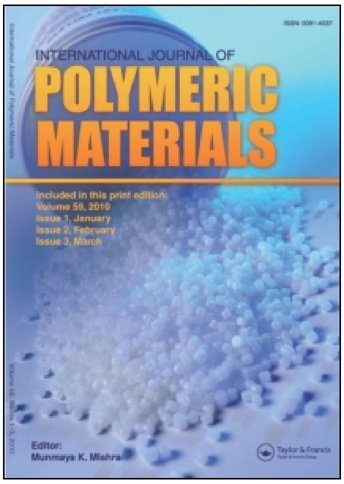

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Mechanical and Morphological Properties of Polypropylene and Regenerated Tire-Rubber Blends

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Mechanical and Morphological Properties of Polypropylene and Regenerated Tire-Rubber Blends

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Mechanical properties and morphology of blends prepared from polypropylene (PP) and 5–20 wt% of regenerated tire-rubber (RgR) were studied. The samples were prepared in a twin-screw extruder. The addition of maleic anhydride-functionalized polypropylene (PP-g-MAH) was also investigated. Tensile and flexural moduli, tensile strength at break, elongation at break and Izod impact resistance at 23°C were increased by the addition of 15 wt% of regenerated rubber and 5 wt% of PP-g-MAH. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) analyses showed some interaction between PP and RgR and considerable modification of the compatibilized mixture morphology. The fracture surface of the blend with PP-g-MAH showed a better interaction between the PP matrix and the regenerated rubber domains, for all blends. Well-dispersed particles of the rubber in the polypropylene matrix were observed. DSC showed that PP crystallizes on cooling at lower temperatures as the RgR content increases. The decrease in crystallization temperature is more evident for blends with 5 wt% PP-g-MAH.

Keywords: mechanical properties, polypropylene, recycling, regenerated rubber, tires

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INTRODUCTION

The automotive and transportation industries are the biggest consumers of elastomers. Rubber waste is generated from the manufacturing process and disposal of post-consumer elastomeric products which consist, mainly, of scrap tires [1].

Seeking to minimize the inadequate disposal of post-consumer tires in Brazil, in 1999, the Brazilian National Environment Council (*Conselho Nacional do Meio Ambiente* – CONAMA) regulated the responsibility of tire manufacturers and importers to collect and dispose of tires in an environmentally correct manner [2–5].

An interesting way to provide a sustainable destination for post-consumer elastomers is to mix them with olefinic thermoplastics, which represents a type of recycling. Generally, researchers use post-consumer ground tire rubber, named recycled rubber [6–12].

Owing to the excellent processing characteristics and the good mechanical properties of polypropylene (PP), it is used in mixtures with several elastomers [5,13,14]. The final product can have thermoplastic and elastomeric characteristics, that is, it may be a thermoplastic elastomer (TPE). The main advantage of TPEs is the possibility for the use of conventional thermoplastics processing techniques, such as extrusion and injection molding, and the main disadvantage is their low resistance to oils and solvents at high temperatures [6,15].

The literature shows that polypropylene and post-consumer rubber with different characteristics are mixed to obtain a material with the good properties of each polymeric component [6–12]. The addition of post-consumer rubber to PP improves the PP mechanical properties, but its crystallinity decreases.

The incorporation of maleic anhydride-functionalized polypropylene (PP-*g*-MAH) as a compatibilizer agent in PP/rubber blends has been studied with the aim of improving the dispersion and interaction of rubber within the PP matrix [13–19].

The dispersion of the rubber domains in a PP matrix has been observed with atomic force microscopy (AFM) and scanning electronic microscopy (SEM) analyses [6,19,20].

No article relating to mixtures of thermoplastics with regenerated rubber could be found in the literature. Regenerated rubber is obtained through chemical modification of the rubber structure, which transforms it into a more plastic and easily reprocessed material. Thus, regenerated rubber can be vulcanized [21,22].

This article focuses on the study of mixtures of polypropylene (PP) and regenerated rubber (RgR). The influence of the addition of 5 wt% of PP-*g*-MAH to the blends was evaluated through their mechanical, morphological and thermal properties, using different RgR contents (5–20 wt%). The advantages of promoting a reduction in the disposal of rubber residues and the preservation of the non-renewable sources of the raw material are discussed.

