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Toughening of PA6/mEPDM Blends by two Methods of Compounding, Extruder and Internal Mixer: Rheological, Morphological and Mechanical Characterization

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Summary

Blends of polyamide 6 with metallocene rubber as dispersed phase and grafted rubber as compatibilizer were prepared by two methods of compounding, extruder and internal mixer. Rheological measurements and morphological analysis were made in order to study the influence of compounding. The ternary blends with the same maleic anhydride content displayed similar rheological behaviour. On the other hand, the developed morphology is related to the compounding process and blend formulation. The better particle size distribution is achieved in both methods of compounding for blends with 20 wt% of EPDM-g-MA. The addition of EPDM-g-MA improves the mechanical properties compared to blends without compatibilizer. The results confirm that the mechanical properties are more influenced by the compounding process than by the blend composition.

Introduction

Polyamides are defined as pseudoductile polymers because their high energy for craze initiation compared to the so-called brittle matrices. Pseudoductile matrices deform under a uniaxial tensile stress state mainly by shear yielding, whereas crazing is in general the deformation mechanism of brittle matrices. Nevertheless, polyamides become brittle in the presence of molding flaws, environmental abuse, poor design, or, more generally, in the presence of a stress concentrator that limits their industrial application.[1]

Blending is a well-known method for modifying polyamide properties. Most of the research and development works in polyamide-6 are directed to the improvement of properties like impact strength by blending with a properly functionalized elastomeric phase.[2-12] Blends of polyamides and unfunctionalized elastomers have low impact toughness because the rubber particles formed during melt blending are relatively

large.[13,14] A compatibilizer, generally the same elastomer functionalized with a reactive group such as maleic anhydride (MA), is used to improve the interfacial adhesion of the PA/elastomer blends.[15,16] Reactive compatibilizers, containing maleic anhydride, form a chemical linkage through the reaction of anhydride groups with the polyamide end groups. This reaction causes the graft copolymer which enhances the interfacial compatibility of immiscible polymer blends.[17] Maleic anhydride grafted ethylene-propylene elastomers, EPR-g-MA, are frequently used for toughening polyamides.[3, 10, 15, 18-19] Commercial products like these typically contain approximately 1% by weight of grafted maleic anhydride and give rise to a rubber particle population in nylon 6 matrix that is in a satisfactory size range for toughening.[19]

On the other hand, the addition of the compatibilizer provokes an increase in the viscosity of the blends due to an increase in interfacial adhesion as a result of in situ copolymer formation. The graft copolymer formed in situ by the reaction of the PA amine end groups with maleic anhydride in mEPR-g-MA acts as a compatibilizer, leading to a very fine dispersion of the polyamide phase in the EPDM matrix.[20-21] The result is a material with stable morphology and good interfacial adhesion. Similar behavior was observed in other polyamide blends when grafted rubbers were used as compatibilizers.[1,15,20]

The factors affecting the evolution of blend morphology during compounding are: (1) temperature, (2) residence time in an internal mixer or in a twin-screw extruder, (3) the intensity of mixing (rotor or screw speed in an internal mixer or twin-screw extruder respectively), (4) grafting degree (MA content in EPDM), (5) viscosity ratio, (6) elasticity ratio, and (7) interfacial tension.[22] The combination of these factors conditioned the final properties of the resulting material.

The mechanical behavior of rubber-toughened plastics depends on the morphology of the blend,[6,18] the characteristics of the rubber and matrix phases[16] and the nature of the interface between these phases.[3,6,16]

In most blends, the enhancement of material toughness is accompanied by a marked decrease of the tensile modulus and/or the yield stress, which limits seriously the applicability of these materials.[8,10,12,23,25] On the other hand, a better impact strength is achieved when the toughness is improved.[9-11,26]

This paper focus on the study of the influence of the compounding process on the microstructure and properties of PA6/mEPDM blends by using an internal mixer and a co-rotating twin-screw extruder. Uncompatibilized and compatibilized blends, using EPDM-g-MA have been studied. The present paper will show the relationships between compounding conditions in both extruder and internal mixer and the morphology and rheology of these blends. Also this paper will deal with the changes in tensile, impact properties and Vicat temperature relating to morphology and composition.

