Rice straw as an alternative reinforcement in polypropylene composites

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Agron. Sustain. Dev. 26 (2006) 251–255
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DOI: 10.1051/agro:2006023

Research article

Rice straw as an alternative reinforcement in polypropylene composites

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(Accepted 22 August 2006)

Abstract – We studied the use of rice straw as reinforcement in maleated polypropylene (PP_m). Composites containing 20 and 30% by weight rice straw were successfully prepared by extrusion and compression molding. The samples were characterized by tensile tests, differential scanning calorimetry (DSC), thermogravimetry (TGA), dynamo-mechanical analysis (DMTA) and scanning electron microscopy (SEM). The results of the mechanical properties showed that rice straw can be used as an alternative reinforcement for polypropylene. Higher tensile moduli (E) were obtained for composites containing higher rice straw content. Thermogravimetric curves of the composites exhibit two-stage decomposition process and slightly higher thermal stability. Higher crystallization (T_c) and melting peak temperatures for composites were detected by DSC analysis (T_{cpp} = 107.8 °C, $T_{cRS/PP(20/80)}$ = 114.5 °C). The renewability of rice straw and the recyclability of thermoplastic polypropylene provide an attractive eco-friendly quality to the resulting composites.

eco-composites / natural fibers / rice straw / polypropylene

1. INTRODUCTION

In the last decade, interest in using natural fiber-reinforced materials has significantly increased due to growing environmental awareness (Yang et al., 2004a). New and stronger environmental policies have forced some industries such as the automotive and construction industries to look for new eco-materials that will be able to substitute traditional composites reinforced with glass or carbon fibers (Yang et al., 2003).

Natural fiber-reinforced materials offer target environmental advantages such as reduced dependence on non-renewable energy/material sources, and less pollutants and greenhouse emissions. Natural lignocellulosic fibers (flax, jute, hemp, etc.) represent an environmentally-friendly alternative to conventional reinforcing fibers (glass and carbon). Advantages of natural fibers over traditional ones are: low cost, high toughness, low density, good specific strength properties, reduced tool wear (nonabrasive to processing equipment), enhanced energy recovery, CO_2 neutral when burned, and biodegradability. Due to their hollow and cellular nature, natural fibers perform as acoustic and thermal insulators, and exhibit reduced bulk density. Depending on their performance, when they are included in the polymer matrix, lignocellulosic fibers can be classified into three categories: (1) wood flour particulates, which increase the tensile and flexural modulus of the composites, (2) fibers of higher aspect ratio that contribute to improving the composites' modulus and strength when suitable additives are used to regulate the stress transfer between the matrix and the fibers, and (3) long natural fibers with the highest efficiency amongst the lignocellulosic reinforcements. The most efficient natural fibers have been considered those that have a high cellulose content coupled with a low microfibril angle, resulting in high filament mechanical properties. Amongst eco-compatible polymer composites, special attention has been given to polypropylene composites, due to their added advantage of recyclability (Yang et al., 2004b). Yang et al. (2004a) studied the possibility of using lignocellulosic rice-husk flour as reinforcing filler in thermoplastic polymer composites. They designed rice-husk flour/polypropylene composites with four levels of filler loading (10, 20, 30 and 40 wt%). The results of a tensile test performed at six levels of temperatures and various crosshead speeds showed that the tensile strength of the composites slightly decreased as the filler loading increased. Tensile modulus was improved by increasing the filler content. Notched and unnotched Izod impact strengths were lowered by the addition of rice-husk flour. The composite became brittle at higher crosshead speeds, and plastic deformation was shown with increasing test temperatures.

Using the method applied in the wood-based panel industry, Yang et al. (2003) tested rice straw for production of composite insulation boards. They compared mechanical properties and the sound absorption coefficient. The composite boards with a specific gravity of 0.8 have a slightly better bending modulus than wood particle boards (as a control board) at a rice straw

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content of 10% wt, and show no differences from the control board at a 20% wt rice straw content. The sound absorption coefficient of rice straw – wood particle composite boards were higher in the middle and high frequency ranges than commercial wood-based material (Yang et al., 2003, 2004a).

