

The Effect of Matrix Composition on the Properties of Cellulosic Fibers–Polyethylene Composites

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ABSTRACT: The solution/precipitation method was used for the preparation of polyethylene (PE)/cellulosic fibers composites. Blends of modified linear low density PE [linear low density PE-grafted maleic anhydride (LLDPE-g-MAH)] with low density PE (LDPE) were used as matrices for the aforementioned composites. Blends of LDPE with a copolymer of LDPE and acrylic acid (AA)/*n*-butyl acrylate (*n*-BA) [(AA/*n*-BA)-LDPE] were also studied for the same purpose. The reinforcing effect of cellulosic fibers in terms of tensile strength is more enhanced when mixtures of the modified polar polymer with pure PE were used as matri-

ces, as compared with that corresponding to matrices consisting of modified PE alone. Regarding the Izod impact strength, composites of LLDPE-g-MAH presented the best performance with an improvement of 135% in comparison with specimens consisting of LDPE matrix, whereas composites of (AA/*n*-BA)-LDPE matrix showed a modest improvement of their impact resistance. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2385–2393, 2008

Key words: polyethylene; composites; mechanical properties; thermal properties; interfaces

INTRODUCTION

Several cellulose-based products and wastes have been used as fillers for thermoplastic composites, in an attempt to design and produce cost-saving materials. Polyolefins, a well known commodity plastic, is often used as matrix for the aforementioned composites. Much of the effort in developing cellulose/polyolefin composites has been concentrated on the improvement of interfacial adhesion, which ensures higher stress-transfer efficiency between the hydrophilic filler and the nonpolar matrix. The incorporation of coupling agents is a well established method leading to better performance of polyolefins reinforced with cellulose-based fibers.

An increase of 59% in tensile yield strength of linear low density polyethylene (LLDPE) reinforced with 30% wood flour and modified with organic peroxide and maleic anhydride (MAH) was reported by Marcovich and Villar.¹ This improvement was attributed to increased interfacial adhesion between fiber and matrix and to more efficient fiber dispersion.

The impact strength of composites reinforced with short fibers is affected by the amount of the incorporated reinforcement. It was observed that the impact strength of LLDPE reinforced with wood fibers

decreased with wood flour content, because of the increase of fiber ends within the composite. The presence of short fibers means that considerable stress concentration takes place near the fiber ends, where microcracks appear and fibers debond from the matrix.

Because of the polarity of lignocellulosic fibers, their dispersion in the nonpolar low density polyethylene (LDPE) matrix is more difficult than the dispersion in polyethylene (PE) modified with polar groups, and therefore, a tendency for aggregation can be expected in the former case. These aggregates are stress concentration spots during an impact test and a possible interpretation of the decreased impact strength of LDPE composites in comparison with composites containing *m*-LLDPE and acrylic acid (AA)/*n*-butyl acrylate (*n*-BA)-LDPE [(AA/*n*-BA)-LDPE].¹

The effect of various types of compatibilizers on the mechanical properties of high density PE (HDPE)/wood flour composites were investigated by Lai et al.² Polyolefins modified with MAH were incorporated to reduce the interfacial tension between the PE matrix and wood filler. It was found that, in general, tensile and impact strengths of the composites increase with the content of the aforementioned modified polymers.

Maldas and Kokta³ studied the effect of defibration method and some other parameters such as fiber size, concentration, and type of additives (e.g., coupling agents, impact modifiers, and fire retard-

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ants) on the mechanical properties of old newspaper fiber/polypropylene (PP) composites. They studied the following coupling agents: (i) polyvinyl alcohol (PValc) and (ii) maleated PP (PP-*g*-MAH) with initiator [dicumyl peroxide (DCPO)] and found that in the presence of PP-*g*-MAH and DCPO, the tensile strength of composites increases with increasing fiber size and content. Both tensile strength and modulus increased with increasing concentrations of PP-*g*-MAH and DCPO, even in the presence of an impact modifier and fire retardants.

Ren and Hon⁴ reported a significant improvement of tensile strength with the increase of the amount of maleated PP in PP/news paper fiber composites, up to 30%, and then a decrease. It was also observed that the modulus of elasticity is not significantly affected by the amount of maleated PP added. On the other hand, the incorporation of ethylene-propylene–diene copolymer (EPDM) in PP/HDPE blends filled with paper fibers was reported to have led to the improvement of impact strength, whereas the tensile properties were deteriorated.⁵

In PP matrix composites reinforced with recycled newspaper fibers, a modified version of the matrix was tested by Sanadi et al.,⁶ in an attempt to improve the interactions between the hydrophobic PP and the highly polar fibers. These researchers used PP-*g*-MAH and AA-grafted PP and found that the molecular weight of the coupling agent and the graft percentage affected the tensile properties of the examined composites.^{6,7}

Regarding the impact test, the experimental results presented by Son et al.⁷ showed that the incorporation of coupling agents improved the fiber–matrix interaction and increased the work of fracture of the interface. The impact strength was doubled at 40% paper loading when 3% MAH was added, whereas in the case of AA an improvement of 10% was observed. The increase of impact strength of unnotched specimens, as compared with that of notched, was attributed to differences in the crack initiation energies.