Experimental

Materials

Polyamide 6 (PA6), commercialized as Akulon F130C supplied by DSM, was used as the matrix phase. The dispersed phase was an ethylene-propylene-diene metallocene terpolymer, (mEPDM) commercialized as Nordel IP3722P and supplied by Dupont. An ethylene-propylene-diene copolymer grafted with maleic anhydride (EPDM-g-MA

Royaltuf 498 from Crompton), which contains 72.5 wt% ethylene, 0.95 wt% ENB and 1 wt % maleic anhydride grafted was used as a compatibilizer. An antioxidant Irganox B1171 (blend 1:1 of Irganox 1098 and Irgafos 168 from Ciba) was employed to diminish the effect of the temperature and compounding conditions in polyamide 6. This antioxidant was used to prepare a polyamide masterbatch, which was added in 0.2 wt% before blend preparation. The compositions of the studied blends are given in Table 1.

Table 1. Blends compositions in the extruder and in the internal mixer.

Blend	Composition (wt%)	Feed Port (TSE)/Stage (IM)	
	PA6/mEPDM/EPDM-g-MA	1	2
PA6-mEPDM(TSE)	80/20/0	mEPDM	PA6
PA6-g-EPDM-mEPDM(TSE)	80/10/10	mEPDM + EPDM-g-MA	PA6
PA6-g-EPDM(TSE)	80/0/20	EPDM-g-MA	PA6
PA6-mEPDM(IM)	80/20/0	PA6	mEPDM
PA6-g-EPDM-mEPDM(IM)	80/10/10	PA6	mEPDM + EPDM-g-MA
PA6-g-EPDM(IM)	80/0/20	PA6	EPDM-g-MA

Blends and test specimen preparation

Prior to the melting processing step, PA6 was dried at 80 ºC for 8 hours in an oven. The preliminary studies of the compounding process allow us to find the better operating conditions to prepare the blends in an intermeshing co-rotating twin-screw extruder (Leistritz 27 GL) and in an internal mixer (Haake PolyLab mixer Rheomix 3000p).
The blends obtained were dried (at 80 ºC for 8 hours) and then injection molded into standard tensile bars in a Margarite JSW110 injection molding machine, using a barrel temperature of 230-250 ºC and a mold temperature of 80 ºC.

Characterization

The flow properties of the blends and the apparent melt viscosity of the different components were determined using a Ceast Rheologic 5000 with a 30 mm L/D capillary die. The raw materials and the blends were dried before this test at 80 ºC for 24 hours in an oven. A Jeol-820 scanning electron microscope was used to research the rubber particle size and particle size distribution. The injection-molded specimens were broken cryogenically in liquid nitrogen and the elastomeric phase was extracted from the surface by etching with boiling xylene during at least 6 hours. After sputter coating with a thin film of gold, the specimens were examined. An accelerating voltage of 20 KV and a magnification range from 1.300x to 10.000x was used.
Notched Izod test were performed at temperatures between 90 ºC and -40 ºC on a Ceast Resil Impactor according to the ISO 180:2000 standard equipped with a thermal chamber. The average values were calculated from seven runs for each sample. Tensile properties were measured according to UNE-EN ISO 527-1 and 527-2 with an Instron Model 5500R60025. Modulus was determined at a crosshead rate of 1 mm/min while tensile strength and elongation at break were collected at 10 mm/min.

Vicat temperature was determined in an HDT-VICAT tester microprocessor (CEAST 6911.000) according to UNE-EN ISO 306, B50 N (50 °C/h heating rate).

Results and discussion

Determination of the compounding conditions

The morphology of immiscible polymer blends depends on the viscosity ratio and melt elasticity of the blend components. If the viscosities of the two phases are closely matched an optimum particle size of the dispersed phase will be achieved.[21-22] The crossing point of the viscosity of neat materials versus shear rate will determine the shear rate more appropriate for extruding the blends, because of the shear rate in reciprocal seconds could be expressed as the same numerical value as the screw revolution by minute (rpm).

The viscosity curves as a function of the shear rate at 230 ºC of the neat polymers was studied. At this temperature, which is the medium extrusion temperature, the crossing point takes place to approximately 145 rpm. Usually, this speed is the most appropriate for achieving the best morphology, but in order to confirm that this value was the best, three blends were made at three different shear rates (85, 145 and 205 rpm), all of them around the shear rate calculated by rheological measurements. The composition of the blends was fixed at 80 wt% of PA6, 10 wt% of mEPDM and 10 wt% of EPDMgMA and the experimental conditions were the same for all the blends.