Kim et al. (2004) analyzed the thermal degradation and thermal stability of rice-husk flour-filled polyolefin composites. They found that as the rice-husk flour content increased, the thermal stability of the composites decreased and the ash content increased, as a logical consequence of the lower thermal stability of the rice-husk flour. Also, as the thermal decomposition proceeded in the studied composites, the activation energy increased slowly in the initial stages until a degradation conversion (α) of $\alpha = 0.3$. Finding that the activation energy of the composites depends on the dispersion and interfacial adhesion of rice-husk flour in the polyolefin's matrix polymers, they recommended the addition of a compatibilizing agent (Kim et al., 2004).

In order to enhance the performance of rice-husk-filled polyolefines, Panthapulakkai et al. (2005) studied the effect of coupling agents on rice-husk-filled polyolefine extruded profiles. They analyzed four different coupling agents based on ethylene-(acrylic ester)-(maleic anhydride) terpolymers and ethylene-(acrylic ester)-(glycidyl methacrylate) terpolymers. The results showed that these coupling agents significantly improved the tensile and flexural strength of the composites. The extent of the coupling effect was dependent on the nature of the interface formed. Incorporation of coupling agents enhanced the resistance to thermal deformation and the water absorption properties of the composite, whereas it reduced the extrusion rate. Toro et al. (2005) studied the compatibilizing effect of polypropylene grafted with monomethyl itaconate (PP-g-MMI) in PP/rice-husk composites. It was shown that in the presence of PP-g-MMI as compatibilizer, the tensile modulus and water absorption of the composite were improved.

In this paper, we report the possibility of using the lignocellulosic material rice straw as reinforcing filler for polypropylene composites, and the preliminary results obtained for the physico-mechanical and thermal properties of the composites.

2. MATERIALS AND METHODS

2.1. Materials

Polypropylene (maleated-(PPm), 5% maleinization, (KA 805)), a product of Montell, was used as a matrix, while the waste rice straw was kindly supplied by the Rice Institute of Kocani, R. Macedonia. Rice straw/Polypropylene (RS/PPm) composites of different rice straw contents (20/80 and 30/70% wt) were prepared by a two-step procedure: extrusion (HAAKE RHEOCORD, 100 rpm, 165 °C) and compression molding (Carver Press, T = 170 °C, P = 50–150 bar). Before the extrusion, the rice straw was vacuum-dried for 24 h to adjust a moisture content of 1–2%.

2.2. Methods

The obtained composites were characterized with tensile and impact tests, differential scanning calorimetry (DSC), thermogravimetry (TGA), dynamic-mechanical analysis (DMTA) and scanning electron microscopy (SEM). Tensile tests were conducted according to ASTM D 638–99 with a Universal Instron Machine (Model 4301). The tests were performed at a crosshead speed of 10 mm/min at room temperature. Each value obtained represented the average of five samples. Morphology of fracture surfaces of composites after the tensile test was analyzed using a JEOL SEM (vacuum Au/Pd alloy deposition of the samples in a Polaron Sputtering apparatus was performed previously). The crystallization behavior of the composites was studied using a Perkin Elmer DSC-7 thermal analyzer. The composite samples of about 10 mg were analyzed in the temperature range from 0 to 200 °C at a scanning rate of 10 °C/min. Differential scanning calorimetry was carried out under a nitrogen atmosphere. Dynamo-mechanical measurements were carried out using a dynamic thermal analyzer (DMTA PE-Diamond system), operating in bending mode at a frequency of 1 Hz. The samples were investigated in the temperature range from –100 to 160 °C at a heating rate of 2 °C/min. The thermal stability of the samples was measured using a Perkin Elmer Pyris Diamond Thermogravimetric/ Differential Thermal Analyzer. About 12 mg of the composite samples were heated from 40 °C to 800 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

3. RESULTS AND DISCUSSION

The obtained results for the mechanical properties of the studied composites show that rice straw can be used as a reinforcement for polypropylene. The increased rice straw content resulted in a higher tensile modulus, E, (E_{PPm} = 914.6 MPa, $E_{RS/PPm(20/80)}$ = 1246 MPa, $E_{RS/PPm(30/70)}$ = 1514 MPa). However, tensile strength was reduced by about 20% by increasing the rice straw content. Obviously, at higher rice straw contents, the interfacial area between the filler and the polymer also increased, which reduced the interfacial bonding between the rice straw (hydrophilic) and polypropylene (hydrophobic) matrix. For irregular shape reinforcements, the strength of the composites decreases due to the inability of the reinforcement to support stress transfer from the polymer matrix (Yang et al., 2004).

