Processing, Properties and Morphology of Polypropylene–EPDM Blends

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SUMMARY: Blends of polypropylene and an elastomer (ethylene propylene diene terpolymer, EPDM) are systematically investigated to determine the effect of the rubber on the polymer properties. Five compositions on the complete range of blend compositions are analyzed. The study reported here is a first of a series which main objective is to analyze in a systematic way the influence of the different factors that determine the effectiveness of EPDM as an impact modifier for PP. In this first part of the study, the processing behavior of the PP-EPDM blends are analyzed and the mechanical properties of the processed blends (tensile, flexural and impact resistance) are examined. Halpin-Tsai and porosity models successfully represent the mechanical behavior of the blends. The model results allow a physical interpretation of the role of the dispersed phase in terms of the aspect ratio and of the stress concentration factors associated to the dispersed particles. Moreover, the mechanical properties are correlated with the morphology of the blends studied by scanning electron microscopy, where two phases are clearly observed in the complete range of compositions. The results show that PP-EPDM blends with at low rubber content present a good processability, without significant deterioration with respect to neat PP and with a considerable improvement of the room and low temperature performance.

Introduction

Polypropylene (PP) is a semicrystalline thermoplastic polyolefin that offers a very attractive combination of physical and mechanical properties at a relatively low cost, which makes it a versatile material with continuously increasing applications. However, the inherently high glass transition temperature and high cristallinity of this resin determine a reduced toughness, which limits its usefulness at low temperatures[1-2]. In order to overcome these limitations, blends of PP with elastomeric polyolefins, typically with EPR (ethylene propylene rubber) and EPDM (ethylene propylene diene terpolymer) have been proposed[3-8]. In particular, the use of thermoplastic elastomeric materials (TPE) based on blends of EPDM and PP, has increased dramatically in recent years. These blends commonly referred as TPOs, are a

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special class of TPE that combines the processing characteristics of plastics at elevated temperatures[9-11] with the physical properties of conventional elastomers at service temperatures[12-13], playing increasingly important roles in the polymer materials industry.
The similarity of the chemical structure of these polymers, together with their different physical properties makes it possible to combine them to produce materials of desired properties. Different aspects of these blend systems, i.e. crystallization[14-15], morphology[16], mechanical[17] and rheological[18-19] properties, have been already reported in the scientific literature by several authors. The main objective of the research reported here is to analyze in a systematic way the influence of the different factors, which determine the effectiveness of EPDM as a modifier impact for PP. In this first part of the study, the processing behavior of PP-EPDM blends in the whole range of compositions will be analyzed and the mechanical properties of the processed blends (tensile, flexural and impact behavior) will be examined. The properties will be correlated with the morphology of the blends studied by scanning electron microscopy.

Experimental

Materials

Polypropylene (PP) (melt flow index 6.0 at 230 °C and density 0.905 gcm^{-3}) was gently supplied by Montell under the trade name C30G. Ethylene propylene diene terpolymer (EPDM), with 5-ethylidene-2-norborene (ENB) as a termonomer (68% ethylene content and density 0.86 gcm^{-3}), was supplied by Bayer under the trade name BUNA EP T 6470P.
Blends of these homopolymers with various compositions were prepared by melt mixing in a Haake Rheomix 90 at a temperature of 190 °C. The blending time was 10 minutes and the rotor rate was set at 60 rpm. Then, the blends were compression molded at 200 °C in a parallel plate press. Samples were cut from the molded plaques for the experimental study of the mechanical properties. The compositions of the blends studied are showed in Table 1.

Measurements

Torque versus time curves were recorded during the processing of the pure polymers and the blends in the Haake Rheomix 90.
Tensile and flexural test were performed at room temperature (25 °C) on a Lloyd LR30K. Tensile test was performed with a cross-head speed of 5 mm/min until a deformation of the

20% and of 50 mm/min at break. The tensile properties (modulus, strength and elongation at break) were calculated according to ASTM D 638M. The initial tangent modulus was determined from the slope of the load-deformation curves. The tensile strength was determined as the maximum load divided by the initial section area of the specimen. The extension at break was recorded as percent elongation. All tensile properties were the average of a least five measurements.