The SEM microphotographs of cryogenically fractured surfaces of an injection-molded sample of the three ternary blends are presented in Figure 1. These microphotographs show the influence of the screw rate in the reached morphology. The three blends show a heterogeneous size distribution with two well defined populations of different sizes due to the presence of both kinds of elastomeric components. Nevertheless, the PA6-g-EPDM-mEPDM(205) blend has exhibited a larger and more heterogeneous dispersed phase as seen in Figure 1(C) because at this speed, the residence time is short, and it is difficult to achieve a good compatibilization. In conclusion, the most appropriate speed for developing these blends in the extruder is 145 rpm due to the results achieved with the morphology and the viscosity curves.

The internal mixer conditions were chosen meticulously in order to develop blends with similar properties to the extrusion blends. Mixer residence times and shear rates are crucial for developing desired morphologies in polymer blends. In order to determine the best conditions for an internal mixer, two blends with rotor speed of 50 and 80 rpm with 6 and 5 minutes respectively of residence time were produced for achieving the better compounding conditions. The raw material used as matrix phase and the masterbatch were added at the stage 1; after 150 seconds, the elastomeric component was added (stage 2). Once the mixing time was finished, the samples were quenched in cold water, like in the extrusion process, to prevent the degradation.

The SEM microphotographs of the ternary internal mixer blends, PA6-g-EPDM-mEPDM(IM50) and PA6-g-EPDM-mEPDM(IM80), are shown in Figure 1D and Figure 1E. The first exhibited a very broad size distribution for the dispersed phase. However, in the blend obtained at 80 rpm, the distribution was narrower, although there are few larger voids distributed along the sample.

Finally, the morphology analysis has showed that 80 rpm and 5 minutes of residence time are the most appropriate operating conditions for the internal mixer.
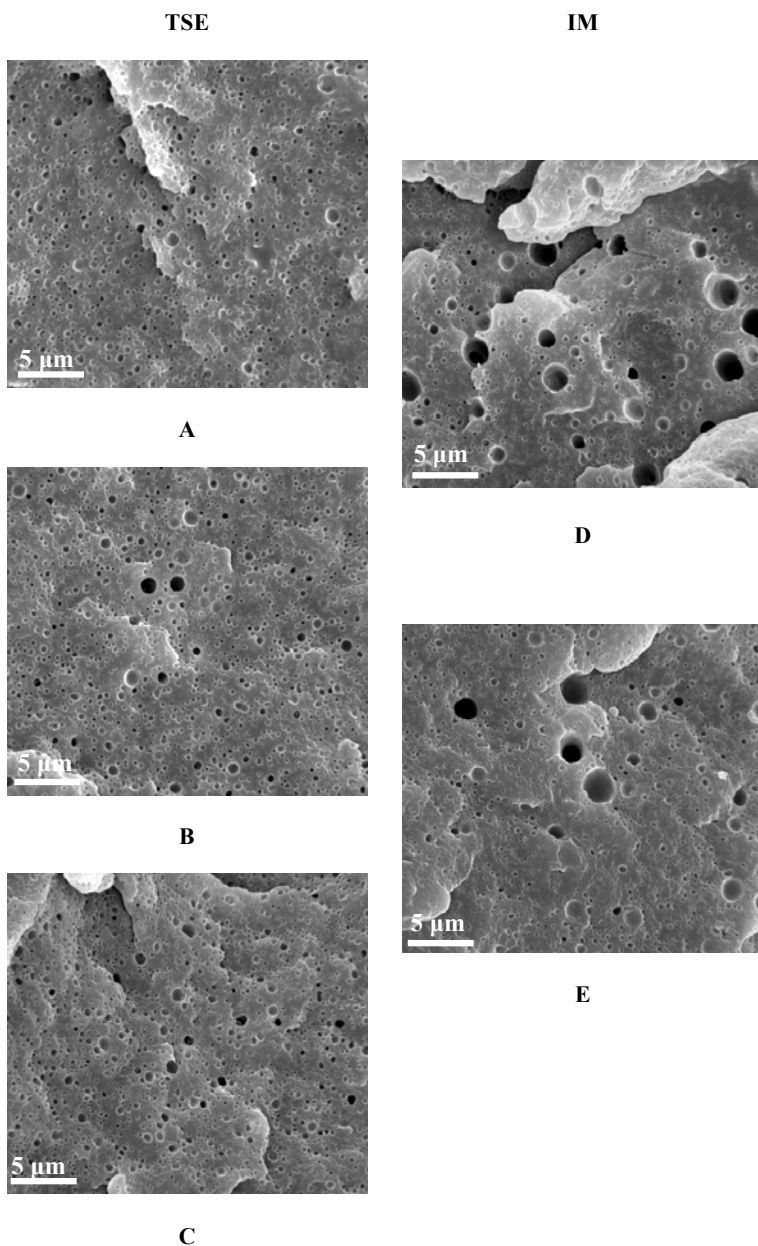
TSE   **IM**