EXPERIMENTAL

Materials

The polypropylene (PP) used was supplied by Ipiranga Petroquímica S.A., Brazil, with a melt flow index and density of 12.0 g/10 min and 0.903 g/cm^3, respectively. The regenerated rubber from passenger car tires (here referred to as RgR) was kindly supplied by a company in Rio de Janeiro, Brazil. This material was obtained from thermal regeneration of ground tire elastomers. It is important to emphasize that these tires are composed of different elastomers, such as styrene-butadiene copolymer (SBR), polybutadiene (BR) and natural rubber (NR). The regenerated sample (50 mesh) was used as received. Maleic anhydride-functionalized polypropylene, PP-*g*-MAH (melt flow index: 11g/10 min, 0.6 mol of maleic anhydride), was supplied by Honeywell, USA.

Preparation of PP/RgR Blends

The polypropylene and regenerated tire rubber were mixed in a Haake twin-screw extruder, at 60 rpm screw speed, with a 170 to 200°C temperature profile, and 5, 10, 15 and 20 wt% rubber content, with and without 5 wt% of the PP-*g*-MAH.

Mechanical, Morphological and Thermal Characterization of PP/RgR Blends

Tensile and flexural tests were performed according to ASTM D 638 and ASTM 790, respectively, using an Instron testing machine (model 4204) upgraded for computerized data acquisition. The Izod impact resistance test was carried out at 23°C using a Resil impact instrument, according to ASTM D 256. The specimens were obtained by injection-molding.

The morphology of the specimens submitted to the tensile test and fracture in liquid nitrogen was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM analysis was performed with a JEOL – JSM 6060 scanning electron microscope and AFM analysis using a Digital Instruments Nanoscope IIIa, at room temperature. Phase contrast images were recorded in the Tapping Mode. The instrumental parameters, such as set point, were adjusted to improve the image resolution. Cross-sections of the samples were cryogenically cut with a microtome from the PP and regenerated rubber blends surfaces. The objective of this test was to obtain some information on the RgR dispersion in the PP matrix and to evaluate the presence of the PP-*g*-MAH in the blends.

The crystallinity (X_c), melting temperature (T_m) and crystallization temperature on cooling (T_{cc}) of PP in the blends were studied through differential scanning calorimetry using a Perkin-Elmer thermal analyzer. The samples were scanned at heating and cooling rates of $10^\circ\mathrm{C\,min^{-1}}$ in nitrogen atmosphere. The melting and crystallization temperatures were analyzed from the second heating and the second cooling curves, respectively. The crystallinity of PP was determined from the ratio of the fusion heat of the blend to that of 100% crystalline PP ($\Delta H^\circ = 138\,\mathrm{J/g}$) [23].

RESULTS AND DISCUSSION

Figures 1 and 2 shows the effects of the regenerated rubber and PP-*g*-MAH contents on the tensile modulus and Shore D hardness, respectively.

Figure 3 shows the results for strength at break of the blends.

The addition of the regenerated rubber (5, 10, 15 and 20 wt%) in PP decreased the tensile modulus of PP (Figure 1). The greatest decrease

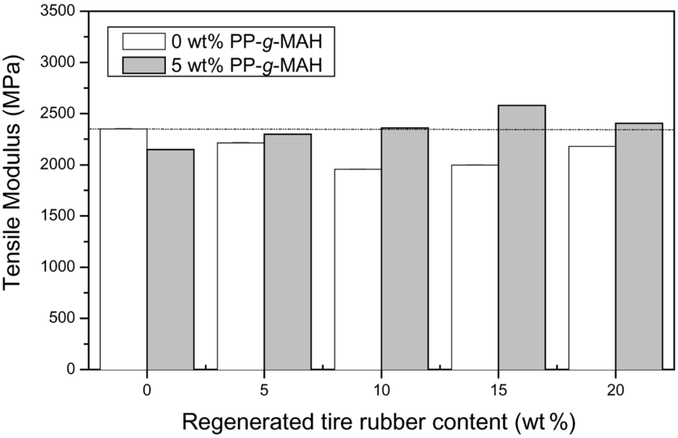

FIGURE 1 Tensile modulus of PP/PP-*g*-MAH/RgR blends.

