J Mater Sci (2008) 43:4443–4449
DOI 10.1007/s10853-008-2661-7

Effect of the processing method on the mechanical properties and morphology of compatibilized PA6/LDPE blends

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Received: 19 January 2008 / Accepted: 15 April 2008 / Published online: 29 April 2008

Abstract In this work, the effect of the processing method on the mechanical properties and morphology of compatibilized PA6/LDPE blends was investigated. The blends were prepared by two processing methods: Injection and Extrusion followed by Injection. The compatibilizers used were polyethylene grafted with acrylic acid (PEgAA) and polyethylene grafted with maleic anhydride (PEgMA). The results showed that in both processing methods the impact strength and elongation at break of the compatibilized blends were greater than those of the uncompatibilized ones. For the blends prepared by injection, the impact strength of PA6/PEgMA/LDPE blend was greater than that of PA6/PEgAA/LDPE blend. For the blends prepared by extrusion followed by injection, the impact strength of the PA6/PEgAA/LDPE blend was greater than that of PA6/PEgMA/LDPE blend. SEM analysis showed that the morphology of the PA6/PEgAA/LDPE blend prepared by extrusion followed by injection was more stable than that of the same blend prepared only by injection.

Introduction

Mixing two or more polymers (Polymer Blends) is an excellent way for developing new materials with good properties and low cost, when compared with the synthesis of new polymers [1]. Blends of Polyamide 6 (PA6) and Polyolefins (POs) combine the thermo-mechanical properties of PA6 with the easy processability and low cost of PE. However, like most of the polymer blends, these blends are immiscible due to chemical incompatibility between the components. PA6 has polar groups while POs have non-polar groups. Diverging polarities generally produce immiscibility [2]. The immiscible blends are characterized by high interfacial tension, lack of adhesion between PA6 and POs phases, and unstable morphology leading to poor mechanical properties [3–6]. One way to overcome the immiscibility problem is through reactive compatibilization where a compatibilizer, which may be a block or graft copolymer, is added to the immiscible blend, reacting chemically with one phase and interacting physically with the other, forming a copolymer in situ at the interface [7, 8]. Many works on PA6/POs blends have been reported in the literature. Dagli et al. [9] described a study on the reactive compatibilization of Polyamide 6 (PA6) and Polypropylene (PP) blends through an acrylic acid grafted PP (PPgAA). They concluded that the carboxyl groups of PPgAA can react with the amino end groups of PA6 forming either amide groups or anhydride groups. Mélo and Canevarolo [10] investigated the in-line optical detection in the transient state of extrusion polymer blending (PA6 and PPgAA) and reactive processing. The optical method confirmed the reactions between the polymers. Piglowski et al. [11] studied the crystallization of PA6/PP blends compatibilized with a modified PA6. They concluded that the rates of crystallization of polymers are reduced in modified blends when compared to unmodified ones. Sacchi et al. [12] studied the morphology of isotactic PP-polyamide 66 blends and their mechanical properties. PPgMA was used as compatibilizer. According to them the presence of PPgMA significantly influences the morphology of the blends inducing finer dispersion and promoting interfacial adhesion, improving the mechanical properties. La Mantia and Mongiovi [13] studied

