Use of Postconsumer Polyethylene in Blends with Polyamide 6: Effects of the Extrusion Method and the Compatibilizer

J. R. Araújo, M. R. Vallim, M. A. S. Spinacé, M.-A. De Paoli

Instituto de Química, Unicamp, Caixa Postal 6154, 13084-970 Campinas, SP, Brazil

ABSTRACT: Blends of polyamide and high-density polyethylene show adequate properties for a large range of applications: they are used for the production of filaments, containers, and molding resins. The effect of the addition of 2 wt % of a compatibilizer, maleic anhydride grafted polyethylene, to the blend was studied and compared to the use of postconsumer polyethylene. The samples were extruded with single- and twin-screw extruders with 25, 50, or 75 wt % f polyethylene, and the test specimens, molded by injection, were characterized by stress–strain tests, thermal properties, and morphologies. Processing the blends with postconsumer polyethylene in both extruders improved the mechanical properties in comparison to the blends processed with high-density polyethylene and the compatibilizer. The morphologies of these blends showed that there was a decrease in the domain size of the disperse phase with the use of the compatibilizer or postconsumer polyethylene. The results indicate that for this blend, postconsumer polyethylene substituted, with advantages, for the necessity of a compatibilizer and the use of the high-density polyethylene. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1310–1317, 2008

Key words: adhesion; blends; compatibilization; interfaces; mechanical properties

INTRODUCTION

The preparation of compatible or miscible polymer blends creates the possibility of new polymeric materials with improved properties. A miscible polymer blend forms a single phase over certain ranges of temperature, pressure, and composition. Polymer miscibility occurs when the free energy of mixing is negative, and this depends on two factors: entropy and enthalpy. Thus, miscible polymer systems only exist when strong intermolecular interactions are present.[1] The large majority of polymeric systems are immiscible because of the large dimensions of the macromolecules. Another characteristic of polymer blends is compatibility. A compatible blend is an immiscible polymer blend that exhibits macroscopically uniform physical properties throughout its whole volume. To improve the interaction and increase the compatibility, it is necessary to use a compatibilizer, which pro-

motes interaction among the blend components. These compatibilizers are block copolymers or polymers modified by grafting. Ideally, they are located at the interface of the blend components. An adequate compatibilizer leads to the formation of a stable disperse phase with a narrow domain size distribution because of the reduction of interfacial tension and precludes phase coalescence in the disperse phase of the blend.[2]

Commercial blends of interest that can be compatibilized are blends of polyamide 6 (PA-6) and high-density polyethylene (HDPE). These blends are prepared because they retain the useful properties of both polymers and do not present the drawbacks of their isolated components. To combine these properties, it is possible to make a two-phase blend in which one of the components, the continuous matrix, contains the other as a disperse phase.[3]

Much effort has been expended to modify the mechanical properties of PA-6 by its blending with different thermoplastics, such as polyolefins. The compatibilization of the PA-6/HDPE blend is important because PA-6 presents high stress and flexural resistance together with good chemical resistance to polar solvents, whereas HDPE presents a high impact resistance and low moisture absorbance.[4] Compatibilization of the immiscible PA-6/HDPE blend is important for applications in food packaging because of the good oxygen barrier properties of the polyamide together with the moisture barrier properties of the polyolefin.[5]

PA-6 presents polar chemical groups in the main chain (amide groups) and amine terminal groups,
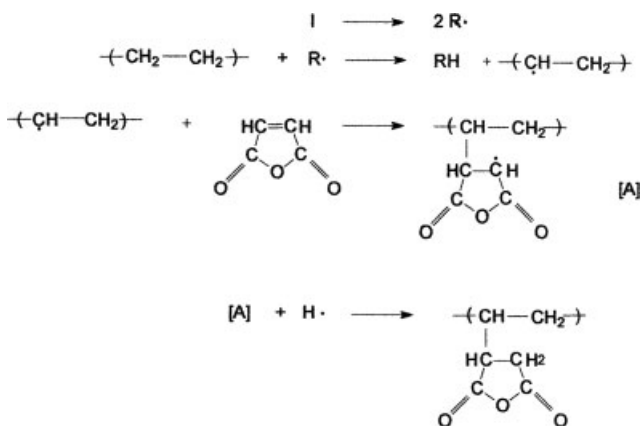
Figure 1 Maleic anhydride grafting reaction with PE.

which may act as reactive centers. HDPE does not present polar groups in its backbone; thus, it cannot interact chemically with PA-6. To promote compatibility, it is necessary to add a compatibilizer to induce interaction between the phases and reduce the interfacial tension, increase the adhesion between the blend components, and promote the reduction of the domain size of the disperse phase, which makes it more homogeneous.[6] The lowering of the interfacial tension depends, to a certain extent, on the presence and concentration of the compatibilizer. The blend interface has an important effect on the control of blend morphology and on the final properties of an immiscible blend.

The use of a compatibilizer can be done in two different ways:

1. By the addition of a functionalized copolymer during processing, such as polyethylene (PE) grafted with an acidic group such as acrylic, maleic, or crotonic group. The acidic groups react with the polