

Rice Husk/Poly(propylene-*co*-ethylene) Composites: Effect of Different Coupling Agents on Mechanical, Thermal, and Morphological Properties

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ABSTRACT: Poly(propylene-*co*-ethylene) composites with rice husk were prepared in a corotating intermeshing twin-screw extruder using four different coupling agents. While modified maleic anhydrides such as maleated polypropylene (MAPP) and maleated polyethylene (MAPE) are commonly used as compatibilizers to improve interfacial adhesion between lignocellulosic filler and matrix, in this study, polypropylene grafted with acid comonomer (CAPP) and high-density polyethylene grafted with acid comonomer (CAPE) were also used. The morphologies and the thermal and mechanical properties of the composites were characterized using scanning electron micros-

copy, thermogravimetric analysis, differential scanning analysis, tensile and impact tests. The results indicate that the base resin of the compatibilizer is an important factor in determining the effectiveness of compatibilizers for composites. Composites with PP-based compatibilizers are more effective than PE-based compatibilizers due to the improved wetting of the former compatibilizer in the matrix polymer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3337–3344, 2012

Key words: composites; compatibilization; fillers; mechanical properties; polyolefins

INTRODUCTION

During the last decade, lignocellulosic materials have been used as reinforcing fillers in commercial thermoplastics to produce composite materials.¹ The addition of filler has a high impact upon economics for thermoplastics, while general improvements in certain properties are also achieved, such as higher rigidity, strength, hardness, and flexural modulus. Natural fillers present some advantages compared to traditional inorganic fillers, including their renewable nature, lower densities, nonabrasive properties during processing, biodegradability, and stiffness.² Yet another attraction is the fact that these materials are obtained easily from natural wastes.

Indeed enormous interest in the development of new composite materials filled with natural filler has been shown by important industries such as the automotive, construction, or packaging industries. Composites are being used increasingly in building products such as decking, fencing, siding, windows, door frames, interior paneling, decorative trim and

interior automotive parts such as door panels, trunk liners, and door trims.³ In recent years, their utilization has increased rapidly, especially in Europe, the USA, and Canada.⁴

Natural fillers such as wood, jute, kenaf, hemp, sisal, pineapple, rice husk, curaua have been successfully used to improve the mechanical properties of thermoplastic composites.^{5–7} In the last year, rice husk filler has been studied due to its significant availability. In fact, as a consequence of the large production of rice, approximately 600 millions tons/year according to FAO statistical data in 2000, there is a large amount of rice husk waste (about 20 wt %).⁸ Therefore, rice filler is promising as a bio-filler in composites to replace various materials in construction, furniture, and many plastic products in a variety of future industrial applications.⁹

However, the use of agro-fillers shows some drawbacks such as their low temperature of thermal degradation due to the presence of cellulose and hemicelluloses. This low thermal degradation limits the allowed processing temperature to less than 200°C and restricts the type of thermoplastics that can be used with agro-filler to some commodity plastics such as polypropylene (PP), polyethylene (PE), poly(vinyl chloride) (PVC), and polystyrene (PS).¹⁰ Another drawback of using natural fillers for reinforcement is the low degree of dispersion and

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low compatibility between the hydrophilic filler surface and hydrophobic polymer matrix.¹¹ This leads to weak interfacial adhesion, which results in poor mechanical properties of the final product. To overcome this obstacle, a compatibilizer is usually added. The compatibilizer most often used for this application is maleated polypropylene (MAPP). Interactions and probably reactions between the anhydride groups of the maleated compatibilizer and the hydroxyl groups of natural fillers can overcome the incompatibility problem and increase the tensile and flexural strengths of natural filler-thermoplastic composites.¹¹ MAPP has been used as a compatibilizer for various polymeric composites which are filled with lignocellulosic materials; however, when polyethylene composites need to be reinforced, MAPPs are not recommended, because of the incompatibility between polyethylene and polypropylene.¹²

In this work, composites of poly(propylene-*co*-ethylene) and rice husk were prepared by melt blending in a corotating intermeshing twin-screw extruder. The objective of the work was to explore the effects of four different coupling agents: MAPP, maleated polyethylene (MAPE), polypropylene-grafted acid comonomer (CAPP), and polyethylene-grafted acid comonomer (CAPE). The results obtained for the mechanical, thermal, and morphological properties are discussed.

EXPERIMENTAL

Materials

Poly(propylene-*co*-ethylene) copolymer (PPc), supplied by Braskem S/A (Triunfo, Brazil), in the form of pellets with a melt flow index of 6 g/10 min (230°C/2,160 g) was used as the matrix for the composites. Its composition consists of 8.5 wt % ethene.