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the effect of thermo-mechanical degradation of uncompatibilized and compatibilized PA6/PP blends. PPgAA and PPgMA were used as compatibilizers. They concluded that the degradation of the blends depends mostly on the type of functional group of PP. Tedesco et al. [14] investigated the effects of PPgMA and PPGMA as compatibilizing agents on the morphological, mechanical, and thermal properties of PA6/PP blends. The results showed that the compatibilizing effect of PPgMA for the PP/PA6 blends is more effective than the PPGMA. In previous work of the present authors [15], the effect of different polypropylenes on the mechanical properties and morphology of PA6/PP blends was investigated. PPgAA and PPgMA were used as compatibilizers. The results showed that PPgMA was more effective than PPgAA and there was no influence of PP MFI on the mechanical properties of uncompatibilized and compatibilized blends. Valenza et al. [16] investigated the effect of PE functionalized with methacrylic acid derivatives on the structure of PA6 and Linear Low Density Polyethylene (LLDPE) blends. The results indicated that the functional groups grafted in the polyethylene chains induce compatibilization phenomena in the blends with respect to blends made with non-functionalized polyethylene. Scaffaro et al. [17] studied the reactive compatibilization of PA6 and Low Density Polyethylene (LDPE) blends with an ethylene-acrylic acid copolymer (EAA) and the effect of the addition into PA6/LDPE/EAA blends of a low molar mass bis-oxazoline (PBO) as the fourth component. According to them, the addition of PBO as the fourth component improves considerably the compatibility of PA6/LDPE Blends. Jiang et al. [18] investigated the effectiveness of polyethylene grafted with maleic anhydride (PEgMA) on PA6/LDPE blends and compared it to that of EAA. The results showed that PEgMA is more effective than EAA copolymers. Yordanov and Minkova [19] investigated the effect of the addition of an acrylic acid functionalized polyethylene (PEgAA) on the Vickers microhardness and thermal stability of PA6/LDPE crystalline blends with different composition and molar mass. According to them, the microhardness of compatibilized blend is lower than that of uncompatibilized ones. The molar mass of LDPE almost does not influence on the hardness values. The thermal stability of compatibilized blends increases due to the strong intermolecular interactions between PA6 and PEgAA and the better dispersion and smaller particle size. Chiono et al. [20] studied the behavior of an ethylene-glycidylmethacrylate (EGMA) copolymer as a compatibilizer for PA6LDPE blends and compared its effectiveness with that of EAA and PEgMA compatibilizers. They concluded that the efficiency of EGMA was comparable to that of EAA copolymers and lower than that of PEgMA. Minkova et al. [21] measured the interfacial tension of uncompatibilized and compatibilized LDPE/PA6 blends by the breaking thread method. The authors evaluated quantitatively the compatibilizing efficiency of PEgAA and maleic anhydride functionalized SEBS toward the blends. They concluded that the addition of the compatibilizers to the uncompatibilized blend reduces significantly the interfacial tension. The aim of this work is to investigate the effect of the processing method (Injection and Extrusion followed by Injection) on the mechanical properties and morphology of compatibilized PA6/LDPE blends. The compatibilizers used were PEgAA and PEgMA, which are two of the most used compatibilizers for PA6/LDPE blends.

Experimental

Materials

Polyamide 6 C216 Natural (PA6) was supplied by Rhodia, Low Density Polyethylene (LDPE) PB 208 (MFI = 22 g/10 min) was supplied by Braskem, High Density Polyethylene grafted with 6% of acrylic acid (MFI = 5 g/10 min) Polybond 1009 (PEgAA) and High Density Polyethylene grafted with 1% of maleic anhydride (MFI = 5 g/10 min) Polybond 3009 (PEgMA) were supplied by Crompton. PA6, PEgAA, and PEgMA were dried under vacuum at 80 °C for 24 h.

Methods

Torque rheometry

Torque rheometry analysis was carried out in an intensive batch mixer Rheomix 600, equipped with roller blades, attached to a Haake System 90, at 240 °C and 50 rpm, for 20 min under air atmosphere. For PA6/LDPE blends the composition was 80/20 (wt%). For PA6/Compatibilizer/LDPE blends the concentration of PA6 was kept fixed at 80 (wt%) and the concentration of the compatibilizers varied from 5 to 20 (wt%). The compatibilizers were added to PA6/LDPE blend after 5 min when PA6 and LDPE were already melt-mixed.

Blends preparation

The blends were prepared by two processing methods: Injection and Extrusion followed by injection. In the first one, after being dry mixed the blends were injection molded at 240 °C using a Fluidmec H 30/40 Injector. In the second one, after being dry-mixed, the blends were melt-mixed in an intermeshing counter-rotating twin-screw extruder, attached to a Haake System 90, at 240 °C in all zones and screw speed of 50 rpm. The obtained material was pelettized, dried under vacuum at 80 °C for 24 h, and injection molded at 240 °C in a Fluidmec H 30/40 Injector.

