

Properties of Thermoplastic Composites Based on Wheat-Straw Lignocellulosic Fillers

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ABSTRACT: Lignocellulosic fractions from wheat straw were used as natural fillers in composites of a polyolefin (a copolymer of polyethylene and polypropylene) and a biodegradable polyester [poly(butylene adipate-co-terephthalate)]. The mechanical properties of these injected composites were investigated with tensile and impact testing. A reinforcing effect of wheat-straw residues was found for both types of composites. Compared with the polyester-based composites, the polyolefin composites were more brittle. The addition of compatibilizing agents (γ -methacryloxypropyltrimethoxysilane, maleic anhydride modified polypropylene, and stearic acid) did not improve the prop-

erties of the polyolefin composites. The surface properties were studied with contact-angle measurements, and poor interfacial adhesion was found between the hydrophilic lignocellulosic filler and the hydrophobic polyolefin matrix. Thermal characterization revealed the formation of low intermolecular bonds between the polyester matrix and the lignocellulosic filler, in agreement with the surface tensions results and scanning electron microscopy observations. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 428–436, 2004

Key words: composites; biodegradable; polyesters; biofibers; interfaces

INTRODUCTION

For several years, natural fibers have been used as reinforcing additives for polymers. Wood fibers have been commonly combined with thermoplastic^{1–7} or thermoset⁸ matrices to enhance mechanical properties such as the stiffness and impact strength. In recent years, annual crop fibers have been increased in value through their incorporation into various polymers. Agricultural waste can originate from different sources, such as sisal, jute, coconut, and flax,^{9–28} and it has significant potential as a source of low-cost reinforcements for polymers, particularly polyolefins such as polyethylene (PE) or polypropylene. However, polyolefins are not the most appropriate matrices for natural fibers because of their nonpolar character and the polar properties of agricultural waste. Several solutions have been proposed to improve interfacial compatibility, such as chemical or physical treatment of the fibers. Different coupling or compatibilizing

agents have been widely used to modify the surface tension of fibers.^{21–29} Another alternative for obtaining good compatibility between natural fibers and a matrix is to use more polar thermoplastic matrices such as poly(methyl methacrylate), polyacrylate, poly(vinyl chloride), and biodegradable polyesters.^{30–38}

Wheat-straw waste is a natural byproduct of the industrial fractionation of wheat straw. To enhance the value of this residue, we propose its incorporation into thermoplastic polymers. Two matrices and different polarities have been tested. Composites based on a hydrophobic matrix such as a polypropylene–polyethylene copolymer require chemical modification, whereas composites based on a more hydrophilic matrix such as a biodegradable polyester are likely to present better interfacial compatibility. The mechanical and thermal properties of these wheat-straw-waste-based composites have been investigated. The crucial importance of interfacial interactions has been studied.

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EXPERIMENTAL

Materials

Two thermoplastic matrices were used. The polypropylene–polyethylene (6%) copolymer was supplied by

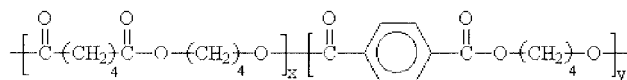


Figure 1 Chemical structure of the polyester (PBAT).

Atofina [Polypropylene 9760 (PP)], and the biodegradable copolyester [poly(butylene adipate-*co*-terephthalate) (PBAT)] was supplied by Eastman (Eastar Bio Ultra Copolyester 14766). The chemical structure of PBAT is drawn in Figure 1.

The lignocellulosic materials used as fillers were byproducts of the industrial fractionation of wheat straw (ARD, Pomacle, France).

Various compatibilizing agents were tested, including γ -methacryloxypropyltrimethoxysilane (A174, Crompton Europe), maleic anhydride modified polypropylene (MAPP; Orevac, Atofina), and stearic acid (Aldrich, Milwaukee, WI).

Lignocellulosic residue (LCR)

Wheat straw was hydrolyzed in an acid medium.³⁹ The soluble fraction was filtered and then refined for further applications, and the byproduct, the insoluble fraction called LCR, was recovered. The particle length was approximately 0–1 mm after the sieving. Lignin and mineral compositions were determined with Klason lignin.⁴⁰ After the hydrolysis of LCR in an acid medium, sugar titration by high-performance liquid chromatography allowed us to quantify the cellulose and hemicellulose contents. LCR was 6% water (3% of residual water), 55% cellulose, 8% hemicellulose, 28% lignin, and 3% ash. The thermal stability was determined by thermogravimetric analysis (high-resolution TGA 2950, Waters TA Instruments) at a heating rate of 5°C min⁻¹. LCR was thermally stable up to 200°C. The LCR density, determined by pycnometry measurements of 10, 20, and 30% LCR filled composite tensile bars, was found to be 1.45 g/cm³ under the assumption that there were no voids in the composite materials.

