

MORPHOLOGY OF POLYPROPYLENE, EPDM RUBBER AND ORGANOPHILIC CLAY NANOCOMPOSITES

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SUMMARY

In this work, nanocomposites of polypropylene and organophilic clay toughened with poly(ethylene-*co*-propylene-*co*-2-ethylidene-5-norbornene) rubber were investigated. Due to the combination of the different components the mechanical properties of the nanocomposites showed a synergistic effect showing characteristic values of supertough blends.

Keywords: polypropylene; nanocomposites; montmorillonite; EPDM

INTRODUCTION

The interest in polymer layered silicate nanocomposites is driven by the possibility of exceptional physical property enhancements at low filler levels. Nanocomposites present an increase in stiffness, tensile strength and barrier properties [1-9]. In such materials, the temperature of ductile-brittle transition and the fragility are however drastically increased with the addition of clay. Therefore, the toughening of nanocomposites becomes an interesting alternative to overcome these problems [9-13].

The mechanical mixture is the most interesting method for preparation of exfoliated nanocomposites presenting potential industrial applications. The clay is incorporated in the polymer during extrusion and the shearing of the material takes to the intercalation or exfoliation of the clay [2,7,8,13,14]. Supertough blends of semicrystalline polymers are prepared with reactive extrusion by the modification of the polymeric matrix or the dispersed elastomeric phase, or by the use of a compatibilizer. The preparation of toughened nanocomposites is viable for conventional methods of mixture and dispersion in the melting state.

The production of a toughened nanocomposite by addition of an elastomer must be carried out through two stages: (1) extrusion of the polymer with the organophilic clay (OMMT) using higher shear rate and (2) extrusion of the prepared nanocomposite with the elastomer for the toughening of the nanocomposite. The addition of the clay in the elastomeric phase does not contribute for the increase of the Young's modulus with the same efficiency that contributes when the clay is present in the polymeric matrix. Moreover, the inserted load in the elastomeric phase diminishes the toughening effect of the elastomer at low temperatures due to the increase of the modulus of this phase [11,12,15,16].

Lim et. al. [15] evaluated the influence of the content of PP-g-MA compatibilizer and organophilic clay in PP nanocomposites toughened by 10 wt% ethylene-octene rubber (POE). These nanocomposites were prepared in a single step by mechanical mixing. The authors observed that the optimum PP-g-MA and clay contents of for this system were 6 wt%, since at higher clay content, the interactions between clay layers resulted in agglomerates that restricted the exfoliation and decreased intercalation degree, not contributing positively for the mechanical properties of the nanocomposites. They also observed that the nanocomposite containing 6 wt% of OMMT and 10 wt% of POE presented impact resistance (8.3 kJ m^{-2}) similar to the value of pure PP (9.3 kJ m^{-2}). This indicates that the incorporation of 10 wt% of POE is enough to compensate the loss in the impact resistance caused by the presence of 6 wt% of OMMT (6.2 kJ m^{-2}). The improvements observed in the mechanical properties are attributed to the presence of PP-g-MA which is capable to interact with clay functional groups and to achieve the desired nanometric dispersion of the clay.

Lee et. al. [16] prepared PP nanocomposites from organophilic clay and ethylene-octene rubber (POE) compatibilized with PP-g-MA (1 wt% of MA) by using the two stage processing method. First, equal parts of PP-g-MA and OMMT were mixed, and later this masterbatch was incorporated to the PP. The nanocomposites presented mixed morphology with combination of intercalated and exfoliated clay. The authors also observed that the increase of the OMMT content results in the reduction of the exfoliation degree of the clay, the reduction in size and the increase in the irregularity of the elastomeric domains. This observation was attributed to two competitive factors occurring during the processing: (1) rheological effect and (2) barrier effect for the coalescence of rubber particles imposed by the presence of the OMMT particles. The reduction in the size of elastomeric domains by the OMMT particles is the explanation suggested by the authors for the increase of the observed toughening at high elastomer contents (30 and 40 wt%). The supertough nanocomposites (impact resistance bigger than 600 J m^{-1}) were obtained for high elastomer content and variable content of OMMT from 1 to 7 wt%.