Based on the data obtained from torque rheometry analysis, the following composition was used: 80/20 (wt%) for PA6/LDPE blends and 80/10/10 (wt%) for PA6/Compatibilizer/LDPE blends.

Samples preparation

Samples for Tensile and Izod Impact Strength tests were obtained by injection molding at 240 °C using a Fluidmec H 30/40 Injector.

Mechanical properties

Tensile strength tests were carried out in an Universal Testing Machine, LR 10KN, of Lloyd Instruments, according to ASTM-D 638 at a crosshead speed of 50 mm/min. Izod impact strength tests were performed according to ASTM-D 256 in notched samples at room temperature using a CEAST RESIL 5,5 equipment. The results reported are the average of 10 tests.

Scanning electron microscopy (SEM)

For the morphology analysis, fracture surfaces of the samples subjected to impact strength tests were coated with gold using a Sputter Coater model BAL-TEC SCD 050 and analyzed by SEM using a JEOL JSM—6360 Digital Scanning Electron Microscope. The voltage used in the filament was 8 kV.

Results and discussion

Torque rheometry

Figure 1 shows the torque rheometry curves of the neat polymers and PA6/LDPE blend (at 240 °C, 50 rpm, and air atmosphere). It may be observed that the torque of PA6 and LDPE (MFI = 22 g/10 min) is similar, indicating that they have almost the same viscosity. The torques of PPgAA and PEgMA are also similar, as they have the same MFI (5 g/10 min). There is almost no difference between the torques of PA6 and PA6/LDPE blend. This was already expected, since PA6 and LDPE have similar viscosities.

Figure 2 shows the torque rheometry curves of PA6/compatibilizer/LDPE blends containing 0–20 (wt%) of compatibilizer. The compatibilizers were added to PA6/LDPE blends after 5 min (as indicated by an arrow), when PA6 and LDPE were already melt-mixed. Figure 2a shows the torque rheometry curves of the blends compatibilized with PEgAA. It may be observed that the torque of the compatibilized blends is greater than that of the uncompatibilized one, which is an