The lignocellulosic material used as the reinforced filler in the composite was rice husk (RH) supplied by WPC Brazil (Pelotas, Brazil) with moisture content of 5% and average particle size of 500 μ m.

Four kind of coupling agents were used in this study. The MAPP was obtained from Kometra (Schkopau, Germany) commercially called TPPP 2112FA, with a melt flow index of 46 g/10 min (230°C/2,160 g). The maleated high-density polyethylene (MAPE) was obtained from Crompton Polybond Co., (USA), commercially called Polybond 3029, with a melt flow index of 5 g/10 min (190°C/2,160 g). PP grafted with acid comonomer (CAPP) and HDPE grafted with acid comonomer (CAPE) were supplied by Braskem S/A, (Triunfo, Brazil), with melt flow indices of 35 g/10 min (230°C/2,160 g) and 11 g/10 min (190°C/2,160 g), respectively.

TABLE I
Formulation of the Composites in Weight Percent

Samples	PPc	RH	MAPP	MAPE	CAPP	CAPE
PPc	100	–	–	–	–	–
PPc/RH	50	50	–	–	–	–
10MAPP	40	50	10	–	–	–
10MAPE	40	50	–	10	–	–
10CAPP	40	50	–	–	10	–
10CAPE	40	50	–	–	–	10

Compounding and sample preparation

Rice husk was oven dried at 100°C for 24 h to adjust the moisture content to 1–3% and then stored over desiccant before compounding. Composites were processed in a corotating intermeshing twin-screw extruder (ZSK 26 Mc, Coperion Werner and Pfleiderer, Stuttgart, Germany) with an *L/D* ratio of 44. In all cases filler and compatibilizing agent were fed together with the polymer matrix into the extruder hopper. The extrusion was conducted at a temperature (from feed to die) of 160°C, 160°C, 170°C, 170°C, 170°C, 180°C, 180°C, 180°C, 180°C, 180°C, and 180°C with a screw speed of 300 rpm. The extruded strand was cooled in a water bath and pelletized. To investigate the effect of different coupling agents on the thermal and mechanical properties, composites samples were prepared with 50 wt % rice husk filler loading with incorporation of 10 wt % of each compatibilizing agent (Table I).

The granulated composites were dried in a conventional oven at 100°C for 12 h and injection molded into test specimens according to ASTM D638 and ASTM D256 for tensile and impact tests, respectively. For all composites, the temperature profile used in the injection molding machine (Alburg, Allrounder M250, Germany) from hopper to nozzle was 180, 185, 195, 200, and 205°C, injection pressure of 1500 MPa, hold pressure of 900 MPa, hold time of 1 s, injection velocity of 15 cm³/s, mold temperature of 50°C, and cooling time of 20 s.

Thermal properties

Thermogravimetric analysis (TGA)

The TGA (TA Instruments 2050, New Castle, DE) was carried out from 25 to 700°C at 10°C/min (under inert atmosphere and argon, 50 mL/min).

Differential scanning calorimetry (DSC)

DSC analysis was carried out using a TA Instrument 2910 (New Castle, DE). Each sample was initially heated at a heating rate of 20°C/min from 25 to 200°C and then maintained at 200°C for 3 min. Then, samples were cooled to –50°C at a cooling

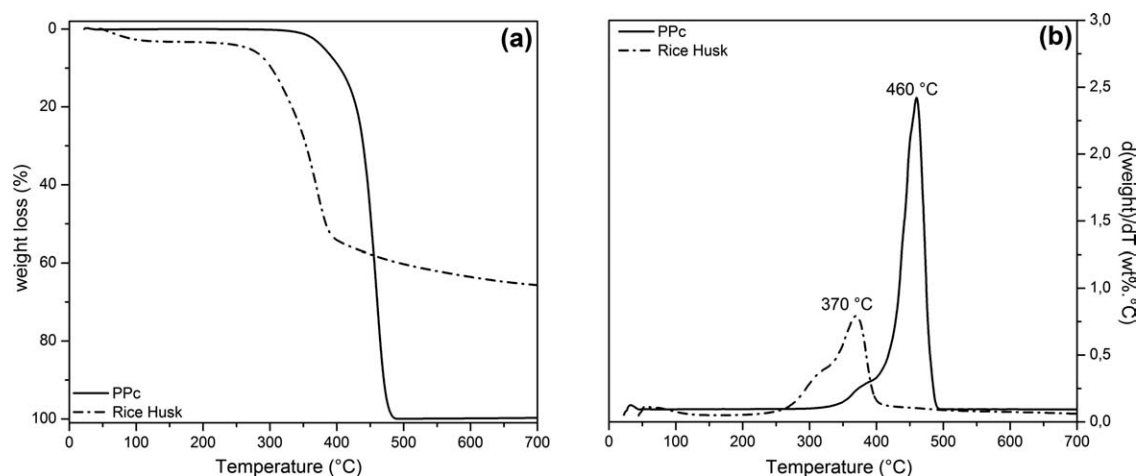


Figure 1 (a) Thermogravimetric curves and (b) the first derivative curves of PPc and rice husk fiber.