Figure 1. SEM microphotographs of preliminary extruder blends (A) PA6-g-EPDM-mEPDM(85), (B) PA6-g-EPDM-mEPDM(145), (C) PA6-g-EPDM-mEPDM(205) and internal mixer blends (D) PA6-g-EPDM-mEPDM (IM50) and (E) PA6-g-EPDM-mEPDM (IM80).

Capillary rheometry

The viscosity curves as a function of the shear rate at 240 ºC for neat polyamide 6 and its blends compounded in the extruder and in the internal mixer are presented in

Figure 2. All blends showed a shear thinning character at the shear rate analyzed. Below a shear rate of 40 s^{-1}, the blends showed a higher value than the neat polyamide 6, while at higher shear rate values the viscosity of the compatibilized blends (PA6-g-EPDM-mEPDM (TSE and IM) and PA6-g-EPDM (TSE and IM)) are greater than the neat polyamide 6. The differences in the viscosity curves are due to the interfacial adhesion between the elastomeric phase and the thermoplastic matrix. This is a consequence of the graft copolymer formed in situ by the reaction of the PA6 amine end groups with maleic anhydride in EPDM-g-MA. The non compatibilized blends, PA6-mEPDM(TSE and IM), have shown similar viscosities although they have been processed by different methods, extruder and internal mixer respectively. The same behaviour is observed in the compatibilized blends with a 10 wt% of functionalized elastomeric component. Nevertheless, the binary blend with a 20 wt% of EPDM-g-MA, obtained in the internal mixer (PA6-g-EPDM(IM)) has shown a higher increase in the viscosity at low shear rates with respect to its equivalent blend compounded in the extruder (PA6-g-EPDM(TSE)). The higher viscosity of PA6-g-EPDM(IM) blend is a consequence of a better linkage between the matrix and the compatibilizer. This result would indicate that the internal mixer improves the interaction between the matrix and the dispersed phase compared to extruder when the blends are completely functionalized.
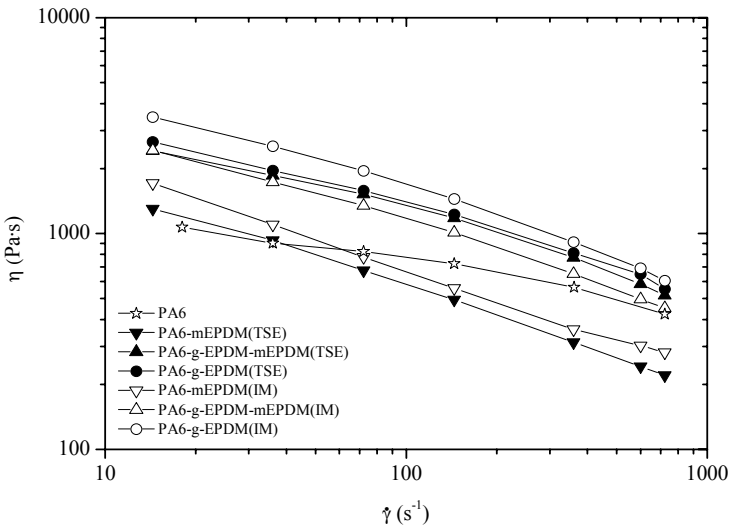

Figure 2. Rheological curves at 240 ºC of PA6 and its blends compounded in both extruder and internal mixer.