Fiber treatment

Silane treatments were achieved through the spraying of aqueous solutions to obtain either a 2 or 5 wt % coating on the fibers.⁴¹ Then, a thermal treatment at 50°C was applied in an oven to promote chemical bonds with the fibers. After the treatment, no solvent extraction was performed to remove the excess silane that was not covalently bonded to LCR. Additional bonds were expected to be created during blending at a high temperature. The weight gain of silane-treated LCR was insignificant. Powdered stearic acid was merely mixed with the fibers before processing⁴² at a

concentration of 8 wt % with respect to the fibers. MAPP pellets dried at 160°C for 5 min⁴³ were mixed with PP-PE copolymer pellets at a concentration of 20 wt %. Environmentally friendly organic solvents with low toxicity were used.

Sample preparation

Before the blending, treated or untreated fibers and thermoplastic granules were dried in an air-circulating oven at 80°C for up to 4 and 1 h, respectively. Blends based on the polymers and various amounts of LCR, from 1 to 30 wt %, for the PP composites were directly added to the feeding zone of a single-screw extruder (S 2032, Scamia, Paris, France). For technical reasons, a maximum concentration of 30 wt % LCR was added to the matrices. For treated PP composites, the LCR content was 10 wt %. The variation of the PP matrix weight between the different blends were negligible. The extrusion temperatures were 135 and 165°C for PBAT and PP, respectively. Strands (3 mm in diameter) were pelletized after air cooling. These granules were extruded once again to improve the fiber dispersion into the matrix.

Standard dumbbell specimens (NFT 51-034-1981) were molded with an injection molding machine (DK Codim NGH 50/100) between 175 and 190°C for PP compounds and at 125 and 140°C for PBAT compounds. The injection-molded specimens were approximately 10 mm wide and 4 mm thick (French Standard NFT 51-0.34 1981).

Characterization

Tensile testing was carried out with an Instron 4204 tensile testing machine according to ASTM D 882-91 at a crosshead speed of 50 mm min⁻¹. Ten samples for each blend were tested. The impact resistance was determined on unnotched samples with an impact tester (JPS, France) according to the Charpy method (French Standard NFT 51-035 1983). Ten samples for each blend were cut from the central parts of the dumbbell specimens (60 mm × 10 mm × 4 mm) and were tested with a 4-J pendulum. The storage conditions for the different samples before testing were 23°C and 50% relative humidity for 5 days.

Contact-angle measurements were carried out on a goniometer (G23, Kruss, Germany). The surface tensions of the solid materials were calculated with the sessile drop method. Water and methylene iodide were used as test liquids because of their different polarities. Wu's method⁴⁴ was used to evaluate the polar (γ^p) and dispersive (γ^d) components of the surface tension (γ). The harmonic-mean equation was used to calculate the work of adhesion (W_{12}) between

TABLE I
Mechanical Properties of LCR/PP Composites

	Tensile modulus (MPa)	Yield stress (MPa)	Strength at break (MPa)	Elongation at break (%)	Charpy impact strength (kJ m ⁻²)
0	860 (20)	22.9 (0.3)	<15	>600	>100
1%	900 (21)	25.0 (0.3)	19.8 (0.6)	27.0 (3.0)	42.0 (6.0)
5%	936 (21)	24.2 (0.3)	21.6 (0.2)	13.0 (1.0)	17.0 (3.0)
10%	1131 (17)	24.0 (0.5)	22.2 (0.5)	11.4 (0.8)	9.9 (2.2)
20%	1477 (23)	23.4 (0.3)	22.5 (0.3)	5.0 (0.4)	4.3 (0.3)
30%	1673 (27)	21.8 (0.3)	21.7 (0.3)	3.8 (0.2)	3.2 (0.3)

Standard deviations are given in parentheses.

the matrix (1) and the natural fibers (2). The interfacial tension (γ_{12}) was then calculated:⁴⁵

$$W_{12} = \frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (1)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - W_{12} \quad (2)$$

The measurements were carried out on tablets (200 mg) molded *in vacuo* at room temperature for natural materials and on injected dumbbell specimens for matrices.

Scanning electron microscopy (SEM) was performed with a Leo Gemini 98 instrument to investigate the morphology and the interface between the filler and matrix. Cryogenic fracture surfaces were observed. SEM micrographs were obtained with a 3-kV voltage.

Differential scanning calorimetry (DSC; DSC 2920, TA Instruments, USA) was used. Samples (10–15 mg) were sealed in aluminum pans. The heating and cooling rates were 10°C min⁻¹. A nitrogen flow (45 mL min⁻¹) was maintained throughout the test. For all materials, the first scan was used for removing the thermal history. For composites based on PBAT, each sample was heated to 150°C and then cooled to -50°C before a second heating scan to 150°C. For PP materials, the temperature limits were -20 and 210°C. The glass-transition temperature (T_g) and melting temperature (T_m) were determined from the second heating scan. The crystallization temperature (T_c) was obtained from the cooling scan because the samples were

not quenched. T_g was determined at the midpoint of heat capacity changes, T_m was determined at the onset peak of the endotherm, and T_c was determined at the onset peak of the exotherm. Three samples for each blend were tested.

