

Influence of reactive compatibilizers on the rheometrical and mechanical properties of PA6/LDPE and PA6/HDPE blends

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Abstract In this work, the influence of reactive compatibilizers on the rheometrical and mechanical properties of polyamide 6/low density polyethylene (PA6/LDPE) and polyamide 6/high density polyethylene (PA6/HDPE) blends was investigated. Polyethylene grafted with maleic anhydride (PEgMA), polyethylene grafted with acrylic acid (PEgAA), and ethylene-methyl acrylate-glycidyl methacrylate (EMA-GMA) were used as compatibilizers. The blends were characterized by torque rheometry, mechanical properties, and morphology. Rheometrical properties results show that PEgMA and PEgAA compatibilizers are more reactive with PA6 than EMA-GMA. Mechanical properties and scanning electron microscopy analysis results show that EMA-GMA compatibilizer is as effective as PEgMA and PEgAA for PA6/LDPE blend. For PA6/HDPE blend, PEgAA and EMA-GMA compatibilizers proved to be as effective as PEgMA. For PA6/HDPE blend compatibilized with PEgAA, an intriguing “web” or “bridge” like structure was observed.

Introduction

Blending two polymers is a different approach for developing new materials with an excellent combination of properties [1, 2]. It is well known that most of polymer blends are immiscible and characterized by high interfacial

tension, poor adhesion between the phases and unstable morphology leading to poor mechanical properties. One way to mitigate the immiscibility problem is through reactive compatibilization, where a compatibilizer, either a block or graft copolymer, is added to the immiscible blend reacting chemically with one phase and interacting physically with the other reducing the interfacial tension, improving the adhesion between the phases, stabilizing the morphology, and forming a copolymer in situ at the interface [3–9]. Blends of polyamide 6 (PA6) and polyethylene (PE) combine the thermo-mechanical and oxygen barrier properties of PA6 with high impact strength at lower temperatures, easy processability, and low cost of PE. These blends are immiscible and a compatibilizer is needed. Effects of different compatibilizers on PA6/PE blends have been studied by various authors. Polyethylene grafted with maleic anhydride (PEgMA), polyethylene grafted with acrylic acid (PEgAA), and ethylene-glycidyl methacrylate copolymer (E-GMA) have been widely used as compatibilizers for PA6/PE blends [10–20]. PEgMA proved to be more effective than PEgAA and E-GMA. However, other compatibilizers have also been used. Silva and Soares [21] have investigated the effect of poly (ethylene-co-vinyl alcohol-co-vinyl-mercaptoacetate) (EVASH) as compatibilizer for PA6 and low density polyethylene (LDPE) blends. The results indicated that the addition of EVASH to the blends improved the mechanical properties and reduced the dispersed phase particle size. Valenza et al. [22] investigated the morphological, calorimetric, rheological, dielectric, and mechanical behavior of blends made with PA6 and linear low density polyethylene (LLDPE) functionalized with methacrylic acid derivatives. The results indicated that the system remained incompatible but the functional groups grafted in the polyethylene chains induced compatibilization phenomena in the

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blends. Minkova et al. [14] 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 towards the blends. They concluded that the addition of the compatibilizers to the uncompatibilized blend reduces significantly the interfacial tension. In previous work [23], the present authors investigated the effect of the processing methods on the mechanical properties and morphology of compatibilized PA6/LDPE blends. The blends were prepared by two processing methods: injection molding and extrusion followed by injection molding. The compatibilizers used were PEGAA and 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. Scanning electron microscopy (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. In the literature, there is lack of works where ethylene-methyl acrylate-glycidyl methacrylate (EMA-GMA) is used as compatibilizer for PA6/LDPE blends. Also, for PA6/high density polyethylene (HDPE) blends, there is lack of works where PEGAA and EMA-GMA are used as compatibilizers. The aim of this work is to investigate the influence of reactive compatibilizers on the rheometrical and mechanical properties of PA6/LDPE and PA6/HDPE blends. PEGMA, PEGAA, and EMA-GMA are used as compatibilizers. For PA6/LDPE blend, the effectiveness of EMA-GMA is compared to that of PEGMA and PEGAA compatibilizers. For PA6/HDPE blend, the effectiveness of PEGAA and EMA-GMA compatibilizers is compared to that of PEGMA.