Qiu et al.⁸ studied the performance of composites of PP, PP-*g*-MAH, and their mixtures, filled with crystalline cellulose. It was observed that the tensile strength decreases when pure PP is used as matrix, whereas the modulus of elasticity increases because of the high modulus of crystalline cellulose. PP-*g*-MAH composites exhibit a strong improvement in both, tensile strength and modulus of elasticity, due to improved interfacial adhesion between fibers and matrix.

In this work, the effect of some modifications of the polymer matrix on the properties of polymer/cellulosic fiber composites was studied. For this purpose, three types of PE matrices were tested: LLDPE, MAH-grafted LLDPE (LLDPE-*g*-MAH), and a copolymer of AA/*n*-BA and LDPE [(AA/*n*-BA)–LDPE].

According to our previous work,^{9,10} the composites were prepared following the solution/precipitation method, a procedure already established for the separation of polymer mixtures and recycling.^{11,12} This method employs modest temperature and shear stresses for producing the mixture of polymeric matrix and fillers. In addition, more efficient fiber dispersion within the polymer matrix can be achieved, because of the elimination of fiber aggregates that are often formed as a result of electrostatic forces. In addition to that, the low viscosity of the polymer solution in comparison with that appearing in the melt-mixing techniques can further assist proper dispersion. Therefore, the study of interactions between functionalized polymer matrices and paper fibers seems a promising step for the optimization of performance of the aforementioned composites.

MATERIALS AND METHODS

Materials

Polymer matrix

The following types of LDPE were used for the preparation of the lignocellulosic fiber-reinforced composites:

1. LDPE (Riblene FL30, Polimeri Europa), with density 0.924 g/cm³ and melt flow rate 2.2 g/10 min, measured at 190°C/2.16 kg. This type of LDPE is recommended for molding of blown film.
2. MAH-grafted LLDPE [LLDPE-*g*-MAH; COESIVE LL15M, MATERIE PLASTICHE BRES-CIANE, Italy] with density 0.910–0.920 g/cm³ and melt flow rate 1.0–2.0 g/10 min. The MAH is introduced by reactive extrusion to the polymer backbone, at a weight ratio of 1%. Typical applications of LLDPE-*g*-MAH are tie layer in multilayer products (pipes, bottles, films) and compatibilizer in PE blends.
3. (AA/*n*-BA)–LDPE (Lucalen A 2920 M, Basell Italy Spa) with density 0.927 g/cm³, melt flow rate 7.0 g/10 min and typical composition: AA comonomer: 4% (DIN 51451), *n*-BA comonomer: 7% (DIN 51451). This copolymer is used as tie layer in extrusion-blown film production.

Blends of the aforementioned types of LDPE were prepared as follows:

4. 20% LLDPE-*g*-MAH + 80% LDPE
5. 50% LLDPE-*g*-MAH + 50% LDPE
6. 20% (AA/*n*-BA)-LDPE + 80% LDPE
7. 50% (AA/*n*-BA)-LDPE + 50% LDPE

Cellulosic fiber reinforcement

The cellulosic fiber reinforcement consisted of chemical fluff pulp from Maritime pine (*Pinus Pinaster*), under the trade name BIOFLUF HD (Tembec Tartas SA, France). It is a chemical pulp bleached with oxygen and oxygen compounds, without any chlorine gas. The average length of the cellulosic fibers is 2.25 cm and their apparent density is 0.57 g/cm³.

Experimental procedure for composite preparation

Compounding of polyethylene with cellulosic fibers

Blends of LDPE and LLDPE-*g*-MAH with composition 50/50 and 80/20, as well as LDPE/(AA/*n*-BA)–LDPE with the same compositions, were loaded with 30% (w/w) cellulosic fibers.

The appropriate quantity of polymer and xylene were fed into the dissolution vessel so that a 5% w/v polymer/solvent mixture was obtained. The mixture was heated with an oil bath, under stirring at 500 rpm up to the dissolution temperature (100°C). After complete dissolution, the cellulosic fibers were added and the resulting mixture was kept at the dissolution temperature for 1 h under stirring at about 700–900 rpm, which ensures satisfactory dispersion of fibers in the polymer solution. The mixture was then slowly cooled to room temperature, still under stirring at 200 rpm. Cooling was achieved by circulation of cooling-water in a coil immersed in the oil bath. Because of the temperature decrease, the polymer precipitates, thus producing a slurry containing the filler fibers. The mixture was filtered under vacuum for solvent removal, and the obtained material was further dried in a vacuum oven for 4–6 h at 80–85°C and 50 mbar.

Preparation of composites by compression-molding

The mixtures of polymer and cellulosic fibers were molded into rectangular sheets (15 × 15 cm²) of about 2-mm thickness using a flash type steel mold on a heated plates hydraulic press. The molding parameters, i.e., pressure, temperature, and time, are presented in Table I.