Ethylene-*co*-propylene copolymer (EPM) and ethylene-*co*-propylene-*co*-diene (EPDM) are the most used impact modifiers for PP [10,15]. The EPDM, as well as its composites and blends, possess high weatherability due to its almost saturated chain. The unsaturation is introduced by the copolymerization of a small amount of diene (5 wt%) with ethylene and propylene.

The objective of this work is to investigate the effect of a organophilic clay on the morphology and mechanical properties of polypropylene/poly(ethylene-*co*-propylene-*co*-2-ethylidene-5-norbornene) (EPDM) blends.

EXPERIMENTAL

Materials

Isotactic polypropylene, iPP (Polibrasil HP 500N), PP-g-MA compatibilizer (Polybond 3200/Chemtura Corporation) with 1 wt% maleic acid-maleic anhydride, organically modified clay, OMMT, Cloisite 20A (Southern Clay Products) and EPDM (Keltan[®] 5508 - DSM Elastomers Ltd) with 69.0 wt% of ethylene, 26.2 wt% of propylene and 4.8 wt% of ENB, were used to prepare the nanocomposites.

Processing

The PP/PP-g-MA/OMMT nanocomposites containing or not EPDM were processed in a Coperion ZSK 26 twin screw extruder with eleven temperature zones in a two-step process. The temperature profile used in the eleven zones was 180 (first to fourth), 190 (fifth and sixth), 200 (seventh to eleventh), and the screw speed was 300 rpm. Before extrusion the materials were dried in a vacuum oven for 12 h. Firstly, the PP/PP-g-MA/organoclay nanocomposites containing 5 wt % of OMMT and 5 wt % of PP-g-MA in relation to PP were prepared. These nanocomposites were then mixed with 30 wt % of EPDM rubber to obtain PP/PP-g-MA/OMMT/EPDM nanocomposites.

Tensile and Impact Resistance Tests

The materials were injection molded into Izod bars (ASTM D256) and dog-bone shaped tensile specimens (ASTM D638) using an Arburg Allrounder molding machine. The following temperatures were kept along the barrel zones: 180, 190, 200, 210, and 200 °C. The mold temperature was kept at 40 °C. At least five injection-molded specimens of each sample were submitted to impact resistance and tensile tests in an EMIC AIC 1 and EMIC DL 200 apparatus, respectively.

Characterization

X-ray diffraction (XRD) measurements were performed using a Shimadzu XRD-6000 diffractometer in a reflection mode with an incident Cu K α radiation ($\lambda = 0.1540$ nm).

The morphology of the nanocomposites were examined in a Carl Zeiss CEM 902 transmission electron microscope. The microscope was operated at an acceleration voltage of 80 kV and equipped with a Castaing-Henry energy filter spectrometer within the column. Ultrathin sections, approximately 40 nm thick, were cut from the central region of the tensile test bar perpendicular to the flow direction at -140 °C in a Leica EM FC6 cryo-ultramicrotome. The images were recorded using a Proscan high-speed slow-scan CCD camera and processed in the iTEM (Universal Imaging Platform) software.

RESULTS AND DISCUSSION

X-Ray Diffraction

The interlayer distances (d_{001}) of the basal reflection peaks of OMMT and nanocomposites were determined from X-ray diffraction. Figure 1 shows the XRD diffraction patterns of PP, OMMT, PP/OMMT and PP/PP-g-MA/OMMT nanocomposites and their blends with EPDM. The XRD parameters calculated from the (001) peaks are summarized in Table 1. The X-ray patterns of neat PP and their blends showed no peaks in this 2θ range and were therefore used as baselines to evidence the existence of diffraction peaks resulting from the dispersed organoclay in the polymeric matrix. The OMMT diffraction pattern reveals a (001) reflection peak at around $2\theta = 3.7$ corresponding to an interlayer spacing of 2.4 nm. The PP/EPDM/OMMT nanocomposite showed the (001) peak between the values of OMMT and the PP/OMMT nanocomposite indicating that the addition of EPDM led to a decrease in the d-spacing in comparison to the nanocomposites after the second step of processing. This indicates that the PP chains intercalated into the galleries of the organophilic clay, but

that the presence of EPDM can cause a decrease in the polymer intercalation. On the other hand, the (001) reflection peaks shifted to lower values in the presence of PP-g-MA compatibilizer, corresponding to an increase in the clay interlayer spacing.