RESULTS AND DISCUSSION

Mechanical properties of the PP/LCR composites

Effects of various amounts of LCR in the PP matrix

Table I shows the tensile and impact behavior of PP/LCR composites. A significant increase in the tensile modulus with respect to that of the unfilled polymer can be observed as a function of the LCR content. The incorporation of a low amount of LCR (1 wt %) causes an increase in the yield stress. For higher LCR contents, an improvement in the stiffness occurs with a decrease in the yield stress. Besides, the more the composites are filled, the better the strength at break is. The incorporation of a low content of LCR causes a drop in the elongation at break and impact properties. The lack of interfacial adhesion, due to the opposite polarities, between the matrix and LCR is responsible for these poor mechanical properties. The incorporation of LCR into polypropylene brings stiffness, toughness, and brittleness.

Effects of the addition of a compatibilizing agent

Grafting is a method used to improve adhesion at the fiber-matrix interface. Compatibilizing agents are ex-

TABLE II
Mechanical Properties of the 10 wt % LCR-Reinforced PP Composites

	Tensile modulus (MPa)	Yield stress (MPa)	Strength at break (MPa)	Elongation at break (%)	Charpy impact strength (kJ m ⁻²)
Untreated LCR	1131 (17)	24.0 (0.5)	22.2 (0.5)	11.4 (0.8)	9.9 (2.2)
Silane 2%	1020 (24)	24.4 (0.2)	22.4 (0.4)	10.7 (1.0)	8.1 (0.5)
Silane 5%	1064 (17)	24.0 (0.1)	22.1 (0.2)	10.2 (0.8)	10.1 (1.3)
MAPP	1008 (22)	27.2 (0.2)	25.3 (0.6)	8.7 (0.3)	9.3 (1.1)
Stearic acid	1125 (18)	23.3 (0.1)	21.1 (0.3)	11.8 (0.8)	10.8 (1.2)

Standard deviations are given in parentheses.

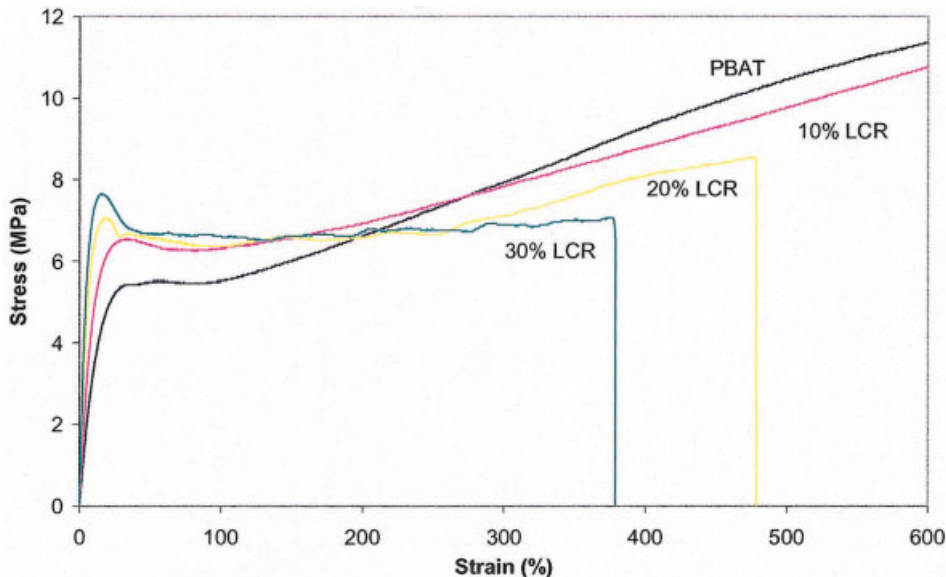


Figure 2 Stress-strain curves for various amounts of LCR in the PBAT matrix.

pected to modify the interface by interacting with both the fibers and the polyolefin matrix. The mechanical properties of polypropylene composites containing 10 wt % LCR with or without a chemical agent are shown in Table II. Silane treatments (2%) applied to LCR have no significant effect on the mechanical behavior in comparison with the untreated materials (considering the standard deviations), except for a tensile modulus decrease. A larger amount of silane brings about stiffness, but the tensile modulus is not as high than as that of the untreated PP composites. On the one hand,

functionalized PP yields a significant improvement in the yield stress and strength at break, 13 and 14%, respectively. On the other hand, the stiffness and ductility decrease. No significant effects on the mechanical properties have been observed with the addition of stearic acid. The same results were obtained by Hornsby et al.,⁴² who used these chemical agents to modify the wheat-straw-fiber surface. Bataille et al.⁴⁶ showed that treatments of cellulose fibers (99.5% pure α -cellulose, hardwood pulp) with A174 silane and MAPP significantly improved the mechanical proper-