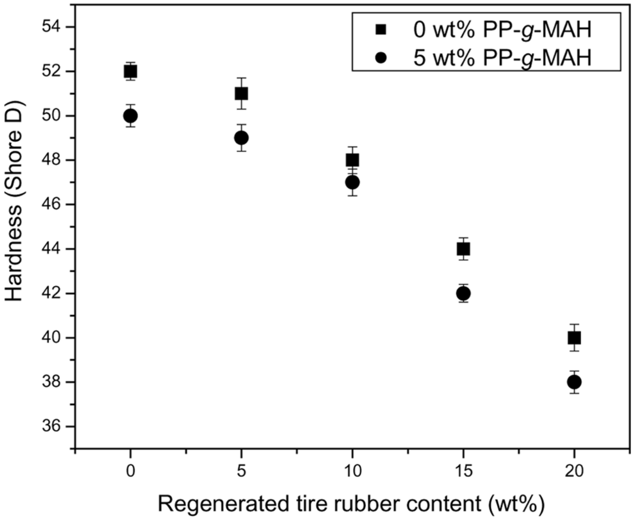

FIGURE 2 Shore D hardness of PP/PP-*g*-MAH/RgR blends.

occurred in 90/0/10 and 85/0/15 wt% PP/PP-*g*-MAH/RgR blends. These results were to be expected, since the addition of rubber to PP promotes a decrease in total rigidity, as is also observed for Shore D hardness behavior (Figure 2).

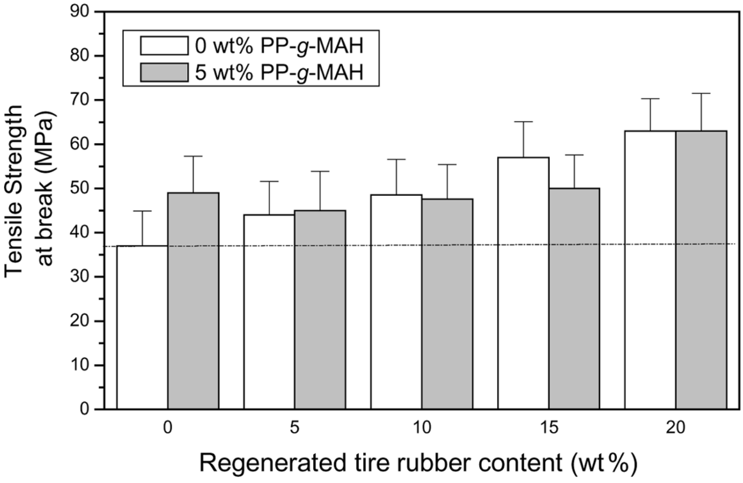

FIGURE 3 Tensile strength at break of PP/PP-*g*-MAH/RgR blends.

The composition with 20 wt% of RgR had a tensile modulus value similar to that with 5 wt% of RgR. This similarity may be due to the presence of non-reacted sulfur and/or chemically active species in the RgR [10,22,23], which can lead to the crosslinking of part of the RgR. This reaction is more likely to occur in mixtures containing a higher quantity of RgR, with more active species. Also, the extrusion conditions (temperature) allow the vulcanization reaction to occur.

Figure 3 shows the tensile strength at break of PP/PP-*g*-MAH/RgR blends as a function of regenerated tire-rubber content. The tensile strength at break increases with the presence of rubber, mainly at higher rubber content. This result was unexpected, because the rubber has amorphous domains that, generally, decrease the tensile strength at break [6,7]. However, as previously suggested, the rubber crosslinking and/or chemical interaction between PP and RgR may be responsible for this behavior in blends with higher rubber content.

The elongation at break decreased with the increase in the regenerated rubber content (up to 10 wt% RgR), but increased with 15 and 20 wt% RgR in the blend (Figure 4). The latter blend gave the highest elongation at break value. It is possible that the RgR acts as an inert filler at low RgR content. But the elongation at break is sensitive to higher RgR content in the blends, possibly due to the occurrence of chemical interactions at blend component interface.