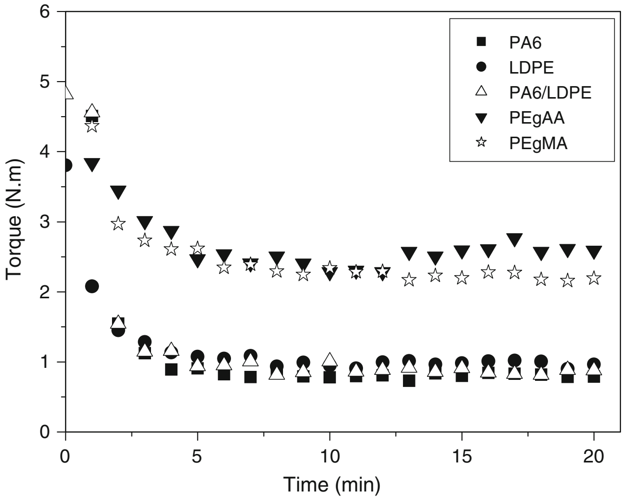

Fig. 1 Torque rheometry curves of neat polymers and PA6/LDPE (80/20) blend

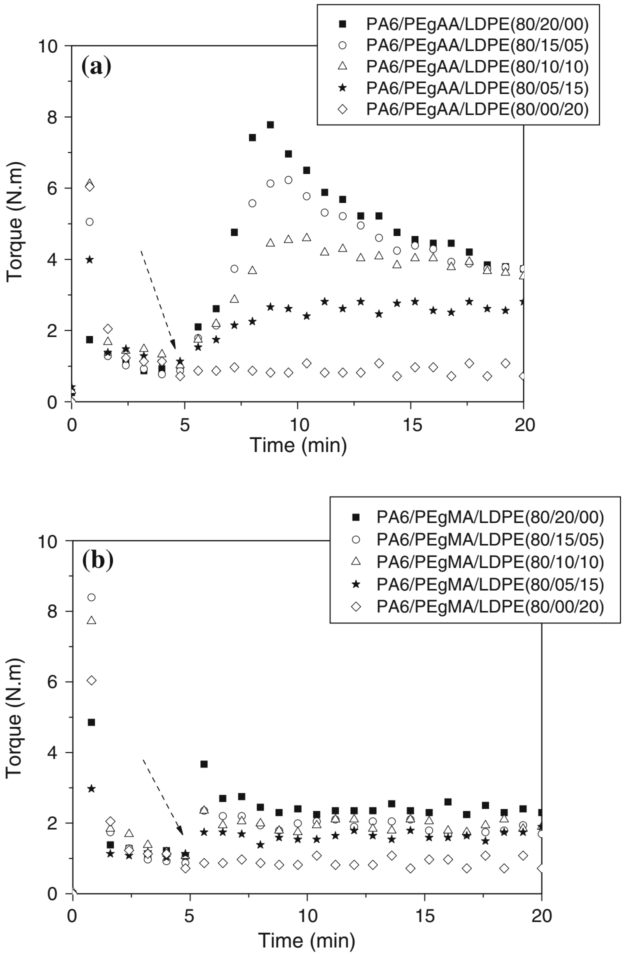

Fig. 2 Torque rheometry curves of PA6/compatibilizer/LDPE blends containing 0–20 (wt%) of: (**a**) PEgAA and (**b**) PEgMA

evidence that reactive compatibilization has occurred. Increasing the PEgAA content, the torque of the blends also increases. However, after some time, approximately 5 min after the addition of PEgAA to PA6/LDPE blend, the torque of the blends containing 10, 15, and 20 (wt%) of PEgAA starts to decrease. According to Filippi et al. [22] and Meier-Haack et al. [23], the carboxyl groups of PEgAA react with the amino end groups of PA6 forming an amide group and resulting in an in situ copolymer formation at the interface. This reaction involves the evolution of water as byproduct. This water leads to a hydrolytic degradation of PA6 by chain scission, reducing its molecular weight. The greater is the PEgAA content the greater is the degradation. Figure 2b shows the torque rheometry curves of the blends compatibilized with PEgMA. It may be observed that the torque of the compatibilized blends is greater than that of the uncompatibilized one, which is an evidence that reactive compatibilization has occurred. According to Jiang et al. [18], Roeder et al. [24], and Bassani et al. [25], the anhydride groups of PEgMA may react with the amino end groups of PA6 forming an imide group and resulting in in situ copolymer formation at the interface. As occurs with the reaction between the carboxyl groups of PEgAA and the amino end groups of PA6, the reaction between the anhydride groups of PEgMA and the amino end groups of PA6 also involves the evolution of water as byproduct [25]. However, almost no degradation of the blends is observed. An explanation for this is that PEgAA has 6% (wt) of acrylic acid content while PEgMA has only 1% (wt) of maleic anhydride content. The torque of the blends compatibilized with PEgAA is greater than that of the blends compatibilized with PEgMA. Figure 3 shows the torque rheometry curves of the blends PA6/PEgAA/LDPE and PA6/PEgMA/LDPE containing 10% of PEgAA and 10% of PegMA, respectively. It may be observed through the slope of the curves (indicated by an arrow) that anhydride groups of PEgMA react more rapidly with the amino end groups of PA6 than the carboxyl groups of PEgAA. It may also be observed that the reaction between the amino end groups of PA6 and the anhydride groups of PEgMA takes less than one minute for completion while the reaction between the amino end groups of PA6 and the carboxyl groups of PEgAA takes almost 4 min.

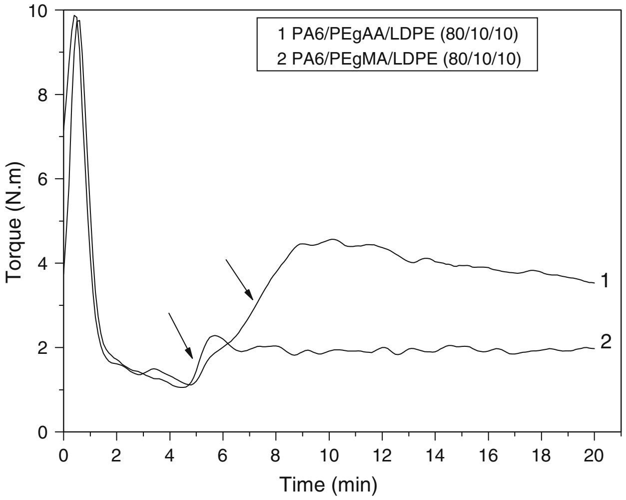

Fig. 3 Torque rheometry curves of PA6/PEgAA/LDPE and PA6/PEgMA/LDPE blends containing 10% of PEgAA and 10% of PegMA, respectively