Table 1. XRD results obtained for the organoclay, PP and PP nanocomposites and blends with EPDM.

Material	2 θ (degrees)	d ₀₀₁ (nm)
OMMT	3.66	2.41
PP	no peak detected	-
PP/OMMT	3.42	2.58
PP/ PP-g-MA/OMMT	3.38	2.61
PP/EPDM	no peak detected	-
PP/EPDM/OMMT	3.60	2.45
PP/PP-g-MA/EPDM/OMMT	3.30	2.68

Transmission Electron Microscopy (TEM)

The morphology of the nanocomposites is quite important because it determines their mechanical performance. The electron micrographs of the bulk thin sections of PP/EPDM blend and PP/EPDM/OMMT nanocomposites are presented in Figure 2. The micrographs of the PP/OMMT nanocomposites showed that the clay particles are not evenly dispersed throughout the matrix; in fact, most of the clay stacks are confined to clusters having micrometric dimensions. The addition of the PP-g-MA compatibilizer promoted a better dispersion of the clay, a decrease in the size of the clay tactoids as well as a partially exfoliated morphology. In this case, the presence of a mixed morphological structure, i.e. combination of intercalated stacks and exfoliated particles, is observed (Figure 2c). TEM images also showed that the presence of tactoids in the PP/EPDM/OMMT nanocomposite did not affect the domain size distribution of EPDM rubber in the PP matrix in relation to the PP/EPDM blend. As expected, the addition of PP-g-MA compatibilizer promoted a significant reduction in the domain size of the EPDM dispersed phase.