Since the industrial manufacturing of the composites proceeds mainly in a nonisothermal regime, analysis of the crystallization parameters and crystallization behavior of rice straw/polypropylene composites is especially important from a practical point of view. For composites based on semicrystalline polymers, the crystallinity is an important factor that determines the stiffness and fracture behavior of the crystallized polymer matrix (Feng et al., 2001). The crystallinity depends upon processing parameters, e.g. T_c, cooling rate, nucleation density and annealing time (Sanadi et al., 1999). Crystallization data for T_c and ΔH_c obtained by differential scanning calorimetry are summarized in Table I.

It is clear that the addition of rice straw to a polypropylene matrix results in an increased crystallization temperature and accelerated crystallization process due to the "nucleating" effect of the rice straw. This could advantageously affect the processing of the composites.

Characteristic dynamic-mechanical data of polypropylene and rice straw/polypropylene composites are shown in Table II and in Figure 1 (tan δ) and Figure 2 (E'). According to the

Table I. Crystallization data for rice straw/polypropylene composites.

Sample	T_c (°C)	Onset T_c (°C)	ΔH_c (J/g)
Polypropylene	107.8	114.1	72.4
Rice straw/Polypropylene (20/80 wt%)	114.5	118.9	67.8
Rice straw/Polypropylene (30/70 wt%)	115.2	119.1	78.3

T_c: crystallization peak temperature (°C); Onset T_c: starting crystallization temperature (°C); ΔH_c: the heat of fusion (J/g).

Table II. Dynamo-mechanical parameters of polypropylene and rice straw/polypropylene composites.

Sample	E' (GPa) at 25 °C	E" (GPa) at 25 °C	tan δ at 25 °C
Polypropylene	3.53	0.08	0.022
Rice straw/Polypropylene (20/80 wt%)	5.37	0.18	0.035
Rice straw/Polypropylene (30/70 wt%)	4.51	0.12	0.026

E': storage modulus; E": loss modulus; tan δ: ratio of loss and storage moduli.

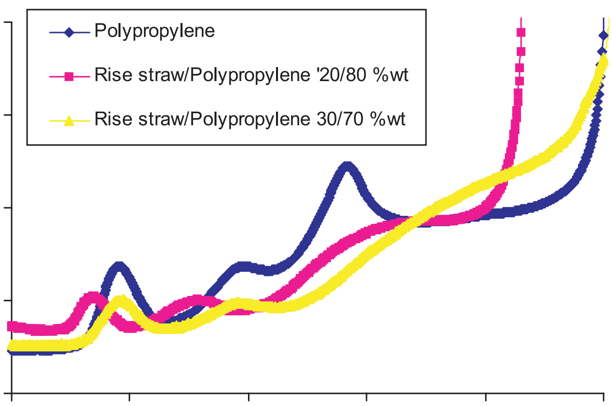


Figure 1. Dynamo-mechanical thermograms for the ratio of storage and loss moduli, tan δ, of polypropylene and rice straw/polypropylene composites .

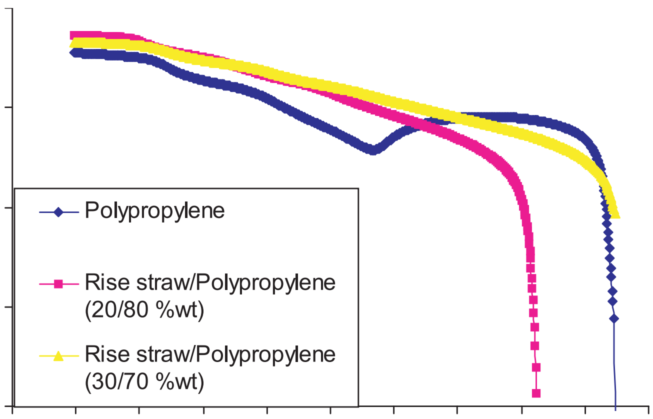


Figure 2. Storage modulus spectra of polypropylene and rice straw/ polypropylene composites.