A Zwick cutting machine (model 7103) was employed for cutting specimens from the obtained sheets, according to the dimensions reported in ASTM D-638¹³ (specimen type IV), to run tensile tests.

For the Izod impact test, the specimen's dimensions were 1.00 cm × 1.00 cm × 7.00 cm.

Materials characterization

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were run in a Perkin Elmer DSC4 differential

TABLE I
Compression Molding Parameters for the Preparation of Polyethylene Matrix Composites Reinforced with Cellulosic Fibers

	Plates' temperature (°C)	Pressure (bar)	Time (min)
Heating	140	2	0
	180	30	10
	185	30 ^a	11
	185	0 → 40 → 0 ^b	12
	190	80	13
	190	150–170	14
Cooling	190 → 25	170 → 0	15–30

^a Leakage of polymer from the flash type matrix.

^b Pressure drop for liberation of trapped air in the mold.

scanning calorimeter. Samples with weight ranging from 7 to 10 mg were accurately weighed and encapsulated in aluminum pans. The samples were heated from 30 to 200°C at a rate of 5°C/min, under nitrogen. The melting temperature and the heat of fusion (ΔH_m) were calculated from the thermographs obtained during heating.

Density

Density measurements were performed according to ASTM D-792¹⁴ specification, using an electronic balance equipped with a stationary support necessary for holding the immersion vessel above the balance pan (Mettler Toledo AB204-S). The density of the composite (d) was calculated using the following equation:

$$d = \frac{A}{P} d_a \quad (1)$$

where A is the weight of specimen, P is the apparent weight of specimen immersed in a liquid, and d_a is the density of immersion liquid (acetone for our experiments, with d_a of 0.791 g/cm³ at 24.1°C).

Mechanical tests

Tensile measurements were run according to ASTM D-638¹⁴ specification. Five specimens from each composition were tested in an Instron tensometer (model 4466), equipped with a load cell of maximum capacity of 10 kN, operating at a grip separation speed of 50 mm/min.

The impact strength (Izod method) was measured at room temperature using a Wolpert PW5 impact tester (Instron UK) according to ASTM D-256,¹⁵ with specimen dimensions 10 mm × 10 mm × 70 mm. At least 10 specimens of each composite were tested, and the impact strength was obtained as the mean value of these measurements.

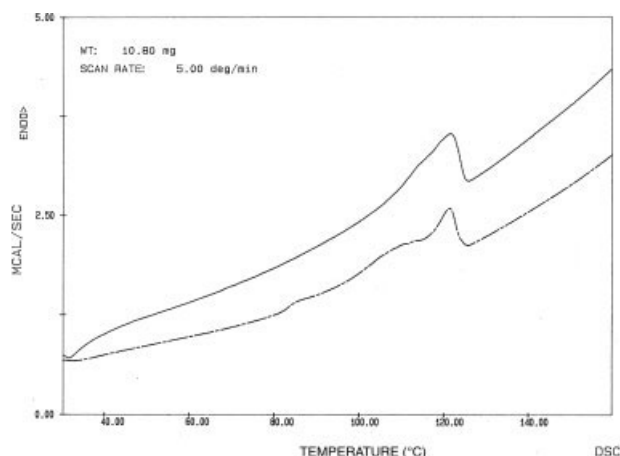


Figure 1 DSC thermographs of virgin LLDPE-g-MAH pellets (—) and LLDPE-g-MAH obtained by the dissolution/precipitation method (— - —).

RESULTS AND DISCUSSION

Thermal characterization

The DSC thermographs of pure LLDPE-g-MAH, treated by the dissolution/precipitation method, provide some information about thermal and structural characteristics of the polymer, and these are presented in Figure 1. A broadening of the peak corresponding to melting transition can be observed, most probably due to the broadening of crystal size distribution within the crystalline phase, since the dissolution/precipitation technique allows the crystallization process to take enough time during precipitation and cooling of the polymer slurry. From the same thermographs, it can be seen that crystallization of LLDPE-g-MAH is better promoted by the dissolution/precipitation process, as compared with conventional melting techniques.

As shown in Figure 2, the DSC scan obtained from blends of LDPE with LLDPE-g-MAH displays

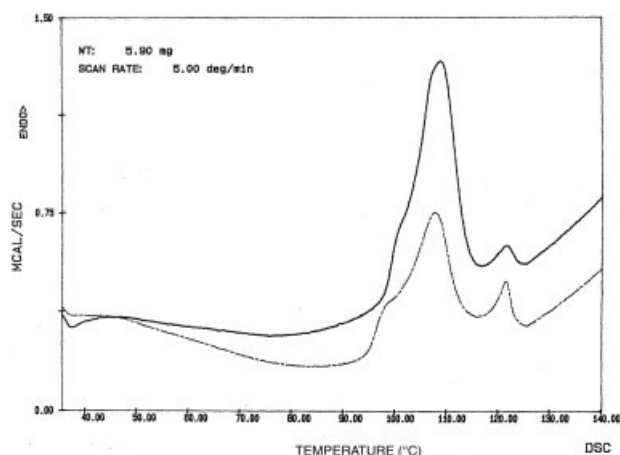


Figure 2 DSC thermographs of LLDPE-g-MAH/LDPE blends. (—): 20/80 w/w, (— - —): 50/50 w/w.