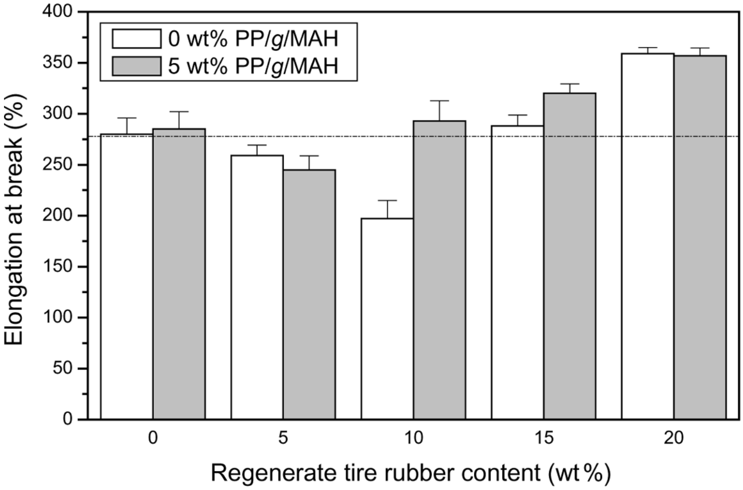

FIGURE 4 Elongation at break of PP/PP-*g*-MAH/RgR blends.

The literature shows different results than those reported here regarding non-regenerated tire-rubber blends. Jain et al. [8] reported a decrease in the tensile modulus and an increase in the elongation at break with an increase in elastomer content. Ismail and Suryadiansyah [6] showed a decrease in the modulus and tensile strength with an increase in rubber content in polypropylene/nitrile rubber/powder tire-rubber blends, whereas the elongation at break exhibited an opposite trend.

PP-*g*-MAH was not efficient as a compatibilizer agent in terms of the tensile properties (Figures 1, 3 and 4). The only exception was for the tensile modulus values for blends with compositions of 85/5/10 and 80/5/15 wt% PP/PP-*g*-MAH/RgR (Figure 1) and for the elongation at break of the 85/5/10 wt% PP/PP-*g*-MAH/RgR blend (Figure 4).

Figure 5 shows the Izod impact resistance at 23°C of PP/PP-*g*-MAH/RgR blends with different compositions of the regenerated rubber.

It can be observed that the incorporation of the regenerated rubber into the PP matrix resulted in an increase in the impact resistance for all blends. This increase was more significant for the samples with 15 and 20 wt% RgR (around 40%). Jain et al. [8] also reported an increase in the impact resistance with an increase in ground tire rubber in the PP matrix. The rubber in the thermoplastic matrix absorbs the impact energy and dissipates this energy as heat.

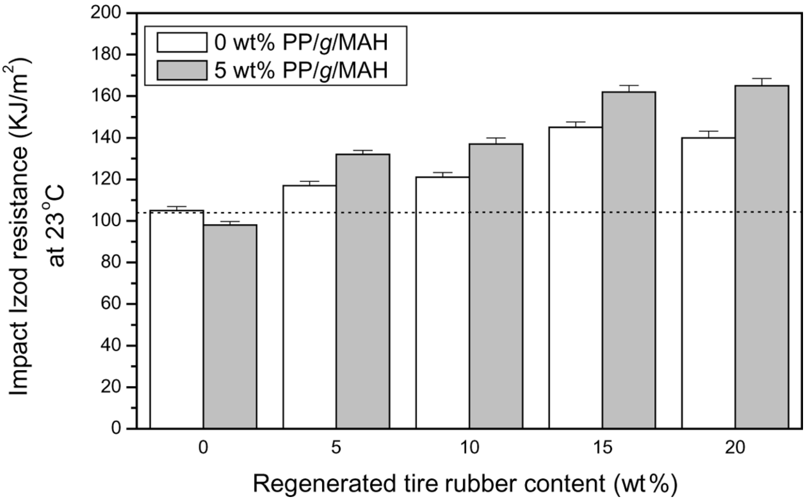

FIGURE 5 Izod impact resistance at 23°C of PP/PP-*g*-MAH/RgR blends.