rate of 20°C/min and kept under isothermal conditions for 3 min. Finally, the samples were reheated to 200°C at a heating rate of 20°C/min. All steps were conducted under an argon atmosphere. All DSC curves shown in this work were normalized with respect to the sample mass. The values of melting temperature (T_m) and the melting enthalpy (ΔH_m) were determined from the second heating scan. The crystallization temperature (T_c) was determined from the cooling step.

Mechanical properties

Tensile test

Before mechanical tests, the specimens were conditioned for 48 h at 23(\pm 5)°C and 50(\pm 5)% room humidity. Tensile tests were carried out in a universal testing machine (EMIC, DL2000, São José dos Pinhais, Brazil), with cross head speed of 50 mm/min, according to ASTM standard D638.

Izod impact test

The Izod impact tests of notched injection-molded specimens were made in an EMIC pendulum-type testing machine (São José dos Pinhais, Brazil), according to ASTM D256. At least five samples for each composite composition were analyzed.

Morphology

Scanning electron microscopy (SEM)

A JEOL JSM-6360 LV scanning electron microscope (Middleton, WI) was used to study the morphologies of the composites. The microscope was operated at a voltage of 20 kV. All samples were maintained for 1 h in liquid N₂ and then microtomed to obtain a

smooth surface. The surface was sputtered with a thin gold layer.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA)

Figure 1a shows the thermogravimetric curves for PPc and rice husk under an argon atmosphere. The matrix is more thermally stable than rice husk under inert conditions.

PPc degrades in a single step from 350 to 500°C with maximum weight loss rate at 460°C [Fig. 1(b)]. The thermogravimetric curve of rice husk exhibits two mass loss steps. The initial mass loss below 100°C is due to the gradual evaporation of absorbed moisture and the second mass loss from approximately 170 to 550°C is due to the decomposition of the three major constituents of the natural filler (hemicelluloses, cellulose, and lignin). The depolymerization of hemicelluloses occurs between 150 and 350°C, the random cleavage of the glycosidic linkage of cellulose occurs between 275 and 350°C, and the degradation of lignin between 250 and 500°C.¹ A residue of around 35 wt % is observed for rice husk at 700°C and it is basically silica.¹

Besides the initial mass loss around 100°C due to adsorbed moisture, the composites exhibit two-step degradation processes (Fig. 2), as confirmed by the presence of two main peaks in the first derivative curves at 349 and 460°C, corresponding to the thermal degradation of rice husk and polymeric matrix, respectively.

Table II shows the temperature corresponding to the maximum weight loss rate (T_{max}) related to PPc and rice husk phases. In this table the first loss weight step around 100°C is omitted.

The composite PPc/RH without compatibilizer presents temperature for both main steps similar to the values observed for pure components. However,

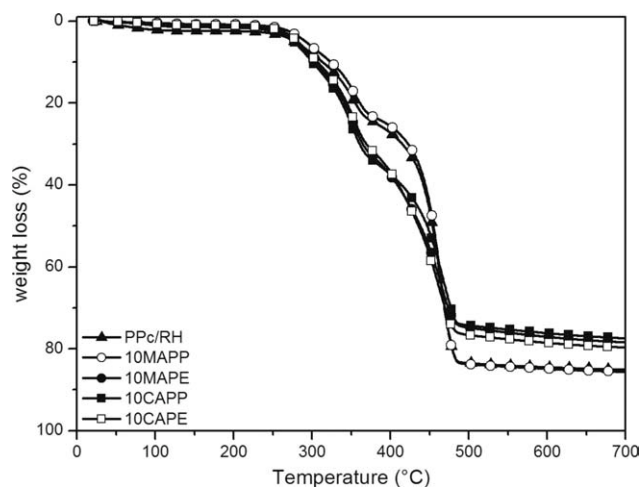


Figure 2 Thermogravimetric curves of the composites.

the temperature corresponding to the maximum weight loss rate is slightly higher for the matrix, probably due to the presence of the residue of the thermal degradation of rice husk (silica).