Experimental

Materials

Polyamide 6 (PA6) C216 Natural was provided by Rhodia. Low density polyethylene (LDPE) PB 208 (MFI = 22 g/10 min) and high density polyethylene (HDPE) JV060U (MFI = 7 g/10 min) were provided by Braskem. Polyethylene grafted with 6% of acrylic acid (PEGAA) Polybond 1009 (MFI = 5 g/10 min) and polyethylene grafted with 1% of maleic anhydride (PEGMA) Polybond 3009 (MFI = 5 g/10 min) were provided by Crompton. Ethylene-methyl acrylate-glycidyl methacrylate (EMA-GMA) terpolymer containing 8% of GMA and 15% of Ester Lotader AX 8900 (MFI = 6 g/10 min) was provided by Arkema.

Methods

Drying of materials

Before torque rheometry analyses and extrusion processing, PA6, PEGAA, and PEGMA were dried under vacuum at 80 °C for 24 h.

Torque rheometry

Rheometrical properties were evaluated through torque rheometry analysis, which was carried out in an intensive batch mixer Rheocord 600 attached to a HAAKE System 90, equipped with roller blades at 240 °C and rollers speed of 50 rpm under air atmosphere during 20 min. The composition of the blends was 80/20 (wt%) for PA6/PE and PA6/compatibilizer binary blends and 80/05/15, 80/10/10, and 80/15/05 (wt%) for PA6/compatibilizer/PE ternary blends. The compatibilizers were added to PA6/PE blends after 5 min when PA6 and PE were already melt mixed. In all compositions, the concentration of PA6 was kept fixed in 80 (wt%).

Blends preparation

To investigate the influence of the reactive compatibilizers on the mechanical properties and morphology, the blends, after being dry-mixed at room temperature, were prepared by melt compounding in a counter-rotating intermeshing conical twin-screw extruder (die diameter of 4 mm), coupled to a Haake System 90 torque rheometer, at 240 °C in all zones and screw speed of 50 rpm. The obtained material was granulated and dried under vacuum at 80 °C for 24 h to be injection molded. The composition of the blends is shown in Table 1.

Samples preparation

Samples for Tensile and Izod impact strength tests were obtained by injection molding at 240 °C using a FLUID-MEC H 30/40 Injector.

Table 1 Composition of the blends (wt%) prepared in a twin-screw extruder

PA6	LDPE	HDPE	PEGAA	PEGMA	EMA-GMA
80	20	–	–	–	–
80	–	20	–	–	–
80	10	–	10	–	–
80	–	10	10	–	–
80	10	–	–	10	–
80	–	10	–	10	–
80	10	–	–	–	10
80	–	10	–	–	10

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 cross head 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

Rheometrical properties

Effect of the compatibilizer type

Figure 1 shows the torque rheometry curves of PA6/compatibilizers/PE ternary blends containing 0–20 (wt%) of PEGAA (Fig. 1a, b), PEGMA (Fig. 1c, d), and EMA-GMA (Fig. 1e, f) compatibilizers. The compatibilizers were added to PA6/PE blends after 5 min (as shown by a dotted line) when PA6 and PE were already melt mixed. It may be observed that when the compatibilizers are added to PA6/PE blends there is an increase in the torque indicating that reactive compatibilization has occurred resulting in the formation of a copolymer in situ at the interface. When the copolymer is formed, there is an increase in the molecular weight of the system and hence there is an increase in the viscosity resulting in the torque increase. It is known that the amino end groups of PA6 may react with the carboxyl groups of PEGAA forming an amide group, and with the anhydride groups of PEGMA forming an imide group [16, 17, 24–26]. The epoxy groups of GMA may react with either amino end groups or carboxyl groups of PA6, forming a copolymer in situ at the interface [20, 26, 27]. The greater the compatibilizer concentration the greater the increase in the torque. A possible explanation is that increasing the compatibilizer content, there are more chances of reactions between the amino end groups of PA6 and the functional groups of the compatibilizers. The increase in the torque was more pronounced for the blends compatibilized with PEGAA. However, after reaching a maximum the torque of the blends containing 10, 15, and

20 (wt%) of PEGAA starts to decrease. It is known that the reaction between the amino end groups of PA6 and the carboxylic groups of PEGAA involves the evolution of water as byproduct. This water leads to a hydrolytic degradation of PA6 by chain scission reducing its molecular weight [17, 25]. The reaction between the amino end groups of PA6 and the anhydride groups of PEGMA also involves the evolution of water as byproduct [26]. However, little or no degradation was observed in this case in the present study. This may be attributed to the fact that PEGMA has only 1% of maleic anhydride content, which may not be enough to produce the amount of water necessary to hydrolyze the PA6 chains during the reaction. For the blends compatibilized with EMA-GMA, only a slight increase in the torque was observed when the amount of EMA-GMA was increased from 5 up to 20% (Fig. 1e, f).