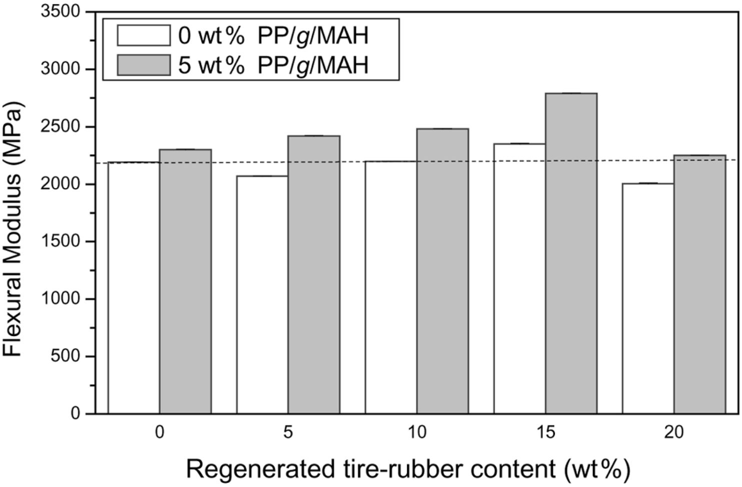

FIGURE 6 Flexural modulus of PP/PP-*g*-MAH/RgR blends.

In the same way, the impact resistance increases for all blends prepared with 5 wt% of PP-*g*-MAH. The grafted PP was effective as a compatibilizer agent in terms of impact resistance.

Figure 6 shows that the addition of regenerated rubber to the PP matrix did not significantly change the flexural modulus. However, a decrease in the flexural modulus with the addition of rubber would be expected. The presence of PP-*g*-MAH promoted a slight increase, mainly for the 80/5/15 wt% PP/PP-*g*-MAH/RgR blend.

Figures 7–9 show the SEM photomicrographs of the tensile fracture surface for the samples with 5, 10 and 15 wt% of regenerated rubber with and without 5 wt% of PP-*g*-MAH.

For all blends, well-defined and well-dispersed rubber domains can be observed in the polypropylene matrix of the PP/RgR blends (Figures 7A, 8A and 9A). The micrographs of these noncompatibilized materials show that the size of the dispersed RgR regions decreases with the increase in the rubber content, suggesting that there is some interaction between the thermoplastic and the regenerated rubber. This result agrees with those obtained for the mechanical properties. It is important to emphasize that the 90/0/10 wt% PP/PP-*g*-MAH/RgR blend showed no interaction between the phases and presented lower values for the mechanical properties.

However, the addition of 5 wt% of PP-*g*-MAH to the blends, besides causing a considerable modification in the morphology of polypropylene (Figures 7B, 8B and 9B), promoted a reduction in the