Tensile test were performed with a length of support span of 64 mm, giving a ratio of support span to specimen depth of 32:1. The flexural properties (maximum strength and modulus) were calculated according to ASTM D-790 M. The results are the average of a least five measurements.

Impact properties were determined according to ASTM D-256 (v-notched) at two temperatures (25°C and –30°C), in an Izod pendulum Ceast mod. Resil 25, with an impact speed of 3.48 ms^{-1} recording the maximum force and stress during the impact test and the energy to fracture. The notches were prepared in a Ceast electrical notching apparatus at a 20% of the thickness and the angle of the "V" side grooves was 45°. In the experiments, carried out at –30 °C, specimens were cooled in liquid nitrogen for at least 20 minutes and then quickly placed in the pendulum and experimented immediately. All results were the average of a least seven measurements.

The morphologies of the compression-molded specimens were observed by scanning electron microscopy (SEM Leica F 360). The micrographs were taken from the cryogenically fractured surfaces (in liquid nitrogen), which were sputtered with gold before microscope observation.

Results and Discussion

Torque versus time analysis

Torque versus time curves obtained during the preparation of the blends in the mixer are reported in Fig. 1 and 2. The torque measured during processing is directly related to the rheological behavior of the blend at the particular processing conditions (temperature and shear rate). Then, the torque value in the plateau region, obtained after stabilization in all cases, can be correlated to the viscosity of the melt. It is possible to observe that the torque increases with the EPDM content in the blend due at higher viscosity of the rubbery component. The dependency of the composition is non-linear and the measured torque is lower than the value predicted by the linear mixture rule of ideal blends, which is represented

by the straight line shown in the Fig.1. This behavior is typical of molten heterogeneous blends.

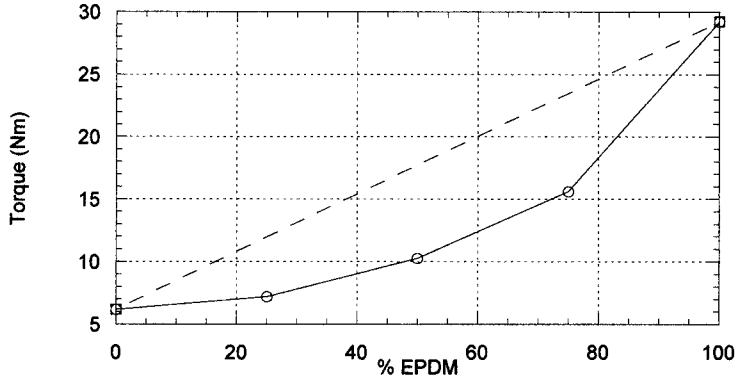

Fig. 1: Torque values of the PP, EPDM and PP-EPDM blends

It is also important to notice that there is not a significant increase of the torque for the PP-EPDM blend with a rubber content of 25% with respect to neat PP. Then, it will possible to take advantage of the eventual better properties of the blend without deterioration of the processing behavior.

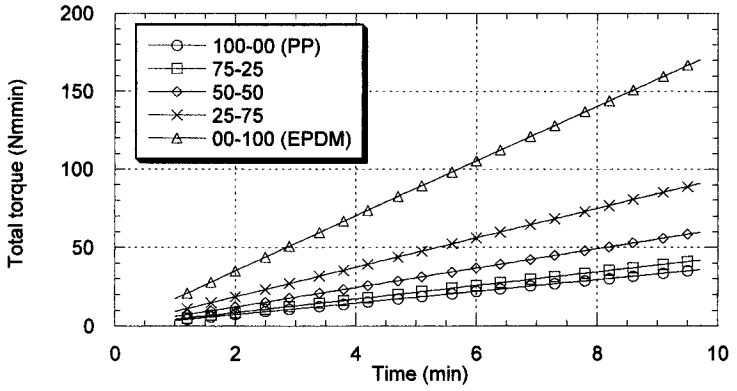

Fig. 2: Total torque curves of the PP, EPDM and PP-EPDM blends.