obtained results for the ratio of loss and storage moduli (tan δ = E″/E′), rice straw/polypropylene composites exhibit higher mechanical properties compared with neat polypropylene in the range of –50 to 50 °C, while they decreased by increasing the temperature above 50 °C. The higher storage modulus of rice straw/polypropylene composites suggested relatively good adhesion between the filler and polymer.

Figure 2 shows the change in the storage modulus, *E*', of polypropylene and rice straw/polypropylene composites. Two variations in *E*' with temperature can be observed for all the systems: a drop in *E*' from –25 °C to 20 °C and a drop in *E*' above 100 °C. The first change between –25 °C and 20 °C is the relaxation associated with the amorphous phase (β relaxation). In this case, the glassy state of the amorphous phase goes through its glass transition and there is a drop in *E*'. Above 80 °C, depending on the system, the reduction in *E*' is less severe until the softening temperature, T_S. In the range of 100 °C to 145 °C the softening temperature of all the system is seen and then the melt region is reached.

The relaxations and the changes in the softening temperatures determined from the loss modulus curves for polypropylene and the rice straw/polypropylene composites are presented in Table III. The β transition peak can be observed between –25 °C and 0 °C, while the α relaxation peak can hardly be seen between 35 °C and 95 °C. The β transition is related to the glass transition, due to the motions associated with unrestricted amorphous polypropylene (Feng et al., 2001). It can be seen that β transition peak temperatures are closed for all three curves (*E'*, *E"*, tan δ) ($T_{g\ PP}$ = –5/–10 °C, $T_{g\ RS/PP(20/80)}$ = –20/ –25 °C, $T_{g\ RS/PP(30/70)}$ = –3/–6 °C).

The presence of rice straw in RS/PPm improved both *E'* and *E"* moduli up to 50 °C, when they showed lower softening temperatures. Higher *E'* values in this range indicate that the rice straw/polypropylene composites still have good fiber/matrix stress transfer.

The obtained DMTA results indicate that further optimization and extended modification is needed in order to improve

Table III. Transition temperatures obtained by dynamo-mechanical analysis of polypropylene and rice straw/polypropylene composites.

	E”	Transition (°C)	Temperature	T_S (°C)
Sample	γ	β	α	
Polypropylene	–60.7	–7.8	95	139
Rice straw/Polypropylene (20/80 wt%)	–65.0	–25	37	108
Rice straw/Polypropylene (30/70 wt%)	–52.0	–5.8	59	145

T_S: softening temperature (°C).

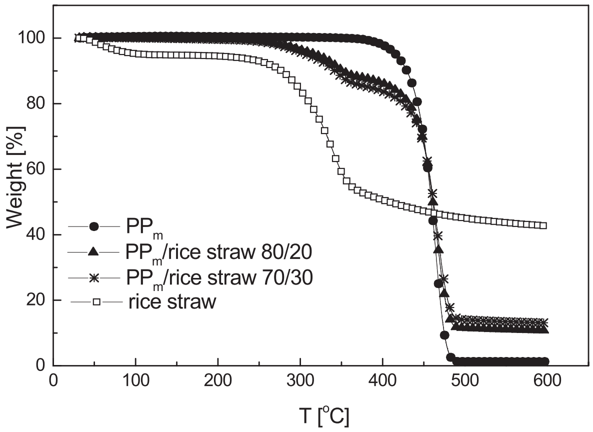
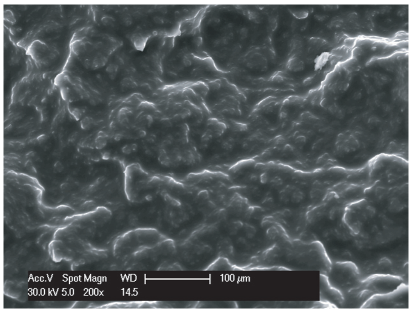