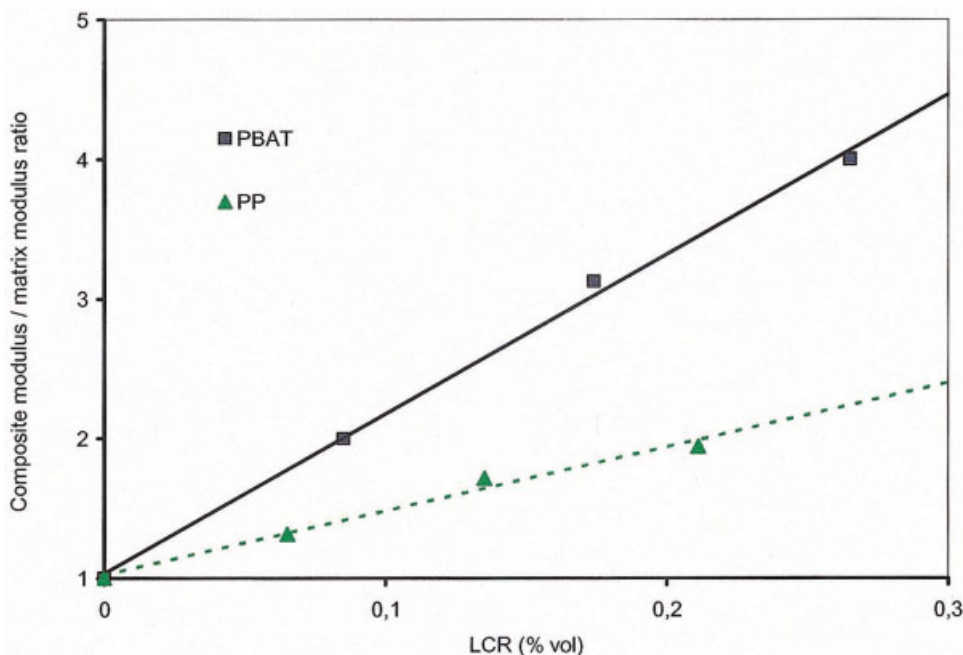


Figure 3 Ratio of Young's moduli (composite modulus/matrix modulus) as a function of the LCR content for PBAT and PP.

TABLE III
Surface Tensions of the Raw Materials

		PP	PBAT	LCR	Cellulose
Contact angle (°)	W ^a	96 (2)	64 (2)	65 (5)	47 (2)
	MI ^a	53 (2)	29 (2)	45 (1)	31 (1)
Dispersive component (mJ m ⁻²)	W/MI	32 (2)	40 (2)	33 (2)	39 (2)
Polar component (mJ m ⁻²)	W/MI	2 (1)	13 (2)	15 (2)	22 (2)
Surface tension (mJ m ⁻²)	W/MI	34 (2)	53 (2)	48 (2)	61 (2)

Standard deviations are given in parentheses.

^aW = water; MI = methylene iodide.

ties of PP composites. Both cellulose and lignin hydroxyls have been presumed to react with coupling agents.⁴⁷

Compared with cellulose, lignins show a reduced hydroxyl concentration and reactivity. We can conclude that not all hydroxyls groups are fully accessible or that operating conditions are not optimal. Besides, LCR shows a lower cellulose/lignin ratio than wheat straw. If the fractionation process of wheat straw in an acid medium modifies the chemical reactivity of lignins, the previous chemical treatments could show low efficiency.

Mechanical properties of the LCR/PBAT composites

The stress-strain tensile curves of the unfilled PBAT and PBAT composites are shown in Figure 2 to illustrate the influence of the LCR content on the tensile properties of the PBAT composites. A 10% LCR content improves the mechanical behavior, including the stiffness and toughness. Compared with unfilled PBAT, this material keeps its ductility. A yield strength improvement and a decrease in the elongation at break occur with an increase in the LCR content. However, the PBAT matrix filled with 30 wt % LCR keeps its ductile character, contrary to the equivalent polypropylene composite. PBAT is likely to promote intermolecular bonds with the LCR because of its polar structure (ester functions).

Influence of the reinforcing effect of the LCR fibers in the PBAT and PP composites

The contributions of LCR as a reinforcing additive have been investigated. Figure 3 shows the gain of stiffness for LCR-filled PBAT in comparison with PP materials. The Young's moduli of PP and PBAT are 860 and 40 MPa, respectively. PBAT is a very ductile matrix, and the addition of up to 27 vol % LCR increases its stiffness dramatically by a factor of 4; for PP composites, the increase is only twofold. These results show that the LCR fibers are efficient reinforcing additives for the PBAT matrix. This is due to the fiber-matrix interactions.