The area under the torque versus time curves gives the total torque, which is a measure of the energy consumption during the blend preparation. These results are reported in Fig. 2. As expected, the energy consumption increases with the EPDM content in the blend. Also, in this case, at relatively low percentages (25%) of rubber in the blend, the energy consumption is similar to that of PP, which indicates that this blend can be processed by methods of thermoplastics processing without higher energy consumption.

Mechanical properties

Tensile Behavior

A typical tensile stress-strain curve of a PP-EPDM blend is represented in Fig. 3. From these curves the Young's modulus, E, the yield stress, the maximum stress, the stress at break (σ_{max}), and the percent elongation at yield and break (ε_{max}, ε_y) were computed.

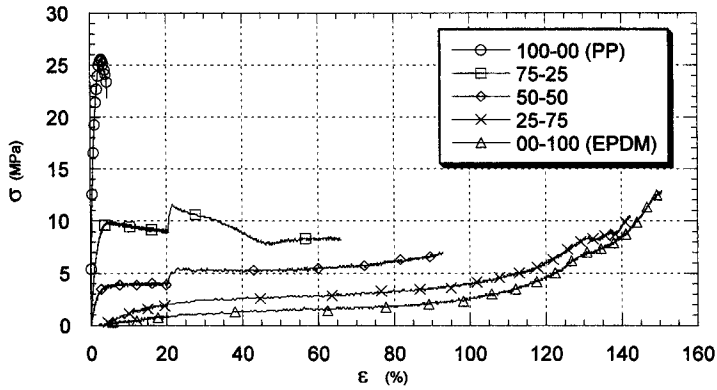

Fig. 3: Variation of tensile properties with the composition of the blend.

The results are listed in Table 1. It can be observed that the modulus and strength of the material is strongly dependent on the matrix composition decreasing significantly with the rubber content. On the other hand, the elongation at break of the material increases with the rubber content in the blend. In general, it can be concluded that, as expected, there is a gradual non-linear increase of the elastomeric behavior of the blends as the concentration of EPDM increases; thus, the modulus and strength decreases but the elongation of the material increases. More specifically, the blends with 25% and 50% of rubber concentration show a

stress-strain curve typically of a ductile polymer with an evident yield point at which permanent plastic deformation takes place. After the yield point a typical "neck" starts to form and then extends in a "cold drawing" process driven by the local heating of the specimen due to energy released during deformation.

Table 1. Tensile properties of materials studied.

Blends PP–EPDM (%)	**Young's Modulus** (MPa)	**Max. Strength** (MPa)	**Def. at max. strength** (%)	**Strength at break** (MPa)	**Def. at break** (%)	**Tensile Yield Stress** (MPa)
100-00	1038	32.1	9	20.7	81	32.1
75-25	597	13.8	26	10.7	97	13.8
50-50	150	12.7	538	12.7	542	3.87
25-75	18	12.6	1159	11.8	1159	2.75
00-100	7	12.4	1216	12.2	1217	1.62

On the other hand, can be observed that the blends with a 25% and 50% of rubber show a stress-strain curve typically of a ductile polymer with a point at which permanent plastic deformation takes place (yield point). During elastic deformation, a "neck" starts to form. The process whereby the neck extends is known as "cold drawing", which is due to local heating of the specimen by the energy expending during deformation. The blends with higher content of rubber present a typical comportment of an elastic material.

The Halpin-Tsai model[20] has been utilized to analyze the behavior of the elastic modulus of the blend as a function of the elastomer concentration. This model, originally developed for short fiber and particulate filled polymers, has been also applied to different polymer blends[21,22]. According to this model, Young's modulus, E_b, of the blends is given by:

$$E_b = E_p\left(\frac{1 + A\eta\phi_r}{1 - \eta\phi_r}\right) \tag{1}$$

where the parameter η is given by:

$$\eta = \frac{\left(E_r/E_p\right) - 1}{\left(E_r/E_p\right) + A} \tag{2}$$

where: E_b is the elastic modulus of the blend

E_p is the elastic modulus of polypropylene

E_r is the elastic modulus of EPDM

ϕ_r is the volume fraction of rubber

A is a constant parameter related to the Einstein's coefficient of the suspension, which is determined by the aspect ratio of the dispersed face.