TABLE II
DSC Analysis of Cellulosic Fiber/LLDPE-g-MAH Systems Prepared by the Dissolution/Precipitation Method

Matrix blend (w/w %) LLDPE-g-MAH/LDPE	Cellulosic fiber loading (% w/w)	ΔH_m (cal/g)	T_{max} (°C)
0/100 ^a	0	16.39	115.59
20/80	0	15.70	108.90
50/50	0	9.33	107.74
100/0 ^a	0	10.67	119.80
20/80	30	18.65	108.17
50/50	30	8.89	107.15

^a Pellets of virgin material.

the melting peak at the temperature of 108°C accompanied with a small peak at 121°C, obviously corresponding to the melting transitions of LDPE and LLDPE-g-MAH, respectively, which suggests that these two polymers act as individual components of a mechanical blend, without further interactions. From the data of Table II, it can be observed that the increase of LLDPE-g-MAH content in the polymer matrix results in a decrease on the melting enthalpy, as indicated by the first peak, which corresponds to transitions mainly deriving from LDPE. On the other hand, an increase in the melting enthalpy displayed by the second peak is evident upon the increase of LLDPE-g-MAH concentration, since this second peak corresponds to transitions of LLDPE-g-MAH.

In Figure 3, where the case of neat blends of LDPE with (AA/*n*-BA)-LDPE is presented, it can clearly be seen that the increase of the content of copolymer results in the enlargement of the right shoulder of the main peak in the DSC thermograph.

The data presented in Tables II and III suggest that cellulosic fibers from maritime pine do not significantly affect the obtained thermograph, when incorporated as a filler in the aforementioned poly-

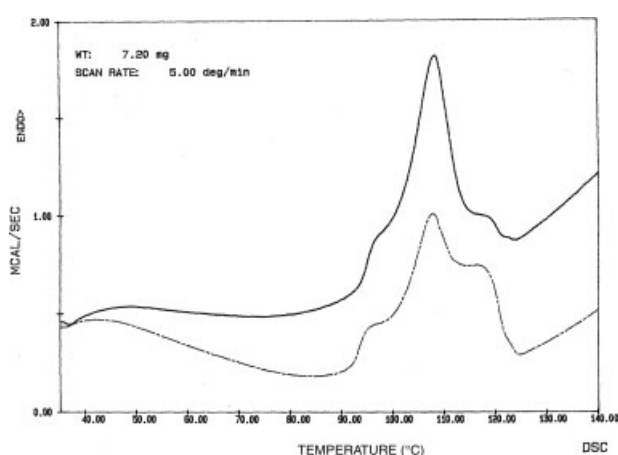


Figure 3 DSC thermographs of (AA/*n*-BA)-LDPE/LDPE blends. (—): 20/80 w/w, (— - —): 50/50 w/w.

TABLE III
DSC Analysis of Cellulosic Fiber/(AA/*n*-BA)-LDPE Systems Prepared by the Dissolution/Precipitation Method

Matrix blend (w/w %) (AA/ <i>n</i> -BA)-LDPE/LDPE	Cellulosic fiber loading (% w/w)	ΔH_m (cal/g)	T_{max} (°C)
0/100 ^a	0	16.39	115.59
20/80	0	20.14	108.39
50/50	0	21.67	107.77
100/0 ^a	0	14.78	123.91
20/80	30	19.64	108.17
50/50	30	20.74	108.83

^a Pellets of virgin material.

meric blend, since their response to thermal transitions is visible at temperatures well beyond the temperature range of the above scan. This can be further observed in Figures 4 and 5, where the thermographs of samples loaded with cellulosic fibers are shown and the obtained curves are identical to those corresponding to their polymer matrices.

Contradictory results can be found in the related literature, regarding the effect of compatibilizers on the thermal characteristics of lignocellulosic fiber composites. Liu et al.¹⁶ observed that upon addition of PE-*g*-MAH into LDPE/starch blends, the crystallization temperature (T_c) remained unaffected, but the melting temperature (T_m) showed a trend similar to that of blends without PE-*g*-MAH.

On the other hand, Qiu et al.⁸ reported that cellulose fibers act as nucleating agents for the crystallization of PP. They claim that crystallization is facilitated by the addition of PP-*g*-MAH in the matrix composition, as a result of the increase of crystallization temperature and rate of PP. However, beyond a

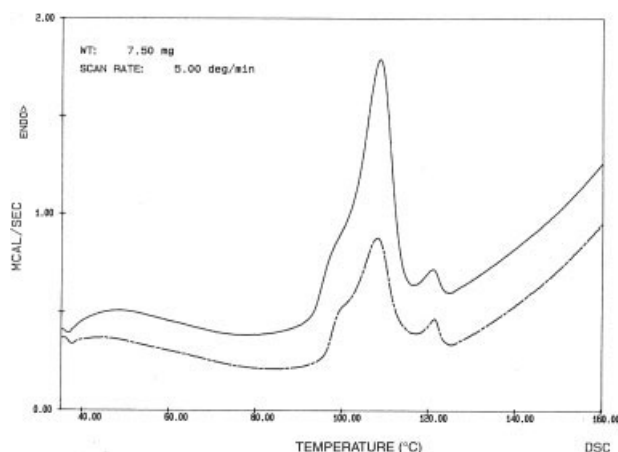


Figure 4 DSC thermographs of LLDPE-*g*-MAH/LDPE blends reinforced with 30% cellulosic fibers. (—): 20/80 w/w, (— - —): 50/50 w/w.

