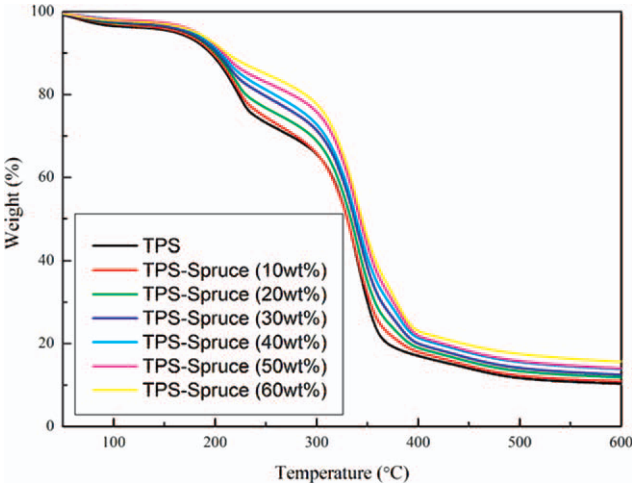

Figure 10 Effect of wood flour content in thermal stability of composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydroscopic constituents.[25] Lignin content is higher in softwoods (spruce 28–30%, pine 27–29%) and lower in hardwoods (beech 21–23%, poplar 18–21%), hemicelluloses content is lower in softwoods (spruce 25–27%, pine 25–28) and higher in hardwoods (beech 30–35%, poplar 33–36%) whereas cellulose content is about the same (44–46%) in both types of wood.[29,30] Thus we can expect that composites rich in hemicelluloses will be more highly hydroscopic, whereas high lignin content would result in lower overall sorption capacity. The above softwood species have also in their composition more hydrophobic extractives (mainly resinous).[30]

Other factors that might also have some effect on water absorption of the composites could be the physicochemical and morphological organization of the chemical constituents within the wood tissues in the various species[24,25] and of wood flour and TPR in the composite matrix. The later could be supported at least partially by the effect of the particle size on water absorption of the composites seen on Figure 9. Increasing particle size from 150 to 750 μm 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 Figs. 1 and 2) and more resistant to water up take and swelling. Low moisture content is important for strong and durable wood composites.[31,32]

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

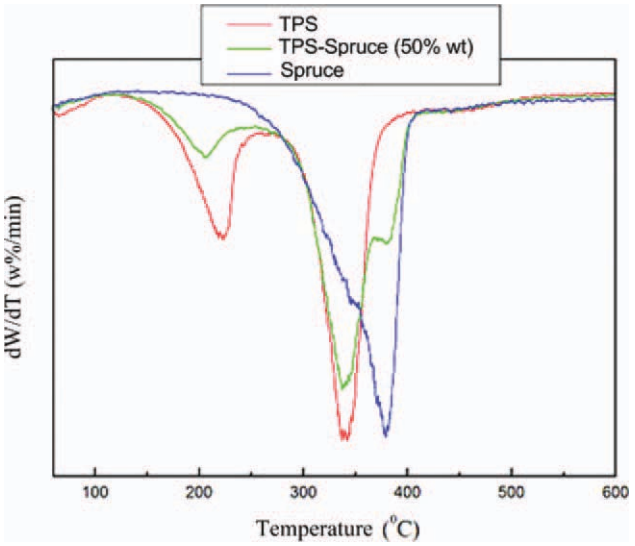

Figure 11 Thermogram derivative of TPS, spruce and composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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 the lignocellulosic material.[6,11,12] Figure 11 shows the derivatives of mass loss of a composite TPS and spruce wood (50% by wt) and its components. The TPS curve exhibits a small decomposition peak at 220–225°C which correspond to the decomposition of glycerol and a large peak at 340–345°C reflecting the decomposition of starch. The spruce wood curve exhibits a large decomposition peak at 370–375°C. The curve of the composite reflects the thermal responses of its components.

Figure 12 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 mainly to the chemical composition of these species. It is known[33] that hemicelluloses are the least stable and decompose at 225–325°C, cellulose decomposes at higher temperatures within the narrower range of 325–375°C and lignin decomposes gradually within the temperature range of 250–500°C. It has also been observed[34] that in softwoods hemicelluloses show lower degradation reactivity and cellulose decomposes within a wider temperature zone than in hardwoods. The thermal behaviour of wood and its composites with TPS apparently reflect the sum of thermal responses of their components.

Surface topography and interfacial bonding between wood and TPS matrix that vary according to wood %, wood species and particle size, are also expected to have an effect on thermal stability analogous to that on strength and water absorption. Though, thermographs of composites made of 50% spruce flour with various particle sizes (<150, 150–250, and 500–750 μm) did not show any measurable differences that could suggest any effect of particle size on thermal stability of the composites. As thermal properties affect the mechanical properties,[35] further studies with more analytical tools (DSC, dynamic mechanical testing etc.) could give more inside on the thermal behaviour and its effect on other properties of TPS-wood composites and the effect of various factors.