Contact-angle measurements

The wetting properties have been determined by contact-angle measurements on the raw materials (PP, PBAT, and LCR). The results are shown in Table III. For comparison with lignocellulosic material data, the same measurements have been carried out on pure cellulose, the references for which are given elsewhere.⁴⁸ As for the contact-angle results, the cellulose substrate shows the lowest contact angles, whatever the test liquid is, and PP shows the highest. The dispersive components of the substrates are only 32–40 mJ m⁻², whereas the polar components vary over a large range, from 2 to 22 mJ m⁻². These variations are related to the polar or nonpolar character of the substrate. The hydrophobic character of PP is shown by its low polar component in comparison with that of PBAT, LCR, and cellulose fibers. The fibers show relatively high values, in agreement with their well-known hydrophilic character. Nevertheless, the LCR polar component is not as high as the neat cellulose one. We can consider that its moderate value is due to the high LCR lignin content (28 wt %), which reduces the polar character of the filler surface. As for the filler surface tensions, the cellulose fibers show the highest values with respect to LCR. The surface tension of PBAT is higher than that of PP.

Table IV shows the work of adhesion and the interfacial tension data for PP/LCR and PBAT/LCR composites. The more compatible the two materials are, the higher the work of adhesion is. Low interfacial tension shows good affinity between the materials. Therefore, the PBAT matrix is apparently one of the best matrices for LCR-based composites. The low interfacial tension in the PBAT composites is indicative of high compatibility. PBAT interacts with the natural

TABLE IV
Work of Adhesion and Interfacial Tensions Between LCR and the Matrix (PP or PBAT)

	PP/LCR	PBAT/LCR
Work of adhesion (mJ m ⁻²)	72	100
Interfacial tension (mJ m ⁻²)	10	1