Mechanical properties and morphology

Table 1 shows the mechanical properties of the blends prepared only by injection. It may be observed that the modulus and tensile strength of the compatibilized blends are similar. The impact strength and elongation at break of the compatibilized blends were greater than those of the uncompatibilized blend, indicating that reactive compatibilization has occurred. The impact strength of the blend compatibilized with PEgMA was greater than that of the blend compatibilized with PEgAA. Figure 4 shows the SEM micrographs of the blends prepared by injection. Figure 4a shows the micrograph of PA6/LDPE blend. It may be observed that this blend is characterized by high LDPE particles average size and poor adhesion between PA6 and LDPE phases, since many LDPE particles were pulled out from PA6 matrix. When PEgAA was added to PA6/LDPE blend (Fig. 4b), there is a considerable decrease in the LDPE disperse phase particles average size and an improvement in the adhesion between PA6 and LDPE phases. However, pull-out of many LDPE particles from PA6 matrix is still observed. When PEgMA was added to PA6/LDPE blend (Fig. 4c), there was a great decrease in the LDPE particles average size and a substantial improvement in the adhesion between PA6 and LDPE phases. No pull-out of LDPE particles was observed. Table 2 shows the mechanical properties of the blends prepared by extrusion followed by Injection. It may be observed that the modulus and the tensile strength of the compatibilized blends are similar. Like the blends prepared only by injection, the impact strength and elongation at break of the compatibilized blends were greater than those of the uncompatibilized blend. The impact strength of PA6/LDPE blend compatibilized with PEgAA was greater

Table 1 Mechanical properties of the blends prepared by injection

Material	E (Gpa)	TS (MPa)	IS (J/m)	ε (%)
PA6	1.80 ± 0.13	49 ± 9	184 ± 24	172 ± 72
PA6/LDPE (80/20)	0.67 ± 0.02	23 ± 4	106 ± 3	61 ± 26
PA6/PEgAA/LDPE (80/10/10)	0.75 ± 0.04	42 ± 1	146 ± 15	219 ± 17
PA6/PEgMA/LDPE (80/10/10)	0.80 ± 0.04	43 ± 3	319 ± 5	233 ± 40

E = Young modulus; TS = Tensile strength; IS = Impact strength; ε = Elongation at break