The addition of compatibilizers to the composites presents little influence on the thermal stability of the materials. The slight shift of temperature for both main degradation steps to higher or lower temperatures observed for compatibilized composites, in comparison to the composite without compatibilizer probably reflects interactions between the polar groups of the compatibilizers and the surface of the rice husk. The thermogravimetric curves for the composites containing maleated PP (10MAPP) as compatibilizer is close to the curve of the composite without compatibilizer. On the other hand, the other composites lose more weight during the first degradation step, and the residue at 700°C is higher in comparison with the composite without compatibilizer. The reason for this behavior is not easy to understand; however, one hypothesis to explain these differences could be possible interactions or reactions between the functional group of the compatibilizers (anhydride and carboxylic acid) and the hydroxyl groups on the surface of the rice husk particles, resulting in polymer chain bonded on the

TABLE II
Temperature Corresponding to the Maximum Weight Loss Rate (T_{max})

Samples	T_{max} (°C)	
	Filler	Matrix
PPc	–	460
Rice husk	349	–
PPc/RH	349	463
10MAPP	355	465
10MAPE	352	464
10CAPP	350	468
10CAPE	352	462

filler. These bonded chains on the rice husk particles can thermally degrade under inert atmosphere resulting in carbon-rich residues, for instance. The esterification reaction between the hydroxyl groups of lignocellulosic materials and the anhydride functional group of MAPP, MAPE, or the carboxylic acid of the CAPP and CAPE is possible and should promote an anchor of the filler on the polymer matrix.¹³ A hypothetical model to illustrate the possible reaction and interaction at the interface of the rice husk-polymer matrix is shown in Figure 3.

Differential scanning calorimetry (DSC)

Since the industrial manufacturing of the composites proceeds mainly in a nonisothermal regime, analysis of the crystallization parameters and crystallization behavior of PPc/RH composites is especially important from a practical point of view. For composites based on semicrystalline polymers, crystallinity is an important factor that determines the stiffness and fracture behavior of the crystallized polymer matrix.¹⁴ Crystallinity depends upon processing parameters, such as cooling rate, nucleation density, and annealing time.

The DSC curves obtained for the coupling agents are shown in Figure 4. The coupling agents present crystallization and melt temperatures at the characteristic temperatures of their predominant components, polypropylene for the MAPP and CAPP compatibilizers, and polyethylene for the MAPE and CAPE compatibilizers.

Figure 5(a) shows DSC curves corresponding to the cooling scan for PPc and its composites. All curves show exothermic peaks corresponding to the crystallization of the polymeric matrix. The addition of rice husk to the PPc matrix does not change the crystallization temperature (T_c), but decreases crystallization enthalpy and, therefore, the crystallization degree. The crystallization behavior of the compatibilized composites depends on the nature of the

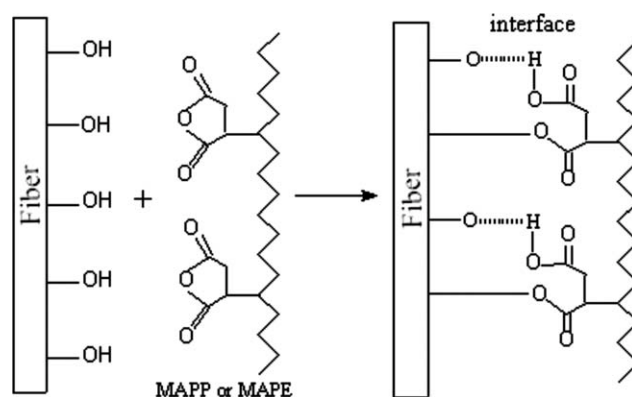


Figure 3 Representation of the interface reaction between the rice husk fiber surface and the coupling agents.

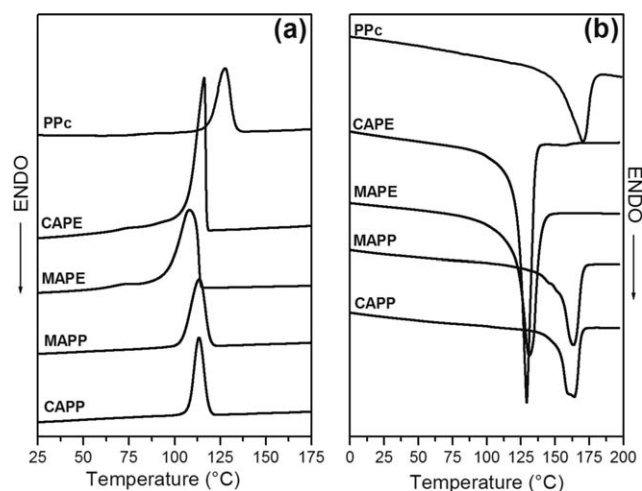


Figure 4 DSC curves for the coupling agents. (a) cooling step and (b) second heating step at 20°C/min.