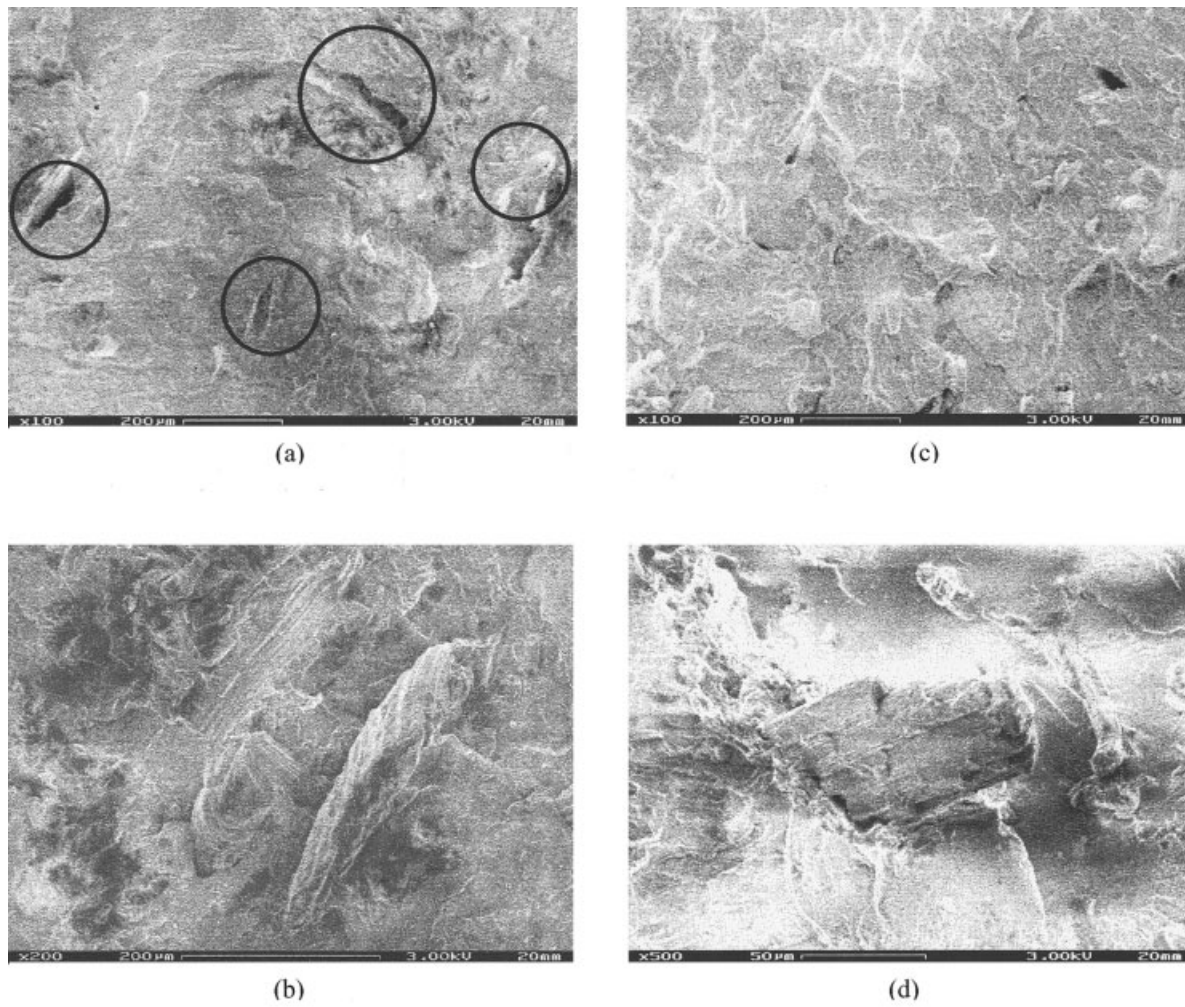


Figure 4 SEM micrographs of cryogenic fractures: (a,b) PP filled with 30 wt % LCR and (c,d) PBAT filled with 30 wt % LCR.

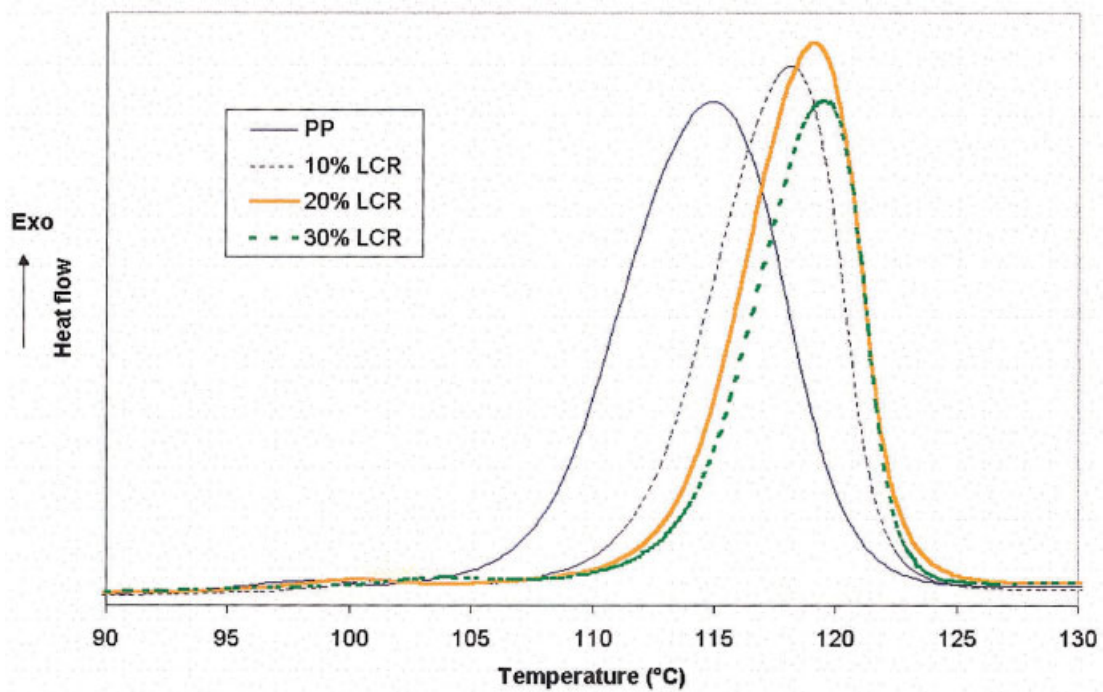


Figure 5 DSC curves for the crystallization of unfilled PP and PP/LCR composites.