Morphology of the blends

Figure 3 shows the SEM microphotographs of the blends compounded in the extruder and in the internal mixer, on the other hand, Table 2 shows the maximum, minimum and mean of rubber particle size. As generally, an increment in the content of compatibilizer provokes a decrease in the size distribution of the dispersed phase.[15,16]

TSE
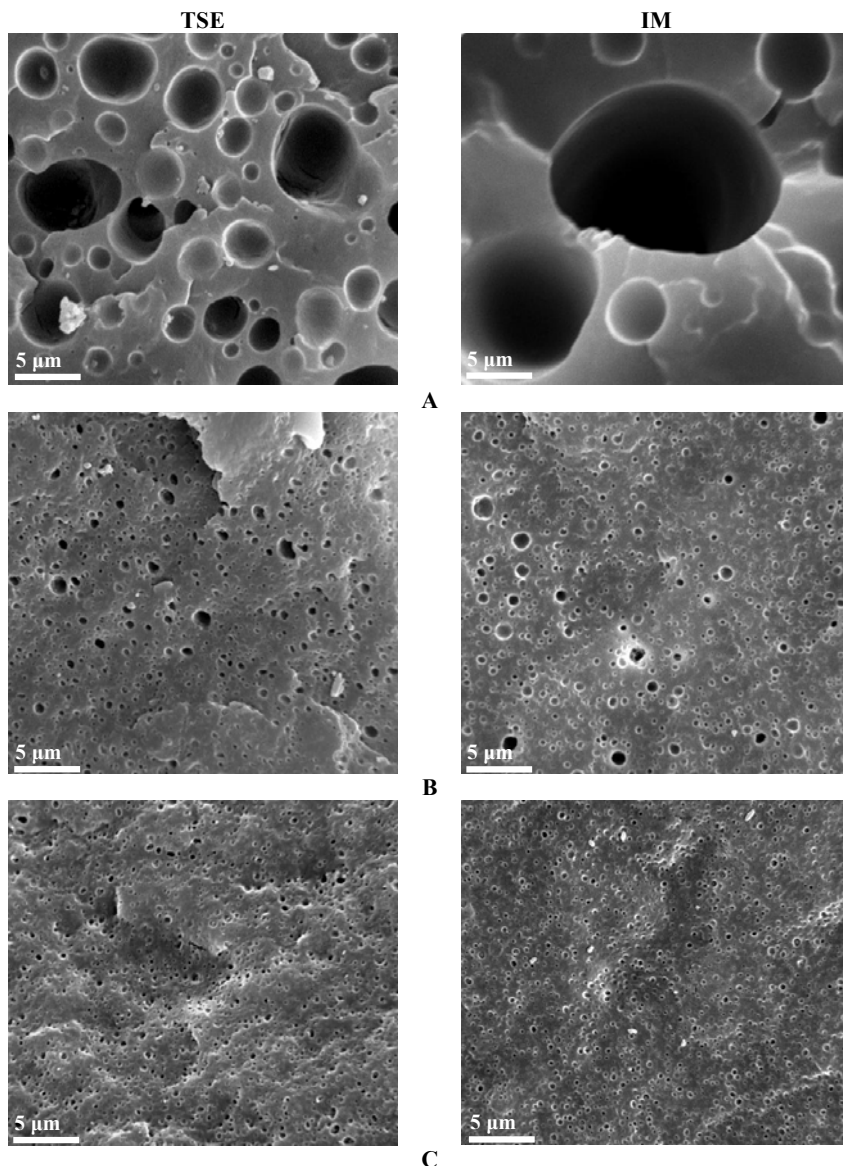
IM

A

B

C

Figure 3. SEM microphotographs of extruder blends (TSE) and internal mixer blends (IM) (A) PA6-mEPDM, (B) PA6-g-EPDM-mEPDM and (C) PA6-g-EPDM.

The microphotograph of the compatibilized PA6-g-EPDM-mEPDM(TSE) blend shows two different population of particle size. In this blend, a decrease in the size distribution has occurred with respect to PA6-mEPDM(TSE) blend due to the increment in the viscosity and because of the presence of elastomeric functionalized with maleic anhydride. This is due to the graft chains formed by reaction of amine groups of the polyamide with maleic anhydride of the EPDM-g-MA material. This can significantly increase the melt viscosity of the blend which in turn leads to higher

shear stresses that tend to make the domain size of the non-maleated mEPDM elastomer smaller.

Table 2. Rubber particle size distribution.