resin of each compatibilizer. For compatibilizers based on polypropylene, only one crystallization peak is observed at 130°C for 10MAPP and 121°C for 10CAPP, temperatures higher and lower with respect to the T_c of pure PPc, respectively. On the other hand, two crystallization peaks are observed for composites based on polyethylene. The peak at lower temperature is significantly less intense in comparison with the second one; therefore, it is due to the crystallization of the compatibilizers based on polyethylene. The peak at higher temperature is due to the crystallization of the PPc matrix, probably the crystallization of PP segments in this copolymer. These results show that the crystallization of both polymeric components in the composites is independent. Despite this, a significant shift of T_c in comparison with the T_c of the pure components, as well as significant changes in ΔH_c , indicate the influence of one component on the crystallization of other component. The values of the

crystallization temperature (T_c), melting temperature (T_m), crystallization enthalpy (ΔH_c), and melting enthalpy (ΔH_m), both of the latter normalized with respect to the PPc content in the composites, are summarized in Table III.

DSC curves in Figure 5(b) show the melting behavior of the composites. The PPc and the composites exhibit melting as a well-defined peak with a minimum around 170°C corresponding to melting of the PP phase in this copolymer. The 10MAPE and 10CAPE composites present two melting peaks related to the melting of the PPc and to the melting of the PE phase in the compatibilizers (MAPE and CAPE).

The melting temperature of PP in the composites is equal to the value for phase PP of the PPc. This indicates that the crystal structure of this phase does not differ from that observed for the matrix, with respect to the thickness of lamella. The melting enthalpy, normalized with respect to the mass fraction of PPc in the composites, was shifted to lower values for all composites. These results show again the interference of rice husk in the crystallinity degree of the composites. For the 10MAPE and 10CAPE composites, two peaks of crystallization, partially overlapped, are observed making it difficult to determine the crystallization enthalpy of each component.

Mechanical properties

Mechanical properties are of major importance for all applications of natural-filled polymer composites. The Young's modulus and tensile strength of the composites are shown in Figure 6.

The tensile strength of the PPc/RH decreases in comparison with PPc, due to the weak interfacial adhesion and low compatibility between matrix and filler. The weak bonding between the hydrophilic lignocellulosic filler and the hydrophobic matrix polymer obstructs the stress propagation and causes the decrease of the tensile strength.¹⁵ To improve the

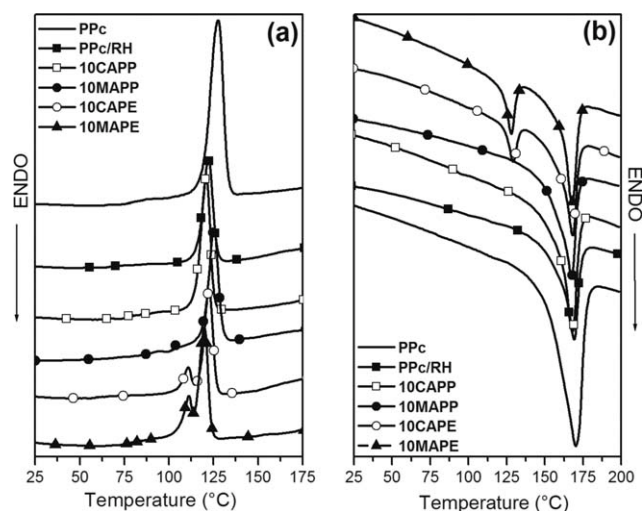


Figure 5 DSC curves for all composites. (a) cooling step and (b) second heating step at 20°C/min.

TABLE III
Values of T_c , ΔH_c , T_m , and ΔH_m of PPc and PPc/RH Composites from DSC Analysis

Samples	T_c (C)	ΔH_c (J/g)	T_m (C)	ΔH_m (J/g)
PPc	127	90	170	92
PPc/RH	127	80	169	80
10MAPP	130	86	167	83
10MAPE	111; 120	97 ^a	128; 168	89; 81
10CAPP	121	89	168	85
10CAPE	111; 123	87 ^a	129; 168	56; 67
MAPP	113	99	163	103
MAPE	131	190	108	183
CAPP	113	81	164	87
CAPE	116	212	129	214

^a Sum of ΔH_c of the crystalline phase of the PPc and of the crystalline phase of the compatibilizing agents.