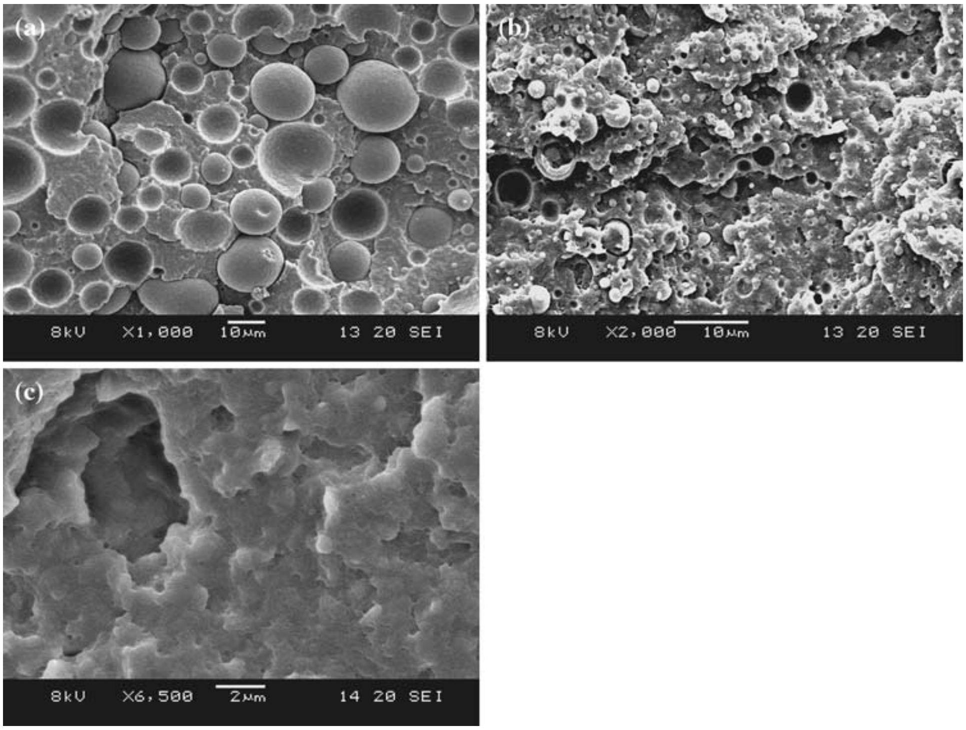

Fig. 4 SEM micrographs of the blends prepared by injection: (**a**) PA6/LDPE (80/20); (**b**) PA6/PEgAA/LDPE (80/10/10); and (**c**) PA6/PEgMA/LDPE (80/10/10)

Table 2 Mechanical properties of the blends prepared by extrusion followed by injection

Material	E (Gpa)	TS (MPa)	IS (J/m)	ε (%)
PA6	1.78 ± 0.10	43 ± 2	73 ± 5	24 ± 7
PA6/LDPE (80/20)	0.96 ± 0.10	30 ± 2	67 ± 4	100 ± 53
PA6/PEgAA/LDPE (80/10/10)	1.26 ± 0.17	33 ± 3	346 ± 24	117 ± 32
PA6/PEgMA/LDPE (80/10/10)	1.38 ± 0.12	32 ± 2	160 ± 15	102 ± 76

E = Young modulus; TS = Tensile strength; IS = Impact strength; ε = Elongation at break

than that of the blend compatibilized with PEgMA. This may be explained by analyzing the morphology. Figure 5 shows the SEM micrographs of the blends prepared by extrusion followed by injection. Figure 5a shows the micrograph of PA6/LDPE blend. Like the PA6/LDPE blend prepared only by injection, this blend is characterized by high LDPE particles average size and lack of adhesion between PA6 and LDPE phases. When PEgAA and PEgMA compatibilizers were added to PA6/LDPE blend (Fig. 5b and c, respectively) there was a great decrease in the disperse phase particles average size and a substantial improvement in the adhesion between PA6 and LDPE phases. It may be observed from Tables 1 and 2 that the impact strength of PA6/PEgAA/LDPE blend prepared by extrusion followed by injection is much greater than that of the same blend prepared only by injection. A possible explanation is that, for the PA6/PEgAA/LDPE blend prepared by extrusion followed by injection, there is sufficient time for the completion of the reactions between the carboxyl groups of PEgAA and the amino end groups of PA6, resulting in a more stable morphology and, hence, increasing the impact strength. The impact strength of PA6/PEgMA/LDPE blend prepared only by injection was greater than that of the same blend prepared by extrusion followed by injection. A possible explanation is that, for the PA6/PEgMA/LDPE blend prepared by injection, the processing time is sufficient for the completion of the reactions between the anhydride groups of PEgMA and the amino end groups of PA6. As explained before (Fig. 3), the reactions between the anhydride groups with the amino end groups of PA6 are more rapid than the reactions between the carboxyl groups of PEgAA and the amino end groups of PA6. The reduction in the impact strength of the PA6/PEgMA/LDPE blend prepared by extrusion followed by injection may be due to degradation of the blend.

Conclusions

In this work the effect of the processing method on the mechanical properties and morphology of compatibilized PA6/LDPE blends was investigated. Torque rheometry analysis shows that there is an increase in the torque of PA6/LDPE blends when PEgAA and PEgAA are added. On increasing the PEgAA and PEgMA content, the torque also increases. For the blend compatibilized with PEgAA, degradation is observed after some time. The greater is the PEgAA concentration the greater is the blend degradation.