Material	Maximum (μm)	Minimum (μm)	Mean (μm)
PA6-mEPDM(TSE)	9.18	0.08	2.05
PA6-g-EPDM-mEPDM(TSE)	1.44	0.08	0.36
PA6-g-EPDM(TSE)	0.92	0.03	0.20
PA6-mEPDM(IM)	15.00	0.10	3.10
PA6-g-EPDM-mEPDM(IM)	1.50	0.09	0.04
PA6-g-EPDM(IM)	0.80	0.02	0.16

If the blends are completely functionalized (20 wt% of EPDM-g-MA), the morphology leads to a homogeneous distribution with a lower particle size than the other blends. However the blends compounded in the extruder show a more homogeneous particle size distribution, while in the internal mixer two different populations of particles have appeared. This behaviour is related to the higher viscosity achieved in the blends produced in the internal mixer, as seen by capillary rheometry, a higher compatibilization, leads to a smaller particles size.

The comparison between the blends obtained with the two compounding methods, shows that the extruder leads to a better distribution of the dispersed phase on the non compatibilized (PA6-mEPDM(TSE) and PA6-mEPDM(IM)) blends. Nevertheless, in both compounding processes the presence of 10 wt% of compatibilizer agent (EPDM-g-MA) leads to a two population of particles due to the presence of two different elastomeric components.

Tensile properties

The tensile properties of the blends including modulus (E), stress at break (σ_b) and elongation at break (ε_b) are presented in Table 3. The Young modulus of a thermoplastic blend depends on the volume fraction of its constituents, on the rigidity of the phases and also on the particle size of the dispersed phase.[23] Therefore, the addition of soft particles like mEPDM and EPDM-g-MA causes a decrease of the modulus of the blends studied as shown in Table 2.

The stress at break (σ_b), the elongation at break (ε_b) and also de Vicat temperature of a thermoplastic blend decreased with the addition of elastomeric phase compared to neat PA6.[8] There are two primary factors involved in this reduction.[2] The first is the rubber particle size, because larger particles lead to an unstable flow which causes premature rupture of the specimen. The second is due to a "network" effect induced by the presence of the compatibilizer, which causes the linkage between the elastomeric and the thermoplastic phases. These two causes can work either separately or jointly. The equilibrium among these two factors would cause the increase in the stress and elongation at break and in the Vicat temperature but this would provoke the lost of any other property such as modulus. According to that, the non-functionalized blends have a lower elongation at break, stress at break and a Vicat temperature than PA6 due to the bigger particle size distribution of the elastomeric phase. The addition of 10 wt% of EPDM-g-MA causes an increase in these properties because of the

reduction in the rubber particle size as seen in SEM microphotographs. Nevertheless, the addition of 20 wt% of functionalized elastomeric phase does not cause the same effect in both compounding processes. That is to say, the blend compounded in the extruder (PA6-g-EPDM(TSE)) shows an increase in these properties, while the blend compounded in the internal mixer (PA6-g-EPDM(IM)) shows a decrease. Vicat temperature achieves a lower increase compared to PA6-g-EPDM(TSE). This is because of the higher viscosity of this blend that implies a greater interfacial adhesion, which renders the system less capable of flowing.

Impact behavior

The notched Izod impact strength for blends compounded in the extruder machine at room temperature (25 ºC) and low temperature (-30 ºC) are shown in Table 3. As expected the notched Izod impact strength increases with the addition of functionalized elastomeric phase at both temperatures. This enhancement is mainly due to the achieve morphology in blends tested at room temperature (25 ºC) and to the interfacial adhesion at low temperatures (-30 ºC).[2,24] On the other hand, the rubber particle size distribution is also a critical factor for the enhancement of the impact strength; is generally accepted that an increase of the Izod impact strength of a thermoplastic PA6 blend is achieved when the rubber particle size is between 0.2 and 1 μm.[1,3,10] The lower level is normally due to the fact that the particles are too small to cavitate, while the upper level is associated with the critical interparticle distance.

Table 3. Tensile, mechanical and Vicat properties of blends compounded in both extruder and internal mixer.