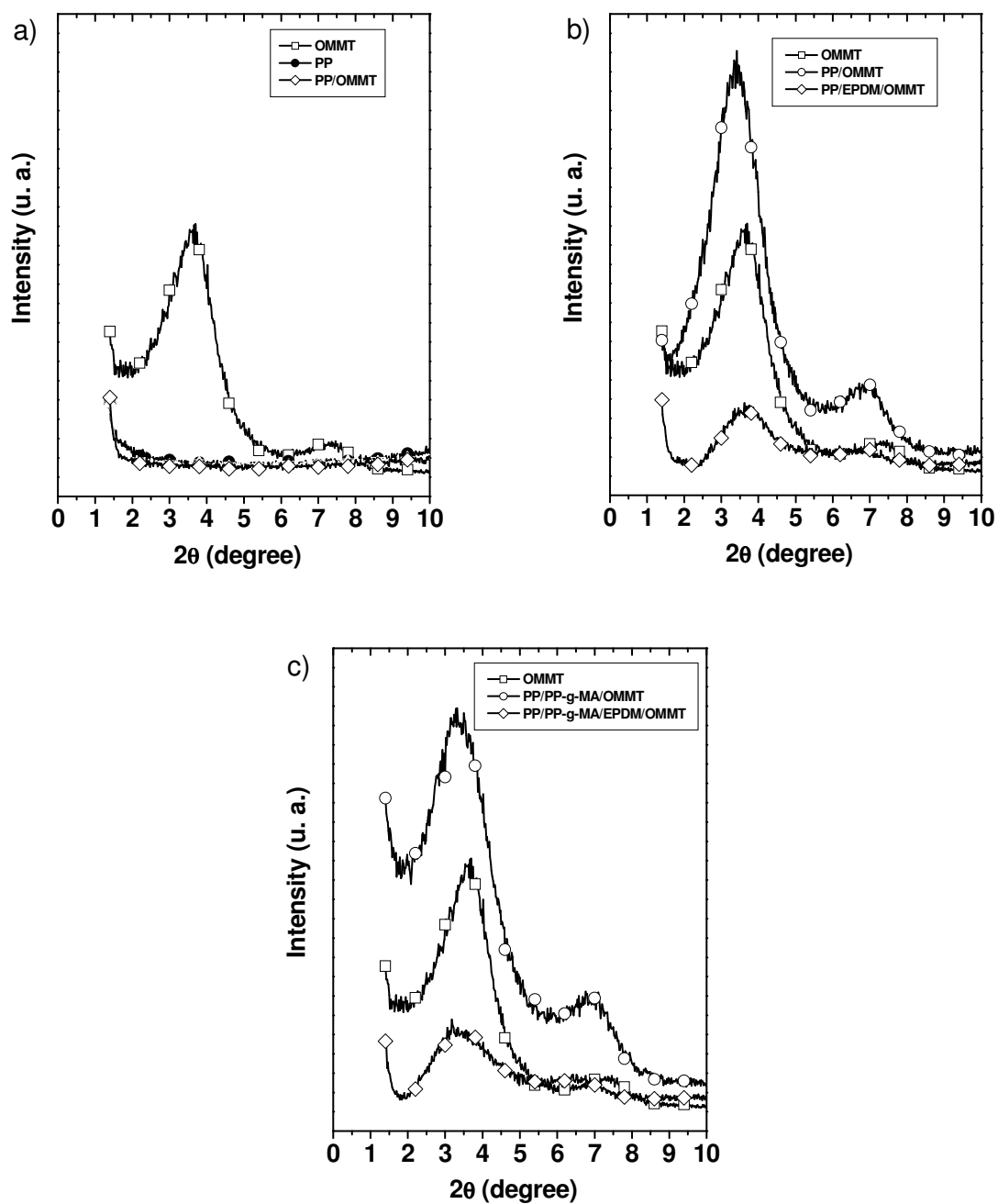


Figure 1. XRD patterns of OMMT and (a) PP, (b) PP/OMMT, (c) PP/PP-g-MA/OMMT and their corresponding blends with EPDM.