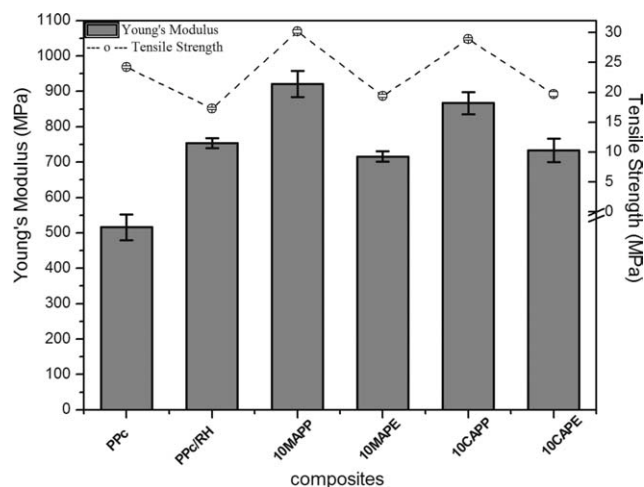


Figure 6 Young's modulus and tensile strength of PPc and PPc/ric husk composites.

interfacial bonding strength between filler and the matrix, coupling agents were used. The enhancement of the tensile strength depends on the nature and structure of the interface formed, which in turn is related to the chemical structure of the compatibilizer. For example, the tensile strength of composites containing MAPP (30.2 MPa) or CAPP (28.9 MPa) as compatibilizer is around 75 and 67%, respectively, higher than the value for PPc/RH. Yang et al.⁴ reported an increase of 43% in tensile strength for PPc/RH composites (70/30 wt %) when 5%wt MAPP was used as a compatibilizer. In relation to the other composites the presence of MAPE and CAPE did not affect significantly the tensile strength in comparison with PPc/RH.

The Young's modulus for all composites with and without compatibilizer is higher than the value for neat matrix, as a consequence of the high modulus of cellulosic filler. The Young's modulus of the composites containing MAPP and CAPP is superior to the value observed for composites containing MAPE and CAPE. One possible reason for this behavior could be related to the compatibility between filler and polymeric matrix (or filler and compatibilizer) and polymeric matrix and compatibilizer. Apparently, compatibilizers based on polyethylene are less compatible with PPc resin, independent of the functional group (anhydride or carboxylic acid). For compatibilizers based on polypropylene, there is also no significant influence of the nature of the functional group on the performance of the compatibilizer. Therefore, these results allow concluding that the compatibility between matrix and compatibilizer is the most important factor in determining the mechanical performance of these composites.

In principle, the better compatibility between a compatibilizer based on polypropylene and PPc resin was expected, because this resin is richer in

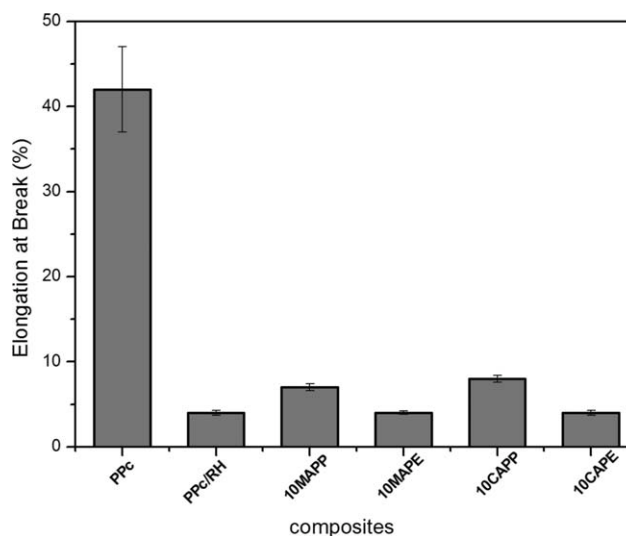


Figure 7 Elongation at break of PPc and PPc/ric husk composites.

polypropylene segments. Therefore, in these composites, the polymer backbone of this compatibilizer diffuses into the polymer matrix and becomes entangled with it.¹¹

Incorporation of the filler resulted in an abrupt drop in elongation at break compared to the polymer matrix (Fig. 7). The steep decline in elongation with incorporation of the filler is obvious, because lignocellulosic fillers have low capability for elongation and therefore restrict polymer chain mobility. This behavior is typical of reinforced thermoplastic in general and has been reported by many researchers.^{10,16} However, the mechanical behavior of these composites reflects not only the stiffness of the filler but also the nature of the resin of the compatibilizers. Again, compatibilizers based on polypropylene confer better properties to their composites as a