Material	Vicat (ºC)	E (MPa)	σ_b (MPa)	ε_b (%)	Notched Izod Impact Strength (KJ/m²)	
					25 ºC	-30 ºC
PA6	195.8 ± 0.4	2663 ± 69	67.3 ± 11.0	240.7 ± 4.0	5.1 ± 0.4	3.5 ± 0.8
PA6-mEPDM(TSE)	148.7 ± 2.3	1453 ± 35	36.3 ± 1.0	99.5 ± 7.0	6.5 ± 0.7	3.7 ± 0.2
PA6-g-EPDM-mEPDM(TSE)	158.9 ± 0.7	1439 ± 4	46.0 ± 1.0	221.4 ± 12.0	49.6 ± 1.2	15.2 ± 0.5
PA6-g-EPDM(TSE)	173.9 ± 2.1	1329 ± 14	50.0 ± 2.0	257.6 ± 24.0	54.9 ± 2.4	17.2 ± 0.8
PA6-mEPDM(IM)	146.8 ± 3.3	1706 ± 19	33.2 ± 2.0	59.2 ± 2.0	5.0 ± 0.4	3.4 ± 0.8
PA6-g-EPDM-mEPDM(IM)	152.7 ± 0.8	1604 ± 7	48.2 ± 2.0	226.4 ± 20.0	42.0 ± 0.9	17.3 ± 2.1
PA6-g-EPDM(IM)	161.4 ± 0.7	1420 ± 13	40.4 ± 1.0	205.6 ± 3.0	37.4 ± 1.1	22.9 ± 3.1

The blend compounded without functionalized elastomeric phase (PA6-mEPDM (TSE)) has a notched Izod impact strength similar to PA6. At room temperature, this behavior is due to the coarse rubber particle size obtained. The absence of polar groups in the rubber hinders the linkage between the PA6 and the elastomeric phase and, consequently, no enhancement in the impact strength at low temperatures can be produced. However, when the interfacial chemical linkage is reached with functionalized elastomers (PA6-g-EPDM-mEPDM(TSE) and PA6-g-EPDM(TSE) blends) an increase in the notched Izod impact strength is achieved at both temperatures studied. The presence of only one type of elastomeric phase, i.e., EPDM-g-MA, causes a lower interfacial tension between the thermoplastic and the elastomeric phases. This removes the coalescence of the rubber phase by steric hindrance and provokes a narrower and homogenous elastomeric particle size

distribution of the elastomeric phase as seen by SEM and an enhancement in the notched Izod impact strength at room temperature.

The notched Izod impact strength at low temperature (-30 ºC) for the extruded blends, is similar for both functionalized blends in agreement with the results obtained in capillary rheometry. At that temperature, the main factor that affects the impact strength is the interfacial adhesion promoted by the reaction between the MA groups present in the elastomeric phase with the amine end groups of the polyamide 6. The slight increase of these parameters for the blend with 20 wt% of EPDM-g-MA could be due to Van der Waals bonds between both phases of the blend because these bonds provide the enough adhesion for improving the impact strength.[16]

The blends compounded in the internal mixer show a similar trend that those observed in the blends compounded in the extruder with the exception of the behavior of the PA6-g-EPDM(IM) blend. The SEM microphotographs discussed above for this blend, showed a slight decrease in the rubber particle size, with a portion of them under the critical lower particle size. Consequently, this leads to a decrease of the Izod impact strength at room temperature because the particles, under the lower level, have not the ability of improve the impact strength of the polyamide 6. A high increase is reached in the impact strength at low temperature (-30 ºC) in the PA6-g-EPDM(IM) due to a greater interfacial adhesion as seen by capillary rheometry.

Conclusions

The addition of an elastomeric component to the PA6 through different compounding methods, i.e., extruder and internal mixer, leads to similar rheological materials except when the elastomeric phase is completely functionalized (PA6-g-EPDM(TSE and IM)). As it is well known, the blends develop different morphologies relate to the compounded process. Thus, the morphology of the non compatibilized blends shows great particles of the elastomeric phase, due to the absence of linkage between PA6 and mEPDM. On the other hand, the greatest viscosity of the PA6-g-EPDM(IM) blend leads to a particle size distribution slightly smaller than those that are in the PA6-g-EPDM(TSE) blend compounded in the extruder.

The compatibilized blends have shown the better Izod impact strength than non-compatibilized blends while the trend in the modulus was the opposite. In general, the PA6-g-EPDM(TSE) blend, made in the extruder, is the one that has the better balanced mechanical properties. In the internal mixer, the better balanced properties were achieved in the blend with only 10 wt% of EPDM-g-MA, although the blend with 20 wt% of EPDM-g-MA found the narrowest and homogeneous elastomeric particle size.

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