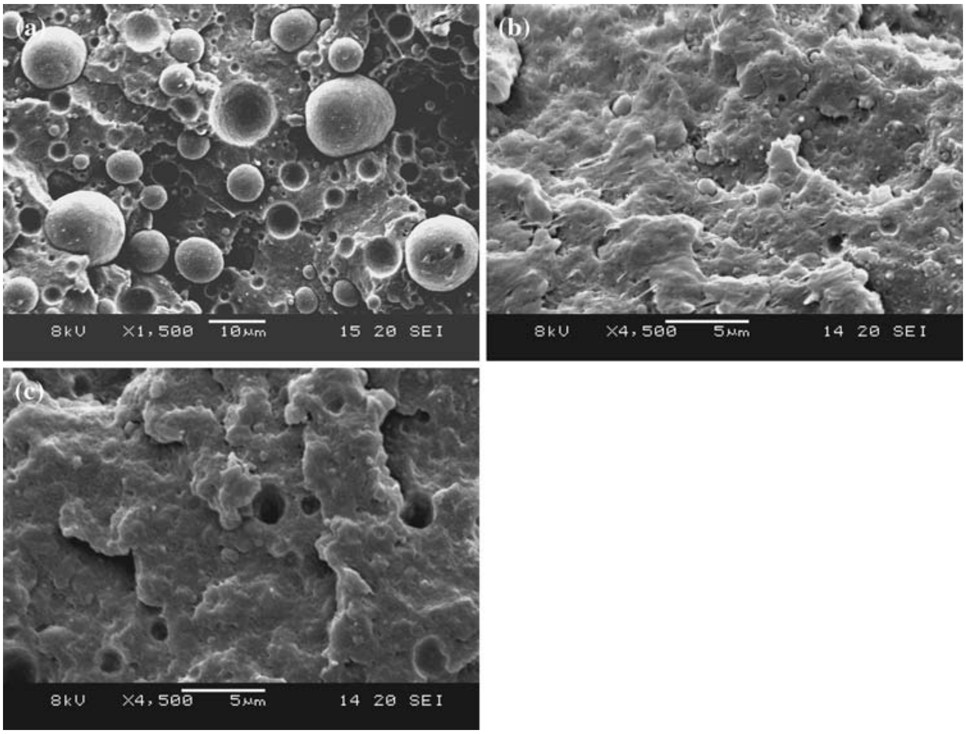

Fig. 5 SEM micrographs of the blends prepared by extrusion followed by injection: (**a**) PA6/LDPE (80/20); (**b**) PA6/PEgAA/LDPE (80/10/10); and (**c**) PA6/PEgMA/LDPE (80/10/10)

The torque of the blends compatibilized with PEgAA is greater than that of the blends compatibilized with PEgMA. In both processing methods (injection and extrusion followed by injection) the impact strength and elongation at break of the compatibilized blends are greater than those of the uncompatibilized ones. For the blends prepared only by injection, the impact strength of the blend compatibilized with PEgMA is greater than that of the blend compatibilized with PEgAA. For the blends prepared by extrusion followed by injection, the impact strength of PA6/PEgAA/LDPE blend is greater than that of the blend compatibilized with PEgMA. The impact strength of PA6/PEgAA/LDPE prepared by extrusion followed by injection is greater than that of the same blend prepared only by injection. The impact strength of PA6/PEgMA/LDPE prepared only by injection is greater than that of the same blend prepared by extrusion followed by injection. SEM analysis shows that in both processing methods, when PEgAA and PEgMA are added to PA6/LDPE blends, the LDPE disperse phase average particles size decreases considerably and the adhesion between PA6 and LDPE phases improves. The morphology of the PA6/PEgAA/LDPE blend prepared by extrusion followed by injection is more stable than that of the same blend prepared only by injection.

Acknowledgements The authors thank Rhodia for supplying PA6, Crompton for supplying PEgAA and PEgMA, Braskem for supplying LDPE, and CNPq for the financial support.

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