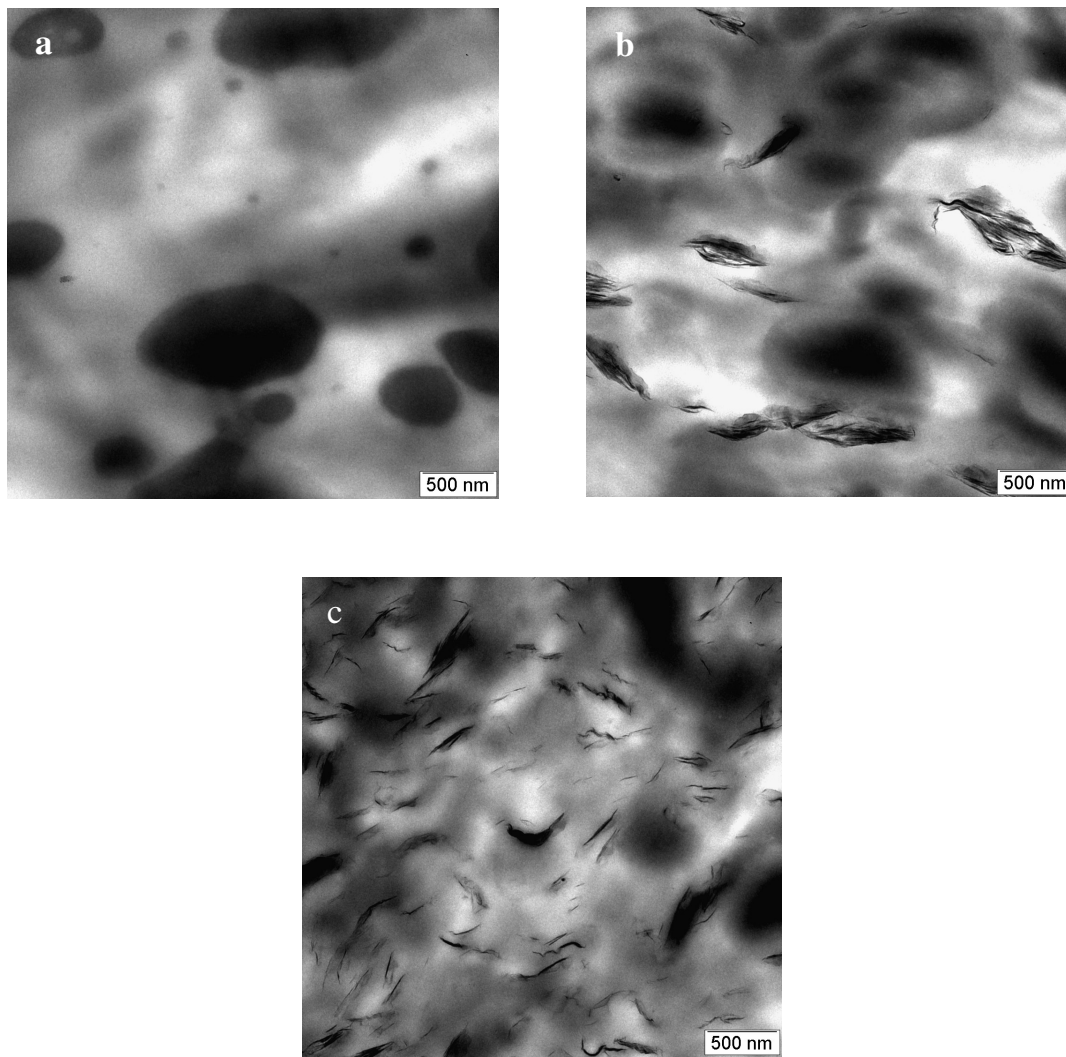


Figure 2: Transmission electron micrographs of (a) PP/EPDM blend, (b) PP/EPDM/OMMT and (c) PP/PP-*g*-MA/EPDM/OMMT nanocomposites.

Tensile and Impact Resistance Tests

Figure 3 shows the representative stress vs. strain curves for PP, PP/OMMT and PP/PP-*g*-MA/OMMT and their blends with EPDM. The values of the mechanical properties are listed in Table 2. The incorporation of EPDM in the PP and PP nanocomposites resulted in a pronounced increase in the strain at break of the material as compared to the respective polymer and polymer blend without clay. The Young's modulus also showed the expected behavior for the addition of rubber in a thermoplastic matrix. The incorporation of 30 wt% of EPDM in PP as well as the PP nanocomposites resulted in a reduction of the Young's modulus of the materials. The impact resistance of PP increased from 22 ± 2 to 128 ± 15 J/m with the addition of EPDM and from 18 ± 3 to 493 ± 43 J/m with the simultaneous addition of EPDM, PP-*g*-MA and OMMT. The

combined use of clay, EPDM and compatibilizer in the PP matrix resulted in a synergistic effect in the impact resistance. In this way, the impact resistance of the PP/PP-g-MA/EPDM/OMMT nanocomposite containing 3.5 wt% of PP-g-MA, 30 wt% of EPDM and 3.5 wt% of clay reached a value corresponding to a supertough blend.