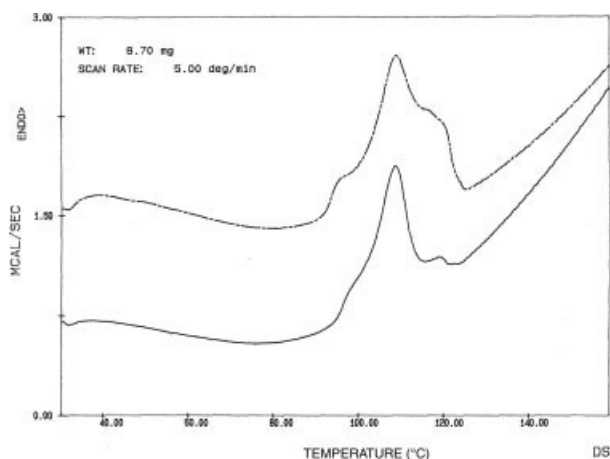


Figure 5 DSC thermographs of (AA/*n*-BA)-LDPE/LDPE blends reinforced with 30% cellulosic fibers. (—): 20/80 w/w, (— - —): 50/50 w/w.

critical concentration, they found that the effect of PP-*g*-MAH is negligible.

The DSC data presented by Espert et al.,¹⁷ who worked with PP modified with ethyl vinyl acetate (PPEVAmoD) and reinforced with cellulose fibers, show that this polymer has approximately the same crystallinity but higher T_c than pure PP. These authors also observed that modification of cellulose with PP-*g*-MAH led to PP composites with higher crystallinity and T_c values, whereas the opposite effect was recorded when cellulose modified with silanes or acetylated cellulose were used as fillers.

Finally, Marcovich and Villar¹ studied composites consisting of a blend of LLDPE, organic peroxide, and MAH reinforced with untreated wood flour, by melt-mixing in a twin-screw extruder. Grafting of MAH onto LLDPE was found as a modification that disturbed initial packing of LLDPE molecules and, therefore, reduced the degree of crystallinity of the original polymer. On the other hand, the authors observed that crystallization process was promoted by the particles of wood flour. This phenomenon was attributed to the nucleation effect of wood flour, which provides sites for heterogeneous nucleation and facilitates the crystallization of the matrix.

TABLE IV
The Increase of Density of Various Polymeric Samples, Due To the Incorporation of 30% w/w Cellulosic Fibers

Matrix	Density increase (%)
LDPE	16.9
LLDPE- <i>g</i> -MAH	14.1
(AA/ <i>n</i> -BA)-LDPE	14.7
LDPE/LLDPE- <i>g</i> -MAH (80/20%)	13.8
LDPE/LLDPE- <i>g</i> -MAH (50/50%)	13.9
LDPE/(AA/ <i>n</i> -BA)-LDPE (80/20%)	13.7
LDPE/(AA/ <i>n</i> -BA)-LDPE (50/50%)	14.8

TABLE V
Experimental and Calculated Density Values of LDPE Blends

Blend	Theoretical value (g/cm ³)	Experimental value (g/cm ³)
50% LLDPE-g-MAH-50% LDPE	0.9259	0.9250 ± 0.0020
20% LLDPE-g-MAH-80% LDPE	0.9298	0.9268 ± 0.0015
50% (AA/n-BA)-LDPE-50% LDPE	0.9328	0.9312 ± 0.0010
20% (AA/n-BA)-LDPE-80% LDPE	0.9326	0.9280 ± 0.0006

Density measurements

As expected, the incorporation of 30% by weight cellulosic fibers into the examined polymer matrices resulted in an increase of the composite density, because of their higher density in comparison with the pure polymers. The increase of density varies from 13.7% for reinforced LDPE/(AA/n-BA)-LDPE 80/20 to 16.8% for the composite of LDPE (Table IV).

The rule of mixtures can be a tool for calculation of the density of the prepared blends (d_c) from the densities of their polymeric components:

$$d_c = \frac{1}{\frac{x_1}{d_1} + \frac{1-x_1}{d_2}} \quad (2)$$

where x_1 is the percentage of the one component by weight, and d_1 and d_2 are the densities of the two polymeric components.

From the data presented in Table V, it is clear that the results obtained by the above equation, calculated by the use of the nominal densities of the blend components, are very close to the experimental results.