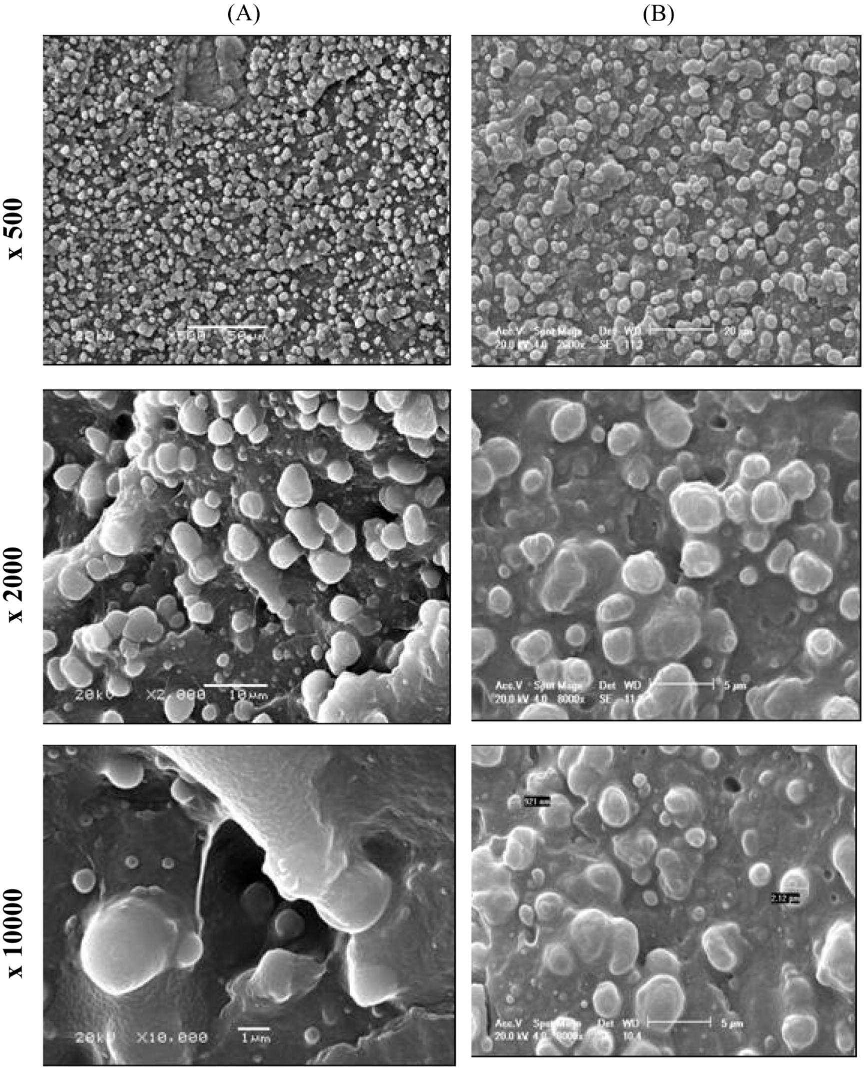

FIGURE 7 SEM photomicrographs of fractured surfaces of PP/PP-*g*-MAH/RgR (wt%) at magnifications of 500X, 2000X and 10000X: (A) 95/0/5 (B) 90/5/5.

domain size, particularly in the case of the 80/5/15 wt% PP/PP-*g*-MAH/RgR blend. This behavior indicates a better interaction between the PP matrix and the regenerated rubber domains through the use of PP-*g*-MAH.

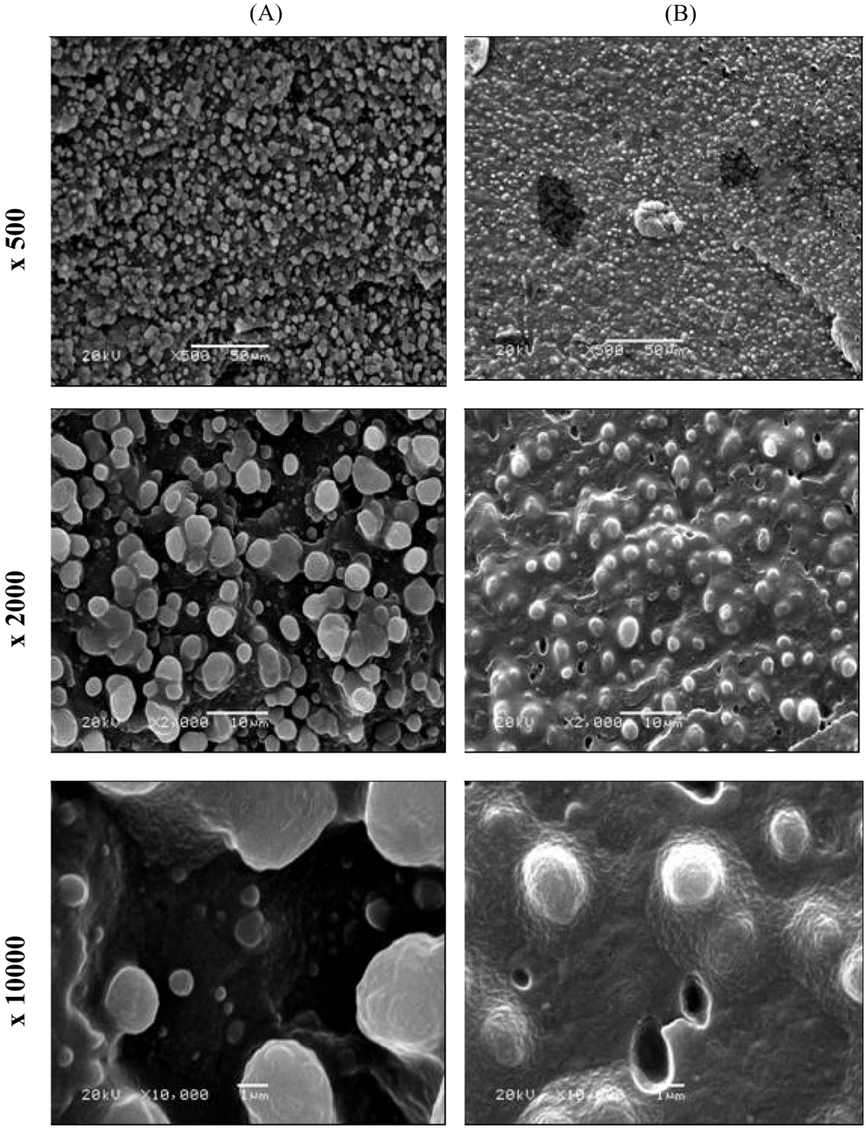

FIGURE 8 SEM photomicrographs of fractured surfaces of PP/PP-*g*-MAH/RgR (wt%) at magnifications of 500X, 2000X and 10000X: (A) 90/0/10 (B) 85/5/10.