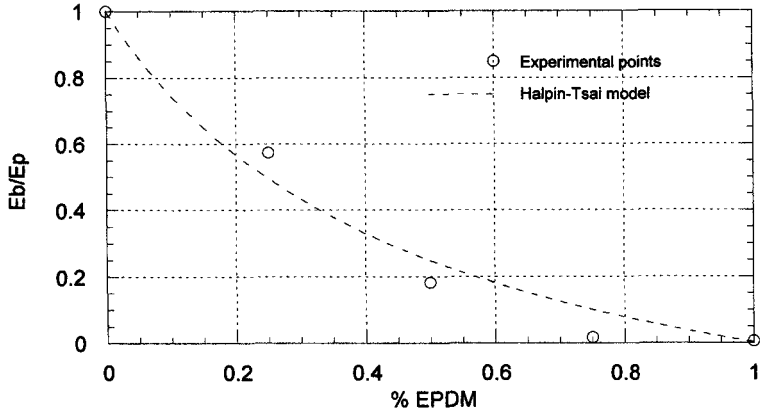

Fig. 4: Normalized Young's modulus as a function of EPDM content compared to Halpin Tsai model.

A non-linear regression has been applied to the experimental elastic modulus values to compute the model parameter A. The results of the model prediction and experimental data are well compare in Fig. 4.

In addition, the experimental values of the maximum stress have been analyzed in terms of the Halpin-Tsai model. In this case, the modeled of the tensile strength of the materials studied is giving by:

$$\sigma_b = \sigma_p \left(\frac{1 + A\eta\phi_r}{1 - \eta\phi_r} \right) \qquad (3)$$

where A is again a constant parameter depending on the aspect ratio of the dispersed phase and η is now given by:

$$\eta = \frac{\left(\sigma_r / \sigma_p\right) - 1}{\left(\sigma_r / \sigma_p\right) + A} \qquad (4)$$

The following symbols have been used in Equations 3 and 4:

σ_b is the maximum strength of the blend

σ_p is the maximum strength of polypropylene

σ_r is the maximum strength of EPDM

The results of the Halpin-Tsai model compared with the experimental results are reported in Fig. 5. A value of A=0.503 was obtained by non-linear regression. As this parameter is related to the aspect ratio of the dispersed phase, a value of the order of the unity, as in this case, indicates that there is not a dominant dimension in the dispersed phase. Then, a compact globular geometry is expected, opposite to the fibrous structure of reinforcing short fibers where very high values of A are obtained.

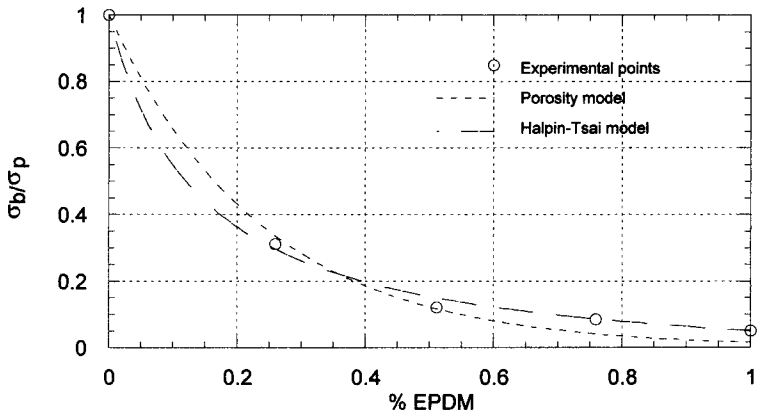

Fig. 5: Normalized tensile maximum strength as a function of EPDM content compared to Halpin-Tsai and porosity equations.