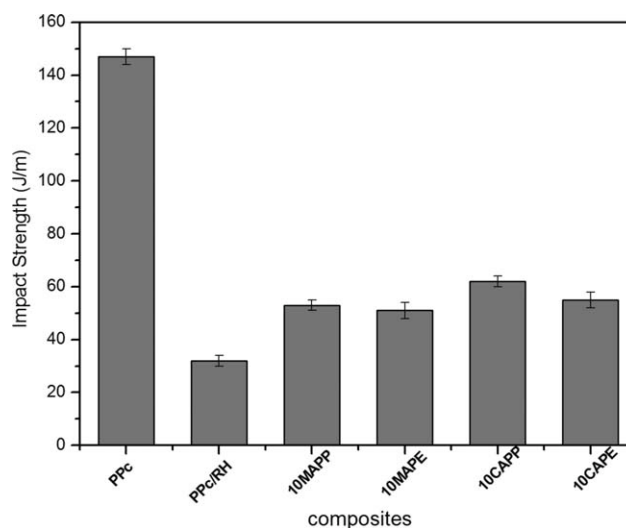


Figure 8 Impact strength of PPc and PPc/ric husk composites.

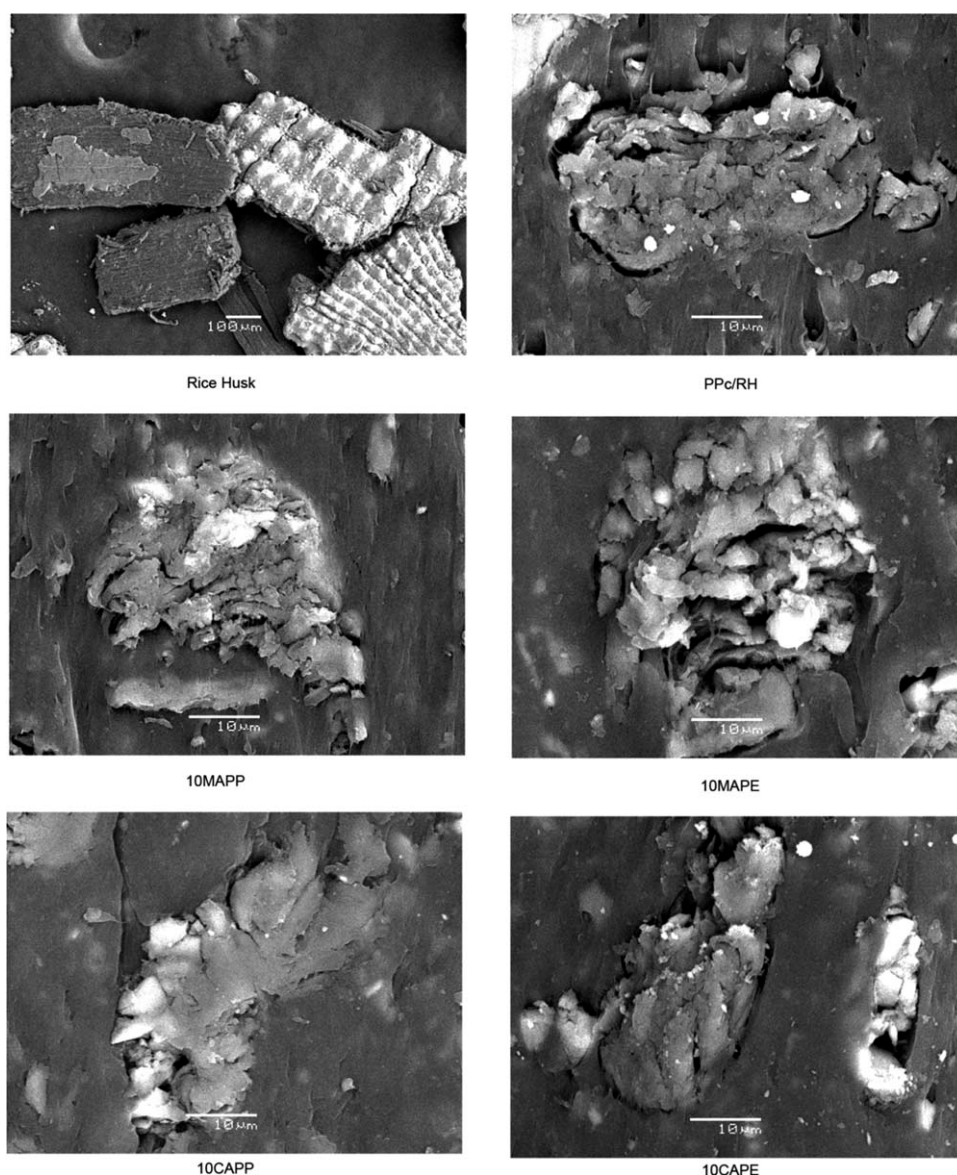


Figure 9 SEM micrographs of the rice husk and of the composites.

consequence of the compatibility between the compatibilizer and the polymeric matrix.

The main goal in the development of reinforced polymers is to improve stiffness with sufficient impact resistance. Izod impact tests were performed on notched samples at room temperature. Figure 8 shows the Izod impact strength of PPc and its composites. PPc presents an impact strength of 147 J/m, which decreases to 32 J/m when 50 wt % rice husk filler are added. Poor interfacial bonding induces microspaces between the filler and matrix polymer, and these cause numerous micro-cracks when impact occurs, which induce crack propagation easily and decrease the impact strength of the composites.¹⁵

On the other hand, the incorporation of compatibilizers results in an increase in the Izod impact strength in comparison with composite without compatibilizer,

indicating the better interfacial adhesion between filler and matrix. The composites containing MAPP, MAPE, and CAPE exhibit similar Izod impact strength, while the CAPP composite presents a higher Izod impact strength, representing a 94% increase over PPc/RH.

The mechanical properties of composites can be affected by the molar mass and grafting of compatibilizers. The maleic anhydride graft (%) of MAPP and MAPE is similar to the acid comonomer graft in CAPP and CAPE. However, the flow index of the CAPP is lower than MAPP; in other words, the molar mass of the CAPP is higher than MAPP. Thus, the higher molar mass of CAPP allows better entanglement with the matrix polymer.³ Kim et al.³ studied the effect of different types of maleic anhydride-grafted polypropylene on the interfacial adhesion properties of bio-flour-filled polypropylene

composites and observed that mechanical properties of the composites are affected according to the MAPP used. The composite treated with MAPP of higher molar mass presents superior tensile, impact, and flexural strengths.

Incorporation of rice husk into PPc resin resulted in higher values of Young's modulus and in lower values of tensile strength and Izod impact strength for the composite without compatibilizer. On the other hand, the composites compatibilized with MAPP present higher Young's modulus and tensile strength than pure PPc resin. Comparison of the mechanical properties obtained in this work with the literature indicates that the values for the composites compatibilized with MAPP are close to those described in the literature. Ashori and Nourbakhsh¹⁷ studied composites of polypropylene (MFI = 7 g/10 min) with rice husk (50/50 wt %) with 2 wt % of MAPP and values of the Young's modulus, tensile strength, and Izod impact strength are 1800 MPa, 27 MPa, and 14 J/m, respectively.

Morphology

The morphology of the composites was studied by SEM. Figure 9(a) shows a scanning electron micrograph of rice husk particles. It presents different outside and inside region morphologies. The outside region is formed by aligned and symmetric bumps composed mainly of silica in the cellulose, while the inside region presents a smooth cellulose surface.⁸

Figure 9(b–f) shows SEM micrographs for the composites. In the case of the composite without any compatibilizing agent it is possible to observe cavities around the filler particles. The presence of these cavities means that the interfacial adhesion between the filler and the matrix polymer is poor and weak. In the case of the composites made with coupling agents, it is possible to observe the decrease in number and in size of the cavities, indicating that the interfacial adhesion between the filler and the matrix polymer is improved. This means the stress is better transferred between the filler and the matrix in the composite incorporating the compatibilizing agent, resulting in materials with higher tensile strength and modulus in response to stress, as observed. The composites made with different coupling agents ((10MAPP and 10CAPP) and (10MAPE and 10CAPE)) show some different characteristics. MAPE and CAPE incorporation in composites has less effects on interfacial adhesion as compared to MAPP and CAPP incorporation due the better wetting of the MAPP and CAPP in the polymer matrix.

CONCLUSIONS

For the modified composites, improvement in interfacial bonding strength, flexural modulus, and other mechanical properties was mainly related to the compatibilizing agent's type, functional group, concentration, and chain structure. The composites 10MAPP and 10CAPP present similar mechanical properties, indicating that the specific functional group does not influence these properties. On the other hand, the composites prepared with MAPP and CAPP exhibited better mechanical properties than composites prepared with MAPE and CAPE, due to the better wetting of MAPP and CAPP to the polymer matrix, which led to stronger interfacial bonding between the filler and the polymer matrix, as confirmed by microscopic observation. Because of the interaction between the different phases, the thermal stability of the compatibilized composites is improved. The increase in mechanical properties demonstrated that MAPP and CAPP are effective compatibilizers for rice husk/poly(propylene-co-ethylene) composites.

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