Effect of the dispersed phase (LDPE or HDPE)

It is worth noting that regardless of the compatibilizers used in this work, the increase in the torque is more pronounced for the blends containing LDPE as a dispersed phase (Fig. 1). However, this increase is more evident for the blends compatibilized with PEGAA, which showed greater increase in the torque, as discussed before. This may be attributed to the lower viscosity of LDPE, which may facilitate the mixing of the components, increasing the chances of reactions between the amino end groups of PA6 and the functional groups of the compatibilizers.

Mechanical properties

Blends containing LDPE as a dispersed phase

Table 2 shows the mechanical properties of the uncompatibilized and compatibilized blends containing LDPE as a dispersed phase. It may be observed that the addition of the compatibilizers leads to a significant increase in the impact strength and elongation at break of PA6/LDPE blend, which is an evidence of reactions between the functional groups of the compatibilizers with the amino end groups of PA6, resulting in a decrease of the LDPE particles average size and improving the adhesion between the PA6 and LDPE phases, leading to an increase in the impact strength. Surprisingly, EMA-GMA compatibilizer was as effective as PEGAA and PEGMA compatibilizers, contradicting the results obtained from the torque rheometry analysis. A possible interpretation is that besides the reaction of the epoxy group of GMA with PA6, the acrylic ester present in EMA-GMA gives flexibility to it and may contribute to the increase in the impact strength of the blend.