Moreover, also the so-called porosity model[23] has been applied to model the maximum stress of the blends. Following this model the strength is giving by the following expression:

$$\sigma_b / \sigma_p = exp(-\alpha \phi_r) \qquad (5)$$

where α is a factor related to the stress concentration factor introduced by the dispersed phase. A value of α = 4.2 has been calculated by regression analysis indicating that PP-EPDM blends constitutes a material with a reduced amplification of the stress. Modeling results are also shown in Fig. 5. Although the Halpin-Tsai model seems to fit better the experimental results, both models give a good representation of the mechanical behavior of the blends as a function of the rubber composition.

Flexural behavior

Stress-strain curves obtained in flexural tests are reported in Fig. 6 for all the compositions analyzed. The flexural mechanical properties of the PP-EPDM blends, computed from equation 1, are reported in Table 2.

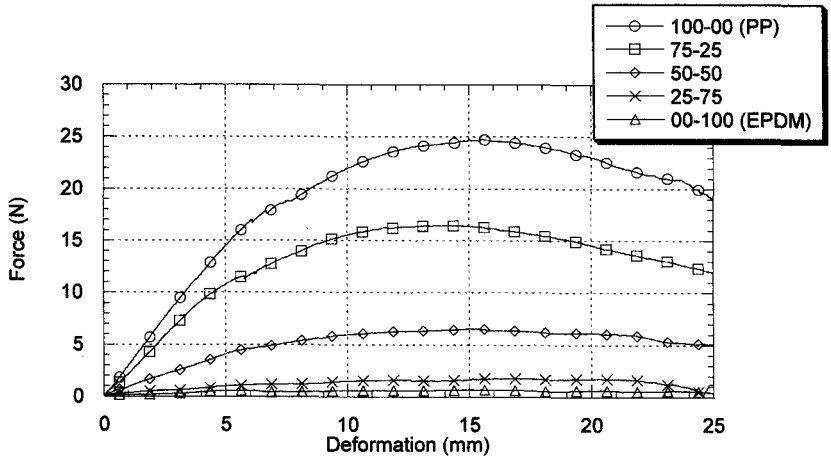

Fig. 6: Variation of flexural properties with the composition of the blend.

It can be concluded from these results that the flexural properties of the materials studied show a similar tendency than the tensile properties characterized by a gradual, but non-linear, increase of the modulus and strength with the PP content in the blend.

Table 2. Flexural properties of materials studied.

Blends PP–EPDM (%)	**Bending Modulus** (MPa)	**Max. Strength** (MPa)
100-00	1078	24.7
75-25	757	16.6
50-50	398	6.5
25-75	42	1.7
00-100	19	0.6

Impact resistance

Impact tests results can be directly related to the toughness of a material. The availability of these properties at different temperatures is very useful for the analysis of the performance of the materials studied at service conditions. The results of impact tests performed at two different temperatures are reported in Table 3.

Table 3. Impact properties of PP-EPDM blends.

Blends PP-EPDM (%)	**Max. Force** **25°C** (N)	**–30°C** (N)	**Impact Strength** **25°C** (KJ/m^2)	**–3°C** (KJ/m^2)
100-00	97	154	3.15	2.63
75-25	83	127	21.05	3.68
50-50	52	104	36.84	11.84
75-25	-	87	-	14.73
00-100	-	76	-	19.68

Experimental results have been used to compute the impact fracture energy given by the area under the force-strain curve measured during the test. The corrected impact strength (U) values were then computed using the following equation[24]:

$$U = U'\left(1 - \frac{U'}{4K_e}\right) \qquad (6)$$

where:

$$K_e = \frac{1}{2} m \upsilon_\circ^2 \tag{7}$$

and $\upsilon_\circ$ is giving by:

$$\upsilon_\circ = (2gh)^{1/2} \tag{8}$$

where g is the acceleration of the gravity, h is the height of fall, K_e is the kinetic energy of the falling mass and U' is the energy displayed by the machine. The impact strength results obtained are reported in Fig. 7 as a function of the blend composition and at the two temperatures used for the tests (25°C and –30°C). From these results, it is clear that there is a strong effect of the temperature on the impact strength of the EPDM and of its blends. On the other hand, the intrinsic fragility of the PP is not further reduced significatively at low temperatures. It can be then confirmed the high effectiveness of the EPDM as toughening agent of PP, although its effectiveness is reduced at low temperatures.

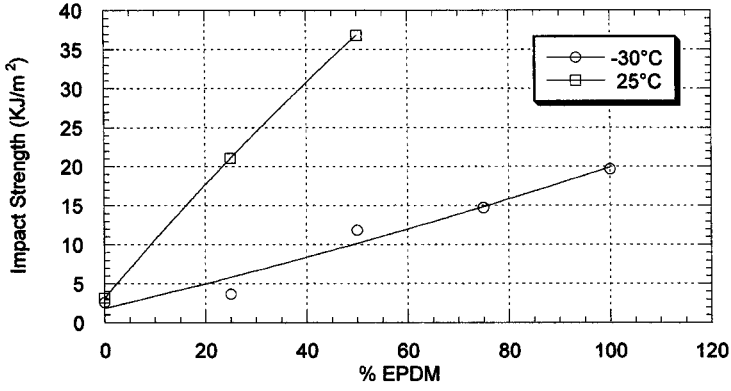

Fig 7: Effect of EPDM on the impact strength PP.

Morphological Study

It is evident that the processing behavior and the mechanical properties of the PP-EPDM blends studied are function of its phase partial immiscibility and distribution, which can be analyzed using conventional electron microscopy techniques. Micrographs of the impact fracture surfaces of compression molded specimens of three blend compositions analyzed, observed by SEM, are reported in Fig. 8-10. It can be shown that in the blend with 25% of EPDM (Fig. 8), the rubber form small particles dispersed in the form of droplets in the polypropylene matrix, which constitute the continuos phase. In blends with a higher rubber content (50%) (Fig. 9), both the rubber and the polypropylene are continuos, phase and their properties are then controlled by both components. At higher percentages of rubber in the blend (75%), the phase inversion has already occurred and the polypropylene form the dispersed phase in the rubbery matrix. At this composition, the rubber mainly determines the properties of the material.

The observed morphology is in agreement with the mechanical properties of the blends studied. The partial immiscibility of both polymers in the whole range of compositions determine a two phase system which properties are mainly ruled by the continuous phase constituted by the polymer present in higher quantity.

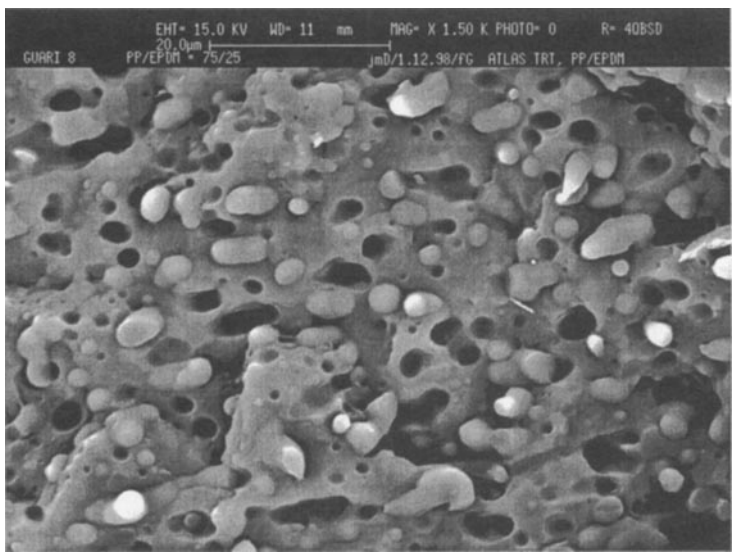

Fig. 8: Fracture surface of PP–EPDM (75-25) blend.