Mechanical properties

Tensile tests

From the data of Table VI, it can be seen that tensile strength of LLDPE-g-MAH shows an improvement

of about 30% with the incorporation of 30% cellulosic fibers (14.51 vs. 11.06 MPa), whereas for the nonpolar matrix of LDPE a drop is observed when the same amount of fibers is added (12.48 and 7.26 MPa, respectively). Similarly, Table VII shows that the (AA/n-BA)-LDPE matrix displays an increase of about 23% in its tensile strength, when 30% of fiber reinforcement is added (17.75 and 21.75 MPa).

Further study of the mechanical properties of cellulosic fiber composites was carried out, using as matrices blends of LDPE with some other types of PE modified with polar groups. Again, a loading of 30% fibers was used for the preparation of composites with the following polymeric blends as matrices:

- 20/80 and 50/50 LLDPE-g-MAH to LDPE per weight and
- 20/80 and 50/50 (AA/n-BA)-LDPE to LDPE per weight.

The obtained results from composite specimens with polymer blends as a matrix are shown in Tables VI and VII, together with those corresponding to reinforced samples of pure LLDPE-g-MAH and LDPE.

From the data of Tables VI and VII, it is evident that the improvement of tensile strength of composites using the above blends is much higher than that of composites with modified LDPE alone as matrix. Composites of 50/50% of LLDPE-g-MAH/LDPE presented the best performance, with a tensile strength of 27.54 MPa. This increase is obviously due to the improvement of adhesive bonding between fibers and the polar LLDPE-g-MAH. However, the sample consisting 100% LLDPE-g-MAH as matrix displays lower strength (14.51 MPa) compared to those with 20/80 and 50/50 LLDPE-g-MAH/LDPE blends. This can probably be explained by the fact that the 50/50 LLDPE-g-MAH/LDPE blend displays an optimum combination of matrix polarity and melt viscosity, since LDPE was reported to have higher MFR than LLDPE-g-MAH. In fact, lower melt viscosity allows better wetting of the reinforcement

TABLE VI
Tensile Properties of LDPE/LLDPE-g-MAH Composites with Cellulosic Fibers

LLDPE-g-MAH (% w/w)	LDPE (% w/w)	Cellulosic fibers (% w/w)	Tensile strength (MPa)	Modulus of elasticity (MPa)	Elongation at break (mm)
0	100	0	12.48 ± 0.229	122.02 ± 2.405	7.70 ± 0.343
100	0	0	11.06 ± 1.348	143.66 ± 5.571	6.82 ± 0.230
20	80	0	12.88 ± 0.923	125.47 ± 3.253	219.82 ± 13.87
50	50	0	16.97 ± 1.283	117.79 ± 3.183	300.00 ± 33.76
0	100	30	7.26 ± 2.187	158.87 ± 42.197	1.16 ± 0.472
100	0	30	14.51 ± 1.825	255.25 ± 32.191	2.27 ± 0.464
20	80	30	25.13 ± 3.612	355.53 ± 30.459	2.54 ± 0.385
50	50	30	27.54 ± 4.303	368.79 ± 74.424	3.03 ± 0.487

TABLE VII
Tensile Properties of LDPE/(AA/*n*-BA)-LDPE Composites with Cellulosic Fibers

(AA/ <i>n</i> -BA)-LDPE (% w/w)	LDPE (% w/w)	Cellulosic fibers (% w/w)	Tensile strength (MPa)	Modulus of elasticity (MPa)	Elongation at break (mm)
0	100	0	12.48 ± 0.229	122.02 ± 2.405	7.69 ± 0.343
100	0	0	17.75 ± 3.968	133.91 ± 6.500	254.35 ± 64.724
20	80	0	12.88 ± 0.923	125.47 ± 3.253	184.13 ± 59.9
50	50	0	16.73 ± 1.15	129.28 ± 4.555	269.65 ± 15.96
0	100	30	7.26 ± 2.187	158.87 ± 42.197	1.163 ± 0.472
100	0	30	21.75 ± 1.402	334.508 ± 25.077	2.01 ± 0.348
20	80	30	21.33 ± 6.65	352.089 ± 67.521	1.64 ± 0.351
50	50	30	26.91 ± 3.935	439.25 ± 57.755	1.84 ± 0.253

during compression-molding and ensures close interfacial contact between fiber and matrix.

The modulus of elasticity displays maximum values for blends of the (AA/*n*-BA)-LDPE copolymer with LDPE, reinforced with 30% cellulosic fibers, as a result of the great improvement in the modulus of (AA/*n*-BA)-LDPE matrix upon the addition of 30% cellulosic fibers. In fact, the data of Table VIII show that the increase of modulus of the (AA/*n*-BA)-LDPE composite is much higher than the increase in tensile strength, which can be attributed to the low deformability of the reinforced material leading to a great reduction of the elongation at break. It was also observed that composites of blends present better performance compared to composites with matrices consisting of pure polar polymers reinforced with 30% cellulosic fibers.