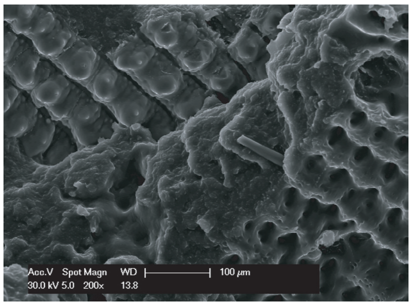
Figure 3. Thermogravimetric curves of rice straw/polypropylene composites.

the fiber/matrix adhesion, which consequently will result in enhanced properties of the studied rice straw/polypropylene eco-composites.

The results obtained by thermogravimetric analysis are presented in Figure 3. The thermogravimetric curve of rice straw exhibits two mass-loss steps: the initial mass loss below 100 °C results from the gradual evaporation of absorbed moisture, while the second mass-loss step in the range of 170 to 550 °C is due to the decomposition of the three major constituents of the rice straw (cellulose, hemicellulose and lignin). The lignocellulosic materials are chemically active and decompose thermochemically between 150 and 500 °C: hemicellulose, mainly between 150 and 350 °C, cellulose between 275 and 350 °C, and lignin between 250 and 500 °C (Kim et al., 2004). Ash in the rice straw (12%) is mainly composed of silica (~96%), and the amount and distribution of silica in the rice straw is likely to be an important factor in determining the properties of the composite products (Kim et al., 2004). The thermogravimetric curve of the rice straw/polypropylene composites also exhibits two main mass-loss steps, the first one of the rice straw and the second one of the polymer matrix. The mass-loss step of the polypropylene matrix occurs slowly below 430 °C, but above 430 °C this process occurs rapidly and is completed at 560 °C. The thermal degradation of polypropylene can take place through random chain scission and a radical chain mechanism. Generally, the rice straw/polypropylene composite showed slightly higher thermal stability; as the rice straw content increased, the thermal stability of the composites increased.



(a)



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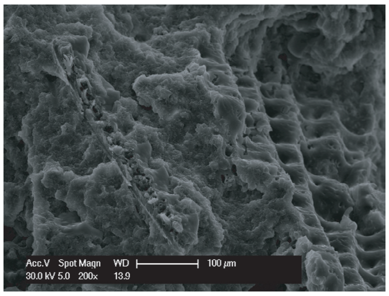

(c)

Figure 4. Scanning electron microscopy (SEM) micrographs of the fracture surfaces of (a) polypropylene matrix (×200), (b) the rice straw/polypropylene composite (20/80) (×200) and (c) the rice straw/polypropylene composite (30/70) (×200).

($T_{d\,\mathrm{PPm}}$ = 466 °C, $T_{d\,\mathrm{RS/PPm}\ (20/80)}$ = 468 °C, $T_{d\,\mathrm{RS/PPm}\ (30/70)}$ = 470 °C).

SEM micrographs of the fracture surfaces of Polypropylene (×200), Rice straw/Polypropylene 20/80% wt (×200) and Rice straw/Polypropylene 30/70% wt (×200) composites after the performed tensile test measurements are shown in Figure 4. The composites mainly represent plastic deformation. A number of holes can be seen in the polymer matrix region. The clean rice straw surface indicates that the adhesion between the rice straw filler and polymer matrix is very weak.

4. CONCLUSION

The properties of the rice straw/polypropylene composites show that rice straw could be used as a biodegradable eco-friendly reinforcement at end-of-use in polypropylene composites, to minimize environmental pollution rather than to perform a strong reinforcing effect. The composites had an acceptable strength up to a rice straw content of 30% wt. The mechanical properties and impact resistance of rice straw/polypropylene composites could be improved by modification of the rice straw, which is a subject of our further research. The cost of the obtained composites is expected to be significantly reduced by adding a cheap lignocellulosic waste product, which permits production of more rigid material compared with polypropylene.

Acknowledgement: This work was supported by a grant of the EU FP6-INCO-WBC program (INCO-CT-2004-509185).

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