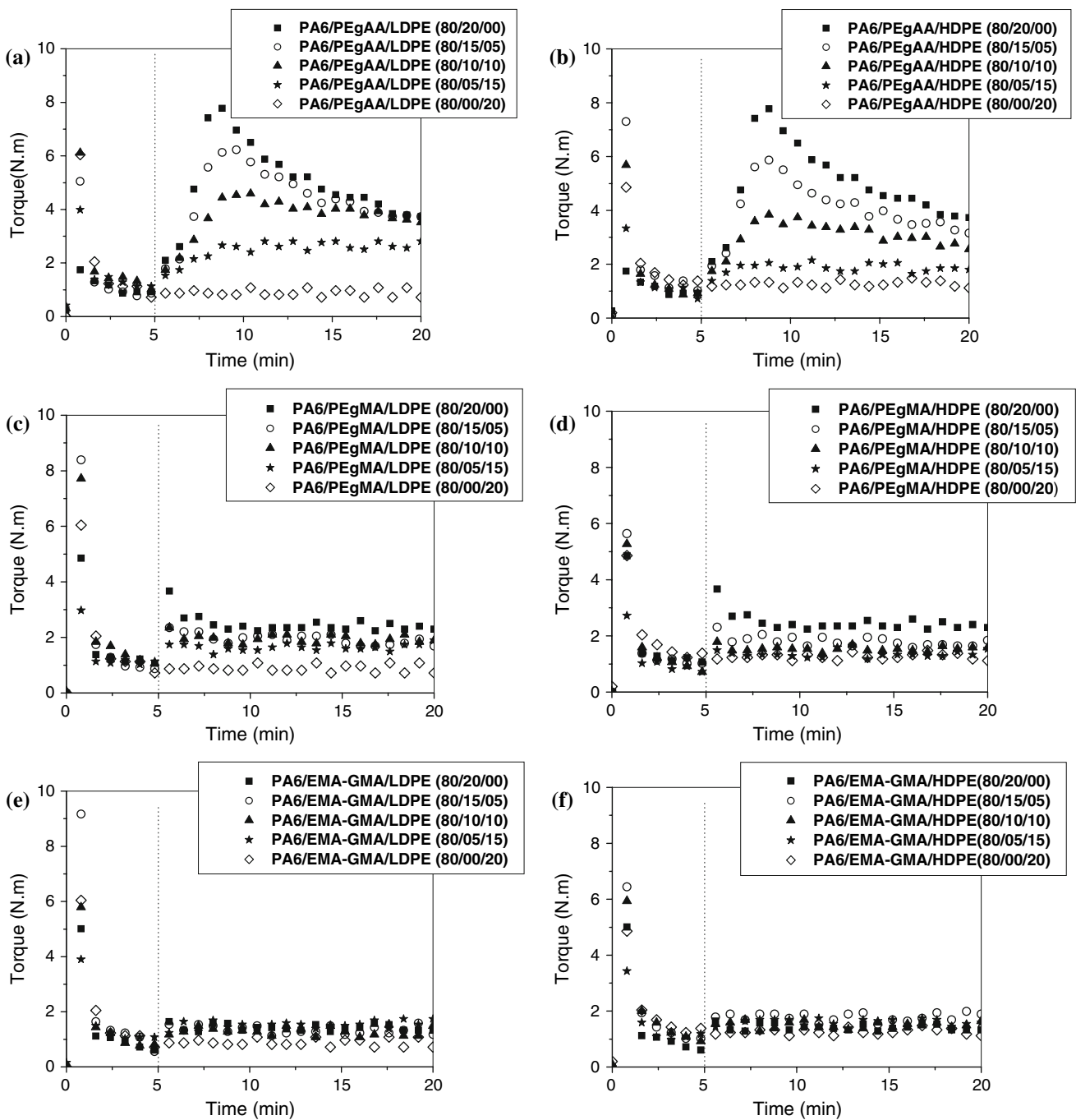


Fig. 1 Torque rheometry curves of PA6/compatibilizers/PE ternary blends containing 0–20 (wt%) of PEGAA (a, b), PEGMA (c, d), and EMA-GMA (e, f) compatibilizers

Blends containing HDPE as a dispersed phase

Table 3 shows the mechanical properties of the uncompatibilized and compatibilized blends containing HDPE as a dispersed phase. As in the blends containing LDPE as a dispersed phase, the addition of the compatibilizers to PA6/HDPE blend significantly improved the mechanical

properties (impact strength and elongation at break), which is an evidence of reactive compatibilization. The impact strength of the blends containing PEGAA and EMA-GMA compatibilizers was greater than that of blend compatibilized with PEGMA, which is the compatibilizer used for PA6/HDPE blend in most of the works. The impact strength of the blends containing LDPE as a dispersed

Table 2 Mechanical properties of the blends containing LDPE as a dispersed phase

Materials	IS (J/m)	ε_b (%)
PA6	72.97 ± 5.38	24.07 ± 6.86
PA6/LDPE (80/20)	66.75 ± 3.71	99.59 ± 53.24
PA6/PEgAA/LDPE (80/10/10)	346.31 ± 23.60	117.17 ± 31.93
PA6/PEgMA/LDPE (80/10/10)	160.33 ± 15.20	102.41 ± 76.15
PA6/EMA-GMA/LDPE (80/10/10)	312.70 ± 14.52	180.65 ± 16.21

IS impact strength; ε_b elongation at break

Table 3 Mechanical properties of the blends containing HDPE as a dispersed phase

Materials	IS (J/m)	ε_b (%)
PA6	72.97 ± 5.38	20.02 ± 4.54
PA6/HDPE (80/20)	77.52 ± 8.71	14.26 ± 6.29
PA6/PEgAA/HDPE (80/10/10)	242.28 ± 11.55	177.17 ± 22.67
PA6/PEgMA/HDPE (80/10/10)	163.42 ± 8.32	149.90 ± 63.12
PA6/EMA-GMA/HDPE (80/10/10)	170.33 ± 17.38	199.65 ± 21.68

IS impact strength; ε_b elongation at break

phase was greater than that of the blends containing HDPE as a dispersed phase. As in the torque rheometry analysis, this may be attributed to the lower viscosity of LDPE.

Morphology

Blends containing LDPE as a dispersed phase

Figure 2 shows the SEM micrographs of PA6/PE uncompatibilized and compatibilized blends containing LDPE as a dispersed phase. It may be observed that the uncompatibilized blend (Fig. 2a) is characterized by poor adhesion between PA6/LDPE phases and large LDPE domains. The addition of the compatibilizers to PA6/LDPE blend has considerably decreased the LDPE domains and improved the adhesion between PA6 and LDPE phases, which is a confirmation that reactive compatibilization has been achieved, resulting in the improvement of the impact strength. Again, EMA-GMA compatibilizer proved to be an effective compatibilizer.