From the above results, it can be concluded that the combination of polar matrices with pure LDPE improves the performance of their composites containing cellulosic fibers, in terms of tensile strength and modulus. Blends of LLDPE-*g*-MAH gave the best results in the tensile strength tests, whereas blends of (AA/*n*-BA)-LDPE showed the highest improvement of modulus of elasticity.

The incorporation of cellulosic fibers in LDPE matrices resulted in significant decrease of the elongation at break, which suggests a transition of the composite material from the ductile behavior corresponding to the thermoplastic matrix to a rather brittle character.

The enhancement of tensile strength is attributed to the stronger interfacial adhesion between modified PE and cellulosic fibers. The carboxyl groups of the MAH contained in LLDPE-*g*-MAH can interact with the hydroxyl group of the cellulosic reinforcement and could form covalent bonds through ester linkages, which would lead to improved interfacial characteristics.^{2,18} In the case of the copolymer, dipole interactions between the ester groups of butyl acrylate and the hydroxyl groups of cellulose would probably create strong interfacial bonding between matrix and fibers. In addition, despite the expected

steric hindrance, the possibility of chemical bonding between the AA and hydroxyl groups still exists.

It is reasonable that the increase of concentration of polar groups within the polymer matrix results in better interfacial adhesion. However, depending on the individual characterization of each specific system, there is a maximum concentration above which a plateau in tensile strength can be observed.

The flow rate of LDPE and LLDPE-*g*-MAH are comparable to that of (AA/*n*-BA)-LDPE, which suggests that molecular weights of these polymers are in the same order of magnitude. This may assist blend miscibility between LLDPE-*g*-MAH and LDPE during the melt-mixing process and consequently contributes to the improvement of mechanical properties.

For composites reinforced with short cellulosic fibers, the tensile strength is strongly dependent on the magnitude of adhesive bonding, whereas the modulus of elasticity of these composites is highly affected by the individual properties of their components as well as by the orientation of fibers.

Impact analysis

Impact tests were performed in composite specimens with various matrices, reinforced with 30% cellulosic

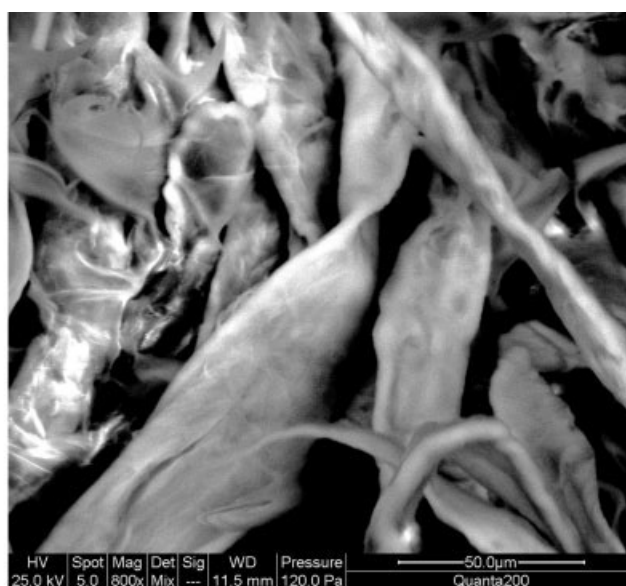
TABLE VIII
Percentage Changes of the Tensile Properties of Various Polymer Matrices After Incorporation of 30% by Weight Cellulosic Fibers

Matrix	Tensile strength	Modulus of elasticity	Elongation at break
LDPE	-41.8	30.2	-84.9
LLDPE- <i>g</i> -MAH	31.2	77.7	-66.7
(AA/ <i>n</i> -BA)-LDPE	22.5	149.8	-99.2
20% LLDPE- <i>g</i> -MAH/80% LDPE	95.1	183.4	-98.8
50% LLDPE- <i>g</i> -MAH/50% LDPE	62.3	213.1	-99.0
20% (AA/ <i>n</i> -BA)-LDPE/80% LDPE	65.6	180.6	-99.1
50% (AA/ <i>n</i> -BA)-LDPE/50% LDPE	60.8	239.8	-99.3

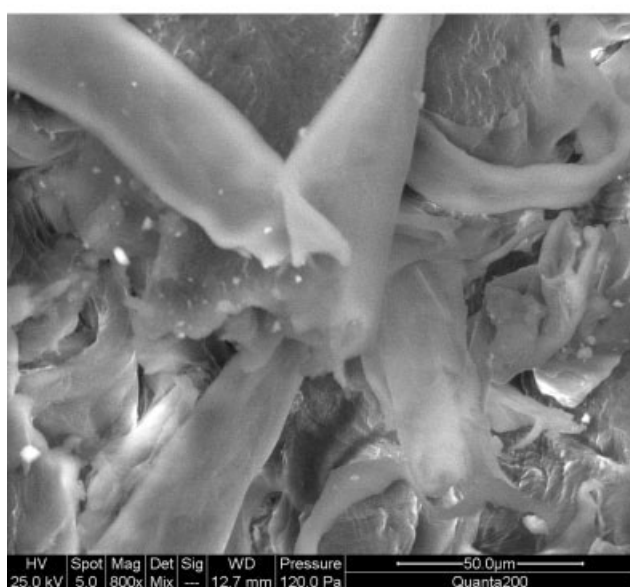
fibers. From the experimental data presented in Table IX, it is clear that composites of pure LLDPE-*g*-MAH display the higher impact resistance, exceeding that of LDPE matrix composites to a 135%. As a result, significant improvement of the impact strength of a composite consisting 50/50 blend of LDPE/ LLDPE-*g*-MAH as a matrix can also be seen in the same table. On the other hand, lower increase (about 20%) was observed when a 50/50 mixture of LDPE/(AA/*n*-BA)-LDPE was used as matrix, which is consistent with the impact strength of samples