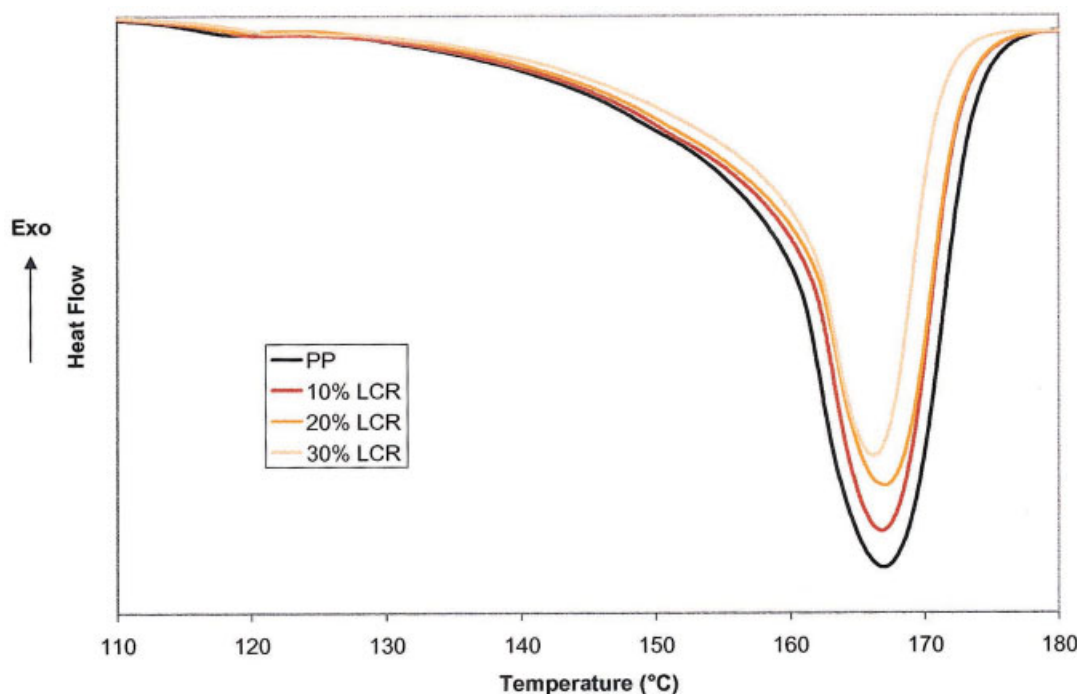


Figure 6 DSC curves for the melting of unfilled PP and PP/LCR composites (the weight percentage increases from the bottom to the top).

fibers because of its hydrophilic character. Hydrogen bonds and electron donor–acceptor interactions between PBAT and LCR are likely to link these two materials. These interactions are considered mainly with the Lewis concept of acid–base behavior.⁴⁹ The mechanical performance of both types of composites is also explained through the interfacial tension values.

Morphological observations

The surfaces of cryogenic fractures of PP and PBAT tensile bars are shown in Figure 4. In Figure 4(a,b), fiber pullout and decohesion can be observed because of poor filler–PP adhesion. The PP composites show adhesive failures. Figure 4(c,d) shows less fiber pullout and decohesion for PBAT composites than for PP composites. In addition to the previous determinations, these micrographs show again that filler–matrix compatibility is better for PBAT composites.

DSC measurements

Thermal characteristics of the PP composites

The crystallization curves of unfilled PP and PP/LCR composites are shown in Figure 5. The addition of small amounts of LCR to PP results in an increase in the matrix T_c . For PP composites, only low variations of T_c can be detected with higher filler contents.

Figure 6 shows the melting curves of unfilled PP and PP/LCR composites. The presence of 6% PE in the

polyolefin matrix can be observed with a light peak. The PE T_m is approximately 120°C, whereas that of PP is about 166°C. The addition of LCR to PP has no impact on these values. Different authors have noticed the same results^{48,50} with cellulose fibers.

The thermal characteristics [heat of crystallization (ΔH_c) and heat of fusion (ΔH_m)] of each PP composite are summarized in Table V. A parameter (P_{xm}) has been defined to estimate the crystallinity evolution of the sample. Equation 1 describes this crystallinity parameter with the percentage of crystallinity (X_c), ΔH_m , the heat of fusion for a 100% crystalline sample (ΔH_m^0), and the weight fraction (w):

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{w} \quad (3)$$

$$P_{xm} = X_c \times \Delta H_m^0 = \Delta H_m \times \frac{100}{w}$$

TABLE V
Crystallization and Heat of Fusion of the Investigated LCR/PP Samples

Sample	ΔH_c (J g ⁻¹)	ΔH_m (J g ⁻¹)	P_{xm} (J g ⁻¹)
PP	99.6 (0.2)	98.9 (0.2)	99
PP/10% LCR	84.8 (0.7)	85.7 (0.6)	95
PP/20% LCR	79.7 (0.7)	81.7 (0.8)	102
PP/30% LCR	65.0 (2.0)	67.0 (2.0)	96

Standard deviations are given in parentheses.

TABLE VI
Thermal DSC Parameters of Unfilled and Filled PBAT

Sample	T_g (°C)	T_m (°C)	ΔH_c (J g ⁻¹)	ΔH_m (J g ⁻¹)	P_{xm} (J g ⁻¹)
PBAT	-39.3 (0.3)	112.2 (0.5)	13.5 (0.2)	13.9 (0.3)	14
PBAT/10% LCR	-38.2 (0.2)	113.2 (0.7)	11.3 (0.1)	11.7 (0.2)	13
PBAT/20% LCR	-36.6 (0.2)	113.8 (0.5)	11.4 (0.2)	11.2 (0.4)	14
PBAT/30% LCR	-35.7 (0.2)	112.2 (0.6)	9.3 (0.5)	10.0 (0.3)	14

Standard deviations are given in parentheses.

The results for the crystallization and heat of fusion with increasing LCR contents show the same evolution. They decrease with higher filler contents because the LCR fibers act as diluents in the PP matrix.³⁹ No significant variation of the crystallinity parameter has been noticed, whatever the LCR content is.