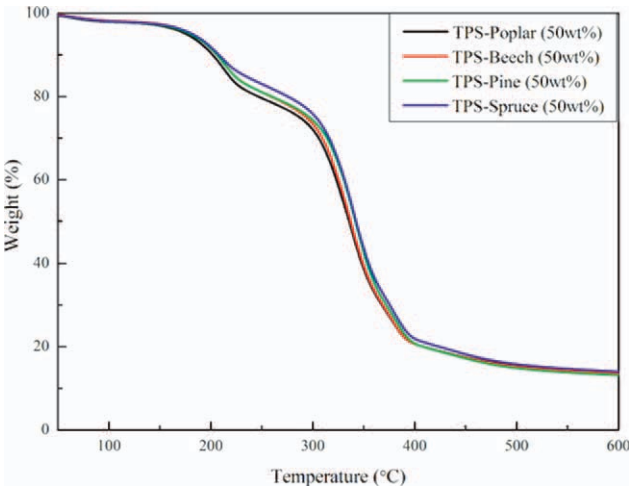

Figure 12 Effect of wood species in thermal stability of composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Biodegradation

Table III gives the results of the biodegradation tests (weight loss after burial for 2 and 10 months in the

TABLE III
Average Weight Loss for TPS and Composites After 2 and 10 Months Burial in the Soil

Composite type	Weight loss (%)	
	2 months	10 months
TPS	7.02	45.21
TPS-spruce (30 wt %)[a]	5.58	36.40
TPS-spruce (50 wt %)[a]	5.52	32.01
TPS-pine (50 wt %)[a]	1.68	30.07
TPS-beech (50 wt %)[a]	5.85	44.23
TPS-poplar (50 wt %)[a]	2.64	32.03
TPS-spruce (<150 μm)[b]	5.48	28.82
TPS-spruce (500–750 μm)[b]	7.11	37.41

[a] Particle size 150–250 μm.
[b] Wood flour content 50%.

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.[24,36] 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 aforementioned species.[24,36]

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 statistically different (t-test 95%). One could expect the small particles to be more susceptible to decay because they provide more surface for the fungal hyphae to develop.[36] The finding in this work supports further the role of interfacial bonding between wood and TPS matrix in developing strength, low water absorption and durability in the wood-TPS composites.

The susceptibility of the composites to biodegradation depends largely on the moisture content of wood and its composites.[24,36] At high level of moisture content the rate of decomposition is rather fast while decomposition does not occur at moisture content levels below 20%. The importance of biodegradation of the TPS-wood composites could be seen from two points of view: product utility and product disposal. In the first case, long lasting products are needed and this could happen if the materials have low water absorptivity and they are not used in humid environments. Moisture is also known to affect adversely the thermal and mechanical properties of biocomposites.[25,26,31] In the second case, a fast degradation of the materials is important to minimize adverse environmental effects from the product disposal. Further studies and longer times of exposures of the composites and of their individual components to various environments and various fungi are needed to get a better inside on biodegradation of TPS-wood composites.

In this work it has been shown that monitoring TPS/wood ratio, species of wood and size of particles in wood flour could allow us to improve water absorption, decay durability, thermal and mechanical properties of the TPS-wood composites. High % of wood in the composite and smaller particles of softwood species result in the greatest improvement of all utility properties of the composites.

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 TPS 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 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 and lower rate of decomposition than beech and poplar. Beech composites were the most 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 750 μm down to 150 μm appears to increase the tensile strength and resistance to biodegradation and decrease water absorption of the composites, but had no obvious effect on thermal stability, modulus of elasticity and elongation at the break point.

References

1. Ramis, X.; Cadenato, A.; Salla, J. M.; Marancho, J. M.; Vallés, A.; Contat, L.; Ribes, A. Polym Degrad Stab 2004, 86, 483.
2. Avérous, L. J Macromol Sci 2004, 44, 231.
3. Aburto, J.; Thiebaud, S.; Alric, I.; Borredon, E.; Bikiaris, D.; Prinos, J.; Panayiotou, C. Carbohydr Polym 1997, 34, 101.
4. Bélard, L.; Dole, P.; Avérous, L. Aust J Chem 2005, 58, 457.
6. Curvelo, A. A. S.; De Carvalho, A. J. F.; Agnelli, J. A. M. Carbohydr Polym 2001, 45, 183.
7. Gáspár, M.; Benkő, Zs.; Dogossy, G.; Réczey, K.; Czigány, T. Polym Degrad Stab 2005, 90, 563.
5. Di Franco, C. R.; Cyras, V. P.; Busalmen, J. P.; Ruseckaite, R. A.; Vázquez, A. Polym Degrad Stab 2004, 86, 95.
8. Johnson, M.; Tucker, N.; Barnes, S.; Kirwan, K. Ind Crops Prod 2005, 22, 175.
9. Avérous, L.; Fringant, C.; Moro, L. Starch/Stärke 2001a, 53, 368.
10. Avérous, L.; Fringant, C.; Moro, L. Polymer 2001b, 42, 6565.
11. Avérous, L.; Boquillon, N. Carbohydr Polym 2004, 56, 111.
12. Ma, X.; Yu, J.; Kennedy, J. F. Carbohydr Polym 2005, 62, 19.