AFM images of cross-sections of PP and regenerated rubber blend surfaces, with 2D and 3D dimensions (Figure 10), verify the results obtained by SEM. SEM and AFM analyses were performed on samples

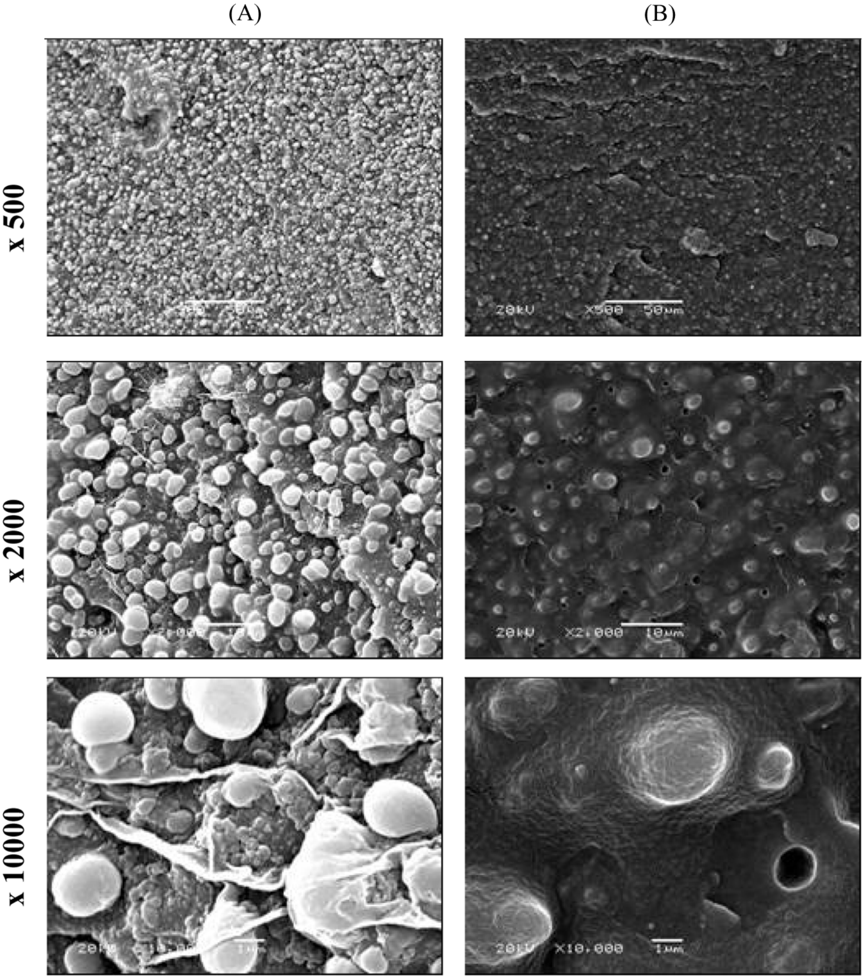

FIGURE 9 SEM photomicrographs of fractured surfaces of PP/PP-*g*-MAH/RgR (wt%) at magnifications of 500 ×, 2000 × and 10000 ×: (A) 85/0/15 (B) 80/5/15.

microtomed perpendicularly to the flow direction of the blend injection process. The results for the characteristics of the rubber particles are expected to be similar using the two techniques [20].

Both Tables 1 and 2 show that the crystallinity of the system decreases with increasing RgR content. This indicates that the formation of crystallites was affected by the presence of RgR. The melting and crystallization temperatures also decreased with the incorporation of RgR.