Blends containing HDPE as a dispersed phase

Figure 3 shows the SEM micrographs of PA6/PE uncompatibilized and compatibilized blends containing HDPE as a dispersed phase. It may be observed that the uncompatibilized blend (Fig. 3a) is characterized by poor adhesion between PA6/HDPE phases and large HDPE domains. As in the blends containing LDPE as a dispersed phase, the addition of the compatibilizers to PA6/HDPE blend greatly decreased the HDPE domains and improved the adhesion between PA6 and HDPE phases confirming that the reactive

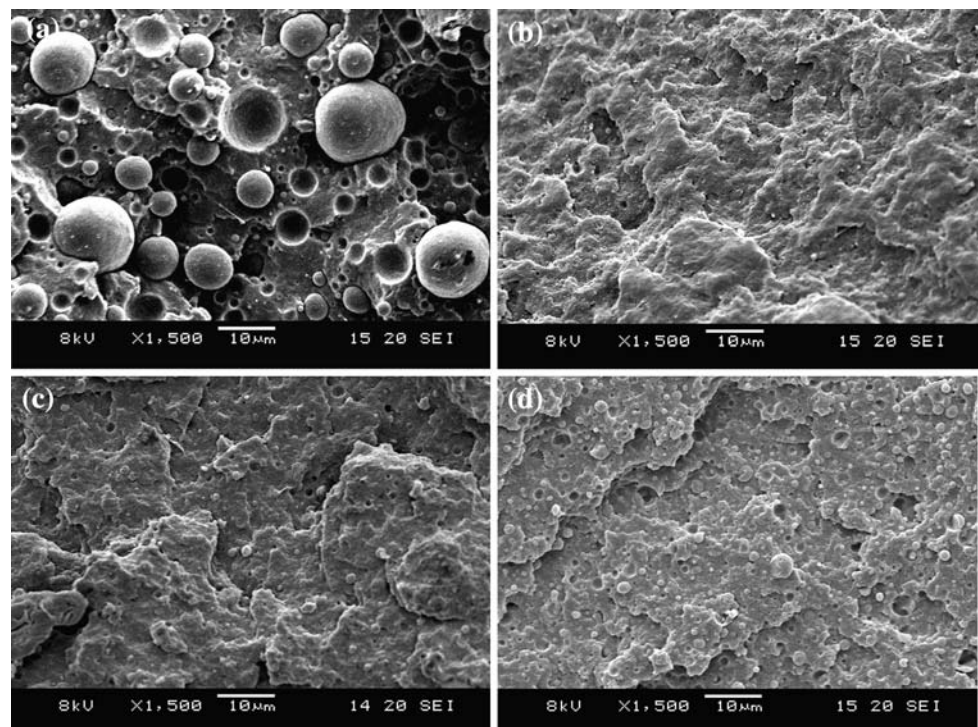
Fig. 2 SEM micrographs of the blends containing LDPE as a dispersed phase: **a** PA6/LDPE; **b** PA6/PEgAA/LDPE; **c** PA6/PEgMA/LDPE; **d** PA6/EMA-GMA/LDPE

Fig. 3 SEM micrographs of the blends containing HDPE as a dispersed phase: **a** PA6/HDPE; **b** PA6/PEgAA/HDPE; **c** PA6/PEgMA/HDPE; **d** PA6/EMA-GMA/HDPE