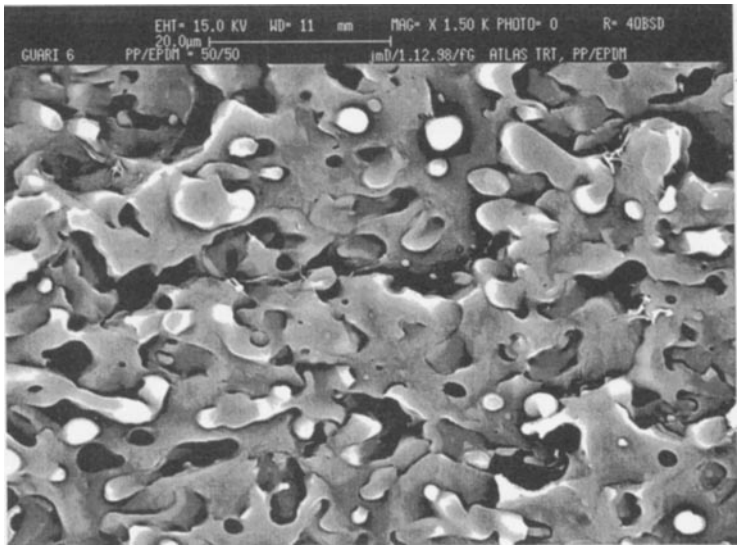

Fig. 9: Fracture surface of PP–EPDM (50-50) blend.

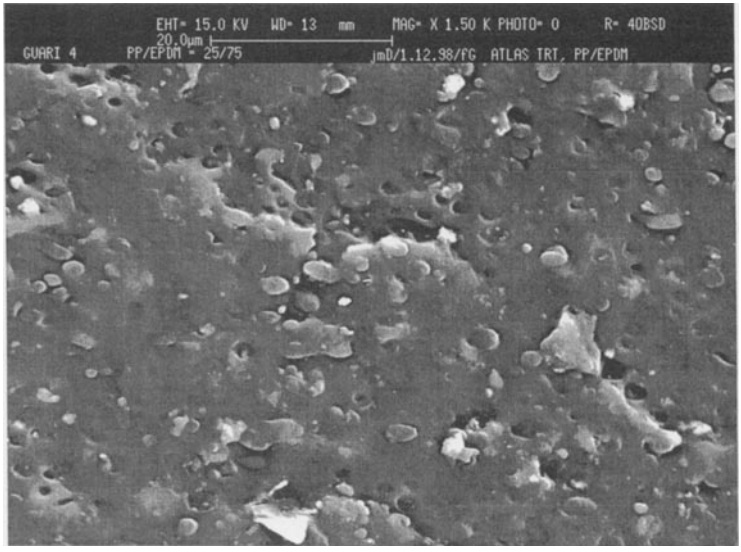

Fig. 10: Fracture surface of PP-EPDM (25-75) blend.

Conclusions

The processing behavior, mechanical properties and microscopic morphology of blends of PP-EPDM in the whole range of compositions have been analyzed in the first part of a complete study of the processing-structure-properties relationships of these materials of continuously increasing industrial interest.

A general processing behavior similar to that of PP has been observed in the blends with medium and low content of EPDM indicating that the same industrial thermoplastic molding processes used for neat PP can be adopted with evident economic advantages. In particular the blend with 25% of EPDM showed practically the same energy consumption during mixing than neat PP indicating that no extra processing costs are expected for this material.

Tensile and flexural properties of the blends show a significant reduction of the elastic modulus and strength of the blends as a function of rubber content, in benefit of an effective increase of the elongation at break. Halpin-Tsai and porosity models have been successfully applied to represent the mechanical behavior of the blends studied as a function of the rubber content. The computed parameters of the models applied confirmed the globular geometry of the dispersed phase (confirmed also by SEM analysis) and the reduced stress concentration factors in this kind of blends. Impact test results confirmed the effectiveness of EPDM as impact modifier of PP with a considerable improvement of the toughness of the blends in the whole range of compositions studied at low and room temperature.

The microscopic morphology of the blends confirmed the main conclusions obtained in the analysis of the processing and mechanical behavior of the blends. Two distinct phases are presented in the whole range of compositions with a phase inversion at about 50%. The main properties of the blends studied are mainly determined by the continuous phase, which is always the polymer with higher content. However, the 50%-50% blend resulted in two co-continuous phases. Thus, the properties are controlled by the morphology of the blend.

Further work is in progress to determine the rheological properties, environmental aging and the behavior as matrix of short fiber composites of the blends reported in this paper.

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