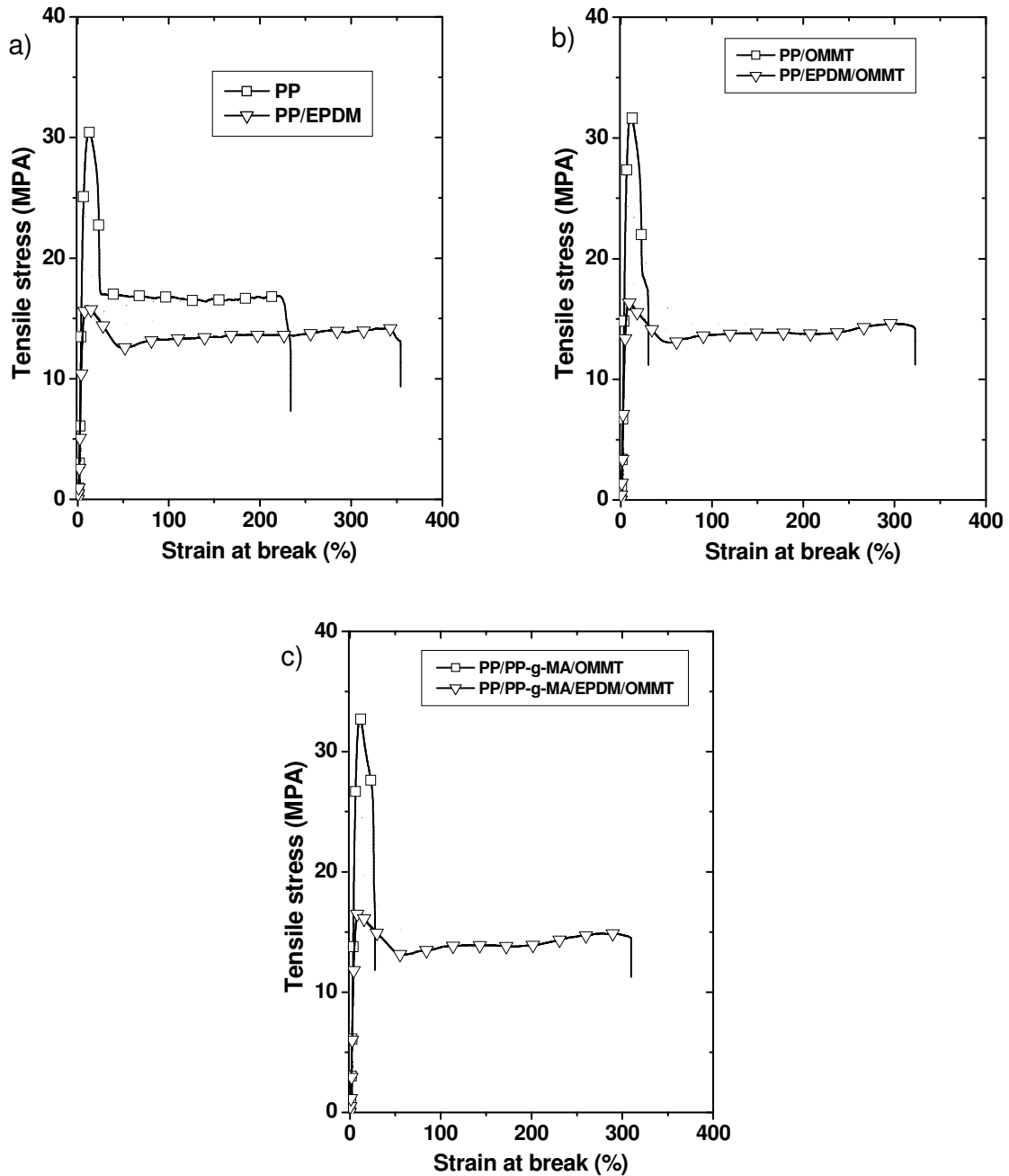


Figure 3. Representative stress vs. strain curves of (a) PP, (b) PP/OMMT, (c) PP/PP-g-MA/OMMT and their corresponding blends with EPDM.

Table 2: Mechanical properties of the materials.

Material	Impact resistance (J m ⁻¹)	Young's modulus (GPa)	Strain at break (%)
PP	22±2	635±20	205±28
PP/OMMT	18±3	683±14	36±24
PP/PP-g-MA/OMMT	18±3	690±13	30±13
PP/EPDM	128±15	388±11	339±35
PP/EPDM/OMMT	509±36	395±7	325±22
PP/PP-g-MA/EPDM/OMMT	493±43	402±4	310±25

CONCLUSIONS

The addition of EPDM in the PP/OMMT nanocomposites caused a decrease in the d-spacing of the clay gallery in relation to the corresponding nanocomposites reaching values close to the d-spacing of the organophilic clay. The XRD results evidenced a low degree of the polymer intercalation in the clay gallery. TEM images showed that the presence of tactoids in the PP/EPDM/OMMT nanocomposite did not affect the domain size distribution of rubber in the PP matrix in relation to the PP/EPDM blend. However, the addition of PP-g-MA promoted the intercalation of polymer in the clay structure and its partial exfoliation as well as a significant reduction in the domain size of the EPDM dispersed phase.

The addition of EPDM to PP increases considerably the impact resistance and the strain at break in comparison with PP. However, the Young's modulus of the blends is lower than the value for PP. The impact resistance of the nanocomposites with 30 wt% of EPDM reached values of supertough polymeric materials: 509±36 J/m and 493±43 J/m for nanocomposites containing 0 and 5 wt% of PP-g-MA, respectively. It is proposed that the clay stabilized the domain morphology and enhanced the blend performance.

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