13. De Carvalho, A. J. F.; Curvelo, A. A. S.; Agnelli, J. A. M. Int J Polym Mater 2002, 51, 647.
14. De Carvalho, A. J. F.; Zambon, M. D.; Curvelo, A. A. S.; Gandini, A. Polym Degrad Stab 2003, 79, 133.
15. Alvarez, V. A.; Ruseckaite, R. A.; Vázquez, A. Polym Degrad Stab 2006, 91, 3156.
16. Alvarez, V. A.; Ruseckaite, R. A.; Vázquez, A. J Thermoplast Compos Mater 2007, 20, 291.
17. Torres, F. G.; Arroyo, O. H.; Gómez, C. J Thermoplast Compos Mater 2007, 20, 207.
18. Wolledorfer, M.; Bader, H. Ind Crops Prod 1998, 8, 105.
19. Romhány, G.; Karger-Kocsis, J.; Czigány, T. Macromol Mater Eng 2003, 288, 699.
20. Soykeabkaew, N.; Supaphol, P.; Rujiravanit, R. Carbohydr Polym 2004, 58, 53.
21. Johnson, R. M.; Tucker, N.; Barnes, S. Polym Test 2003, 22, 209.
22. Georgopoulos, S. T.; Tarantili, P. A.; Avgerinos, E.; Andreopoulos, A. G.; Koukios, E. G. Polym Degrad Stab 2005, 90, 303.
23. Lodha, P.; Netravali, A. N. J Mater Sci 2002, 36, 3657.
24. Tsoumis, G. Science and Technology of Wood: Structure, Properties, Utilization; Van Nostrand Reinhold: New York, 1991.
25. Schniewind, P.; Berndt, H. In Wood Structure and Composition; Lewin, M., Goldstein, I. S., Eds.; Marcel Dekker: New York, 1991; Vol.11, pp 435–476.
26. US Forest Service. Wood Handbook—Wood as an Engineering Material; U.S. Department of Agriculture, Forest Service: Madison, WI, 1999.
27. Stark, N. M.; Berger, M. J. In Proceedings of the fourth International Conference on Woodfiber-Plastic Composite; Effect of particle size on properties of wood-flour reinforced polyprolylene composites; Forest Products Society: Madison, 1997; p 134.
28. Dufresne, A.; Vignon, M. R. Macromolecules 1998, 31, 2693.
29. Pettersen, R. C. In The Chemistry of Solid Wood, Rowell, R. M., Ed.; Advances In Chemistry Series 207, American Chemical Society: Washington, 1984; p 57–126.
30. Fengel, D.; Wegener, G. Wood Chemistry: Ultrastructure, Reactions; Walter de Gruyter: Berlin, 1984.
31. Klysov, A. Wood-Plastic Composites; Wiley: New York, 2007.
32. Sombatsompop, N.; Chaochanchaikul, K. Polym Int 2004, 53, 1210–1218.
33. Shafizadeh, F.; Chin, P. P. S. O. In Wood Technology: Chemical Aspects; Goldstein, I. S., Ed.; American Chemical Society: Washington, 1977; pp 57–81.
34. Markova, I. In Wood Structure and Properties' 98; Kurjatko, S.; Kuleda, J., Eds.; Arbova Publishers: Zvolen, 1998; pp 121–123.
35. Gronli, M. G.; Varhegyi, G.; Di Blasi, C. Ind Eng Chem Res 2002, 41, 4201–4208.
36. Zabel, R. A.; Morrell, J. J. Wood Microbiology: Decay and its Prevention; Academic Press: San Diego, 1992.
37. Berger, M. J.; Stark, N. M. In Proceedings of the Fourth International Conference on Woodfiber-Plastic Composite; Investigations of Species Effects in an Injection-Molding-Grade, Wood-Filled Polyprolylene; Forest Products Society: Madison, 1997, p 19.
38. Sretenovic, A.; Müller, U.; Gindl, W. Composites Part A 2006, 37, 1406.
39. Myers, G. E.; Chahyadi, I. S.; Coberly, C. A.; Ermer, D. S. Int J Polym Mater 1991, 15, 21.