Thermal properties of the PBAT composites

Chang and Tsai⁵¹ prepared different random copolyesters with various compositions. According to their results, the selected PBAT would be about 20–25% poly(butylene terephthalate) and 75–80% poly(butylene adipate). In agreement with the results shown in Table VI and Figure 7, Chang and Tsai showed that random copolyesters of poly(butylene terephthalate-co-adipate) present a single transition for T_g , T_c , and T_m .⁵¹

As shown in Table VI, the addition of increasing amounts of LCR results in a slight but significant increase in T_g of PBAT. According to Avella et al.,³³

this tendency may be explained by intermolecular interactions between the hydroxyl groups of the fibers and the carbonyl groups of the PBAT ester functions. These hydrogen bonds would probably reduce the polymer mobility and then increase T_g values.

PBAT–LCR composites do not show any significant variation of T_m , in agreement with Avella et al.'s³³ data. The crystallization and heat of fusion decrease (diluent effect). An increase in the amount of LCR does not affect the matrix crystallinity. Figure 6 shows crystallization curves of unfilled PBAT and PBAT/LCR composites. The incorporation of LCR induces a slight but significant increase in T_c that is probably linked to the low T_g increase, that is, to the reduction of the polymer mobility.

CONCLUSIONS

Composites based on lignocellulosic fillers from wheat straw and two matrices with different polar and non-polar characteristics have been prepared. According to

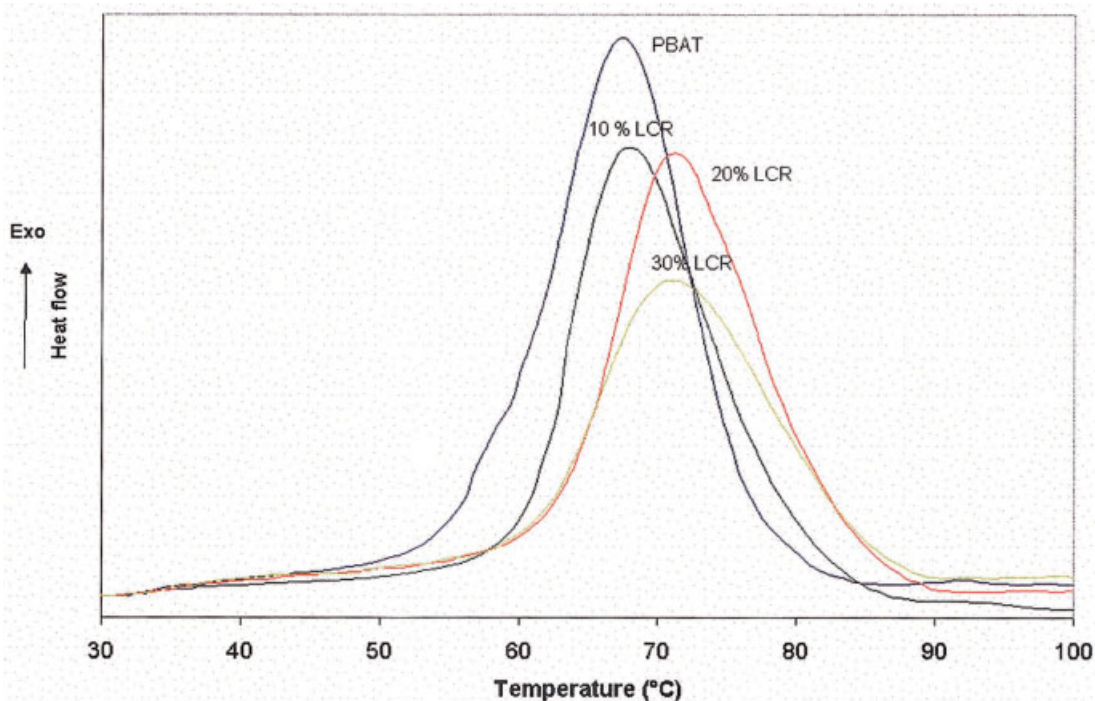


Figure 7 DSC curves for the crystallization of unfilled PBAT and PBAT/LCR composites.

the mechanical properties, the PP/LCR composites are brittle, and this has been correlated to the interface properties. The interfacial tension of the composites is too high for good adhesion. No significant effect has been found with the addition of compatibilizing agents. The mechanisms have not been studied but will require further investigations. The low interfacial tension of the PBAT/LCR composites induces good filler-matrix compatibility. The slight increase in T_g with increasing LCR contents reveals the likely presence of low intermolecular bonds between the lignocellulosic fibers and the matrix. The compatibility between the LCR fillers and PBAT allows us to consider the applications of such composites (e.g., short-term agricultural products).

In this study, a chemical fraction from wheat straw (LCR) has been used. In further investigations, fractions from LCR will be prepared to account for the natural biological variability of agricultural fibers. Fractionation in an alkaline medium allows better separation of different macromolecular fractions of LCR, such as the lignocellulosic matrix and cellulosic fiber fractions, according to previous work.^{52,53} Considering the well-known variability of lignins^{54,55} and the lignocellulosic preparation recently reported,⁵⁶ we can expect large variations in the chemico-mechanical properties of plastic-agricultural fiber composites.

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