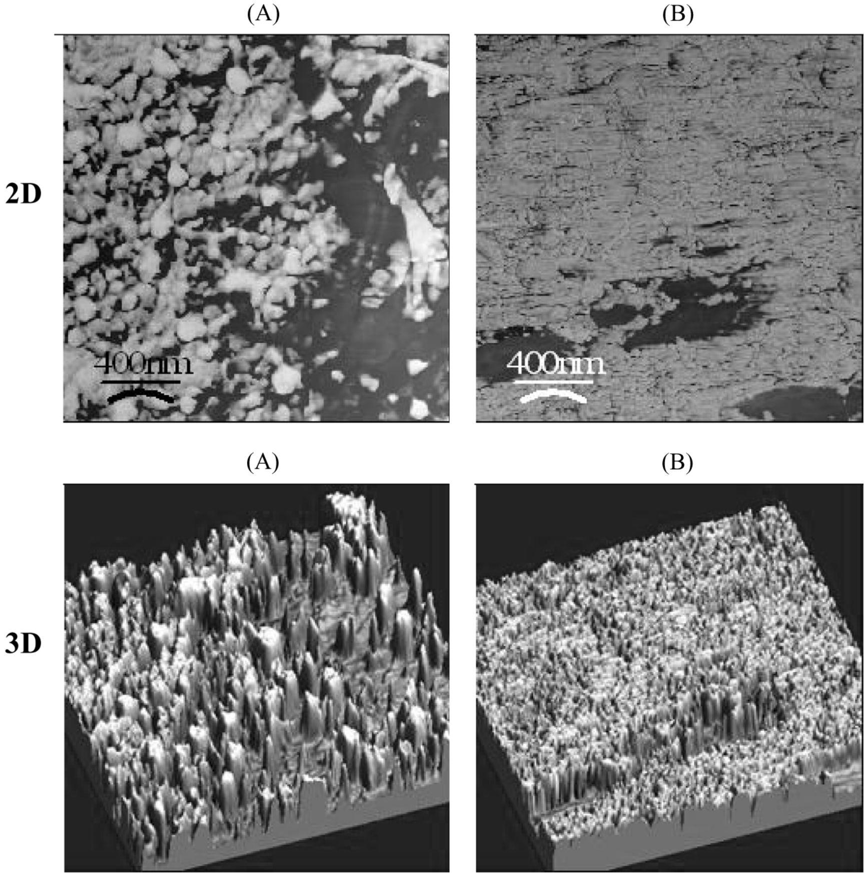

FIGURE 10 AFM images on the cut face of PP/ PP-*g*-MAH/RgR with 2D and 3D dimensions – (wt%): (A) 85/0/15 (B) 80/5/15.

TABLE 1 Thermal Properties of PP and PP/RgR Blends

PP/PP-*g*-MAH/RgR (wt%)	Tc (°C)	Tm (°C)	Xc (%)
100/0/0	124	169	46
95/0/5	115	166	35
90/0/10	110	164	32
85/0/15	104	162	30
80/0/20	106	161	32

TABLE 2 Thermal Properties of PP and PP/ PP-*g*-MAH/RgR Blends

PP/PP-*g*-MAH/RgR (wt%)	Tc (°C)	Tm (°C)	Xc (%)
100/0/0	124	169	46
95/5/0	120	168	48
90/5/5	109	165	32
85/5/10	107	162	26
80/5/15	102	160	24
75/5/20	103	161	23

CONCLUSIONS

The mixture of PP and regenerated tire rubber is important to minimize the inadequate disposal of used tires. The presence of the regenerated tire rubber in PP blends resulted in an increase in the impact resistance for all blends, this being more significant for the samples with 15 and 20 wt% RgR. This result is highly significant in terms of automobile industry applications, for example, in the use of these mixtures in bumpers.

The presence of the regenerated rubber seems to promote an interaction between the domains of the rubber and the polypropylene. It was observed, unexpectedly, that the tensile strength at break and the tensile modulus did not decrease considerably with higher RgR content. This may be due to two processes: the vulcanization of rubber domains and/or the interaction of PP with the regenerated rubber domains during extrusion. These processes will be further investigated in future studies.

The use of 5 wt% of PP-*g*-MAH in the PP and RgR mixtures did not promote a notable improvement in the mechanical properties, except for 85/5/10 wt% and 80/5/15 wt% PP/PP-*g*-MAH/RgR blends. A significant change in the morphology of the mixtures was observed through SEM and AFM analyses.

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