TABLE IX
Impact Properties of Cellulosic Fibers Composites

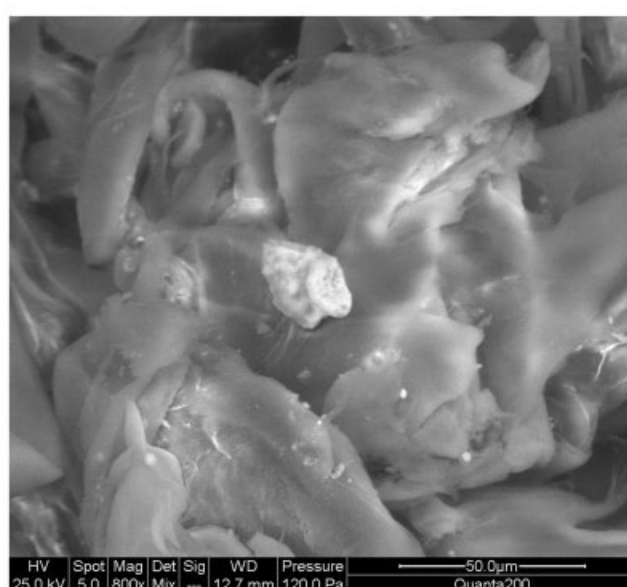
Matrix	Cellulosic fibers (% w/w)	Energy at break (J/mm ²)	%
LDPE	30	1.423 ± 0.288	–
LLDPE- <i>g</i> -MAH	30	3.350 ± 0.604	135.4
(AA/ <i>n</i> -BA)-LDPE	30	1.832 ± 0.412	28.7
50% LDPE/50% LLDPE- <i>g</i> -MAH	30	2.441 ± 0.308	71.5
50% LDPE/50% (AA/ <i>n</i> -BA)-LDPE	30	1.702 ± 0.390	19.6



(a)



(b)



(c)

Figure 6 SEM micrographs of the fracture surface of impact specimens: (a) LDPE, (b) LLDPE-*g*-MAH, and (c) (AA/*n*-BA)-LDPE matrix composites.

consisting of reinforced LDPE and (AA/*n*-BA)-LDPE.

It is evident that the improved compatibility of cellulosic fibers with the modified LDPE matrices results in strong adhesion and proper stress transfer. This leads to better energy absorption when these composites are subject to an impact shock. It has also been reported that higher interfacial adhesion between matrix and filler requires higher energy for the initiation and propagation of crack during the impact test.

An additional support to the aforementioned are SEM observations of the fracture surface of unnotched Izod specimens, indicating some differences between composites with matrices consisting of different types of LDPE, with respect to their interfacial fiber-matrix interactions. Fracture surfaces of composites with pure LDPE as a matrix [Fig. 6(a)] show some fiber pull-out and fairly clean fiber surfaces. On the other hand, composites prepared using LLDPE-*g*-MAH and (AA/*n*-BA)-LDPE show little fiber pull-out and polymeric fragments remain on the broken fibers surface, as it can be seen in Figure 6(b) and Figure 6(c), respectively.

CONCLUSIONS

Cellulosic fibers show increased reinforcing capacity when incorporated into blends of modified and pure LDPE, in comparison with matrices of modified PE alone. Composites with LLDPE-*g*-MAH blend as matrix presented the higher tensile strength values, whereas (AA/*n*-BA)-LDPE blends gave best results in terms of modulus of elasticity.

The improved mechanical properties of LLDPE-*g*-MAH systems can be attributed to chemical reaction between the carboxyl groups of the modified polymer and the hydroxyl groups of cellulosic fibers. In the case of (AA/*n*-BA)-LDPE, the improvement of mechanical properties can be primarily attributed to dipole interactions between the ester groups of butyl acrylate and the hydroxyl groups of cellulose, assisted by possible chemical bonding. These interactions promote interfacial bonding and therefore lead to an increase in tensile modulus.

Based on the above, an interpretation of the improvement of impact resistance can be made. Composites of LLDPE-*g*-MAH presented the best performance, with an improvement of 135% in comparison with the LDPE matrix composites, because of their increased interfacial bonding, whereas specimens of (AA/*n*-BA)-LDPE matrix, where dipole interactions are primarily expected to take place, showed a modest improvement in their impact resistance.

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