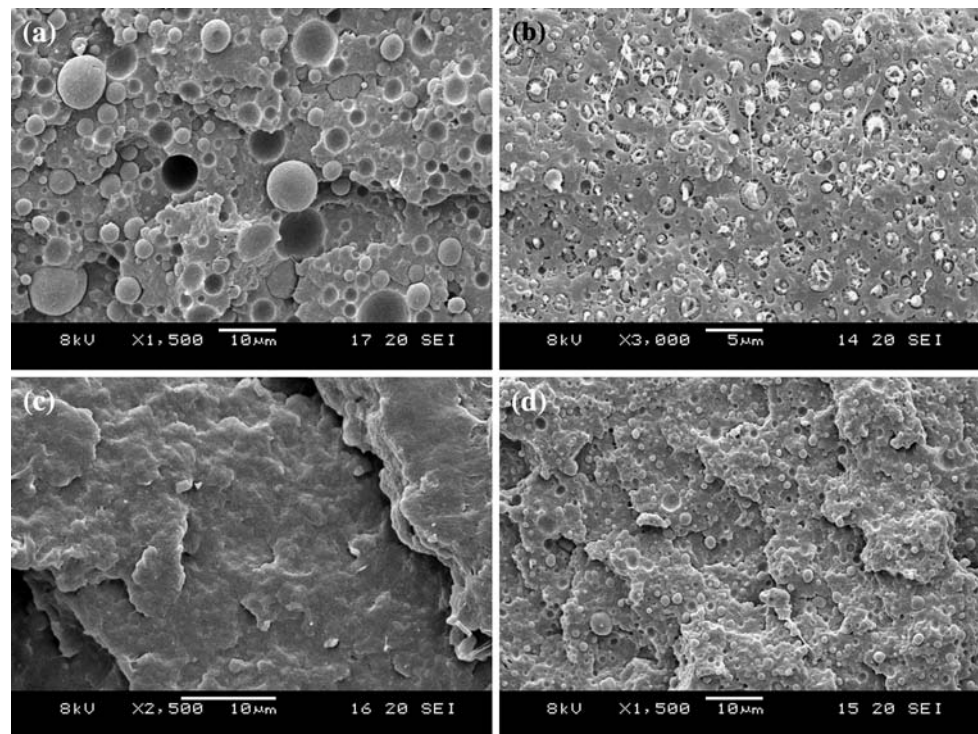
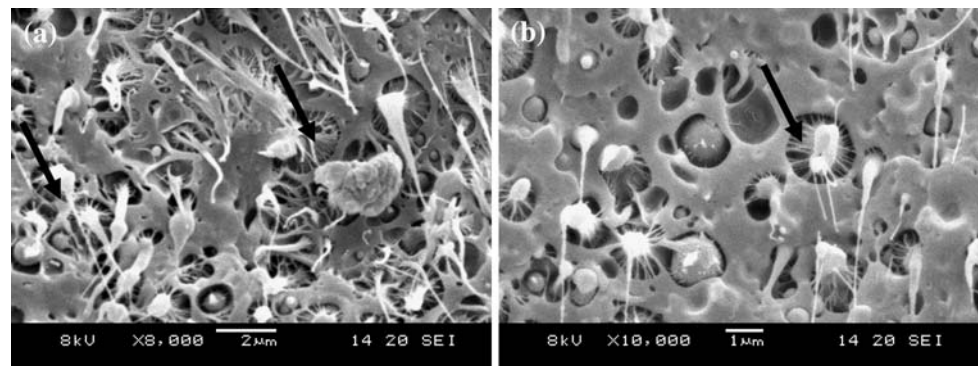


Fig. 4 Magnified SEM micrographs of PA6/PEgAA/HDPE blend: **a** $\times 8,000$; **b** $\times 10,000$



compatibilization has been achieved. The consequence was the improvement of the impact strength of the blend. When PEGAA was added to PA6/HDPE blend (Figs. 3b, 4), an intriguing “web” or “bridge” like structure (indicated by an arrow) linking PA6 to HDPE was observed. This structure was observed only in the blend containing HDPE as a dispersed phase compatibilized with PEGAA and may be attributed to the copolymer formed in situ at the interface between PA6 and HDPE phases. PEGAA and EMA-GMA compatibilizers proved to be effective compatibilizers for PA6/HDPE blend when compared to PEGMA.

Conclusions

In this work, the influence of reactive compatibilizers on the rheometrical and mechanical properties and morphology

of PA6/LDPE and PA6/HDPE blends was investigated. Rheometrical properties were investigated through torque rheometry analysis. The results showed that there is an increase in the torque of the blends with the increase in the amount of compatibilizers. This increase is more pronounced for the blends containing LDPE as a dispersed phase. PEGAA and PEGMA compatibilizers are more reactive with PA6 than EMA-GMA. The values of impact strength for the compatibilized blends are greater than those for the uncompatibilized ones, indicating that the reactive compatibilization was achieved. SEM analysis showed that the addition of the compatibilizers to PA6/PE blends significantly decreases the PE domains and improves the adhesion between PA6 and PE phases improving the impact strength. Mechanical properties and SEM analysis also showed that EMA-GMA compatibilizer is as effective as PEGMA and PEGAA for PA6/LDPE blend and for

PA6/HDPE blend, PEGAA and EMA-GMA compatibilizers proved to be as effective as PEGMA. For PA6/HDPE blend compatibilized with PEGAA, an intriguing “web” or “bridge” like structure is observed. This structure is an indicative that a copolymer in situ was formed at the interface, improving, through this “web” or “bridge” the adhesion between the blend phases and hence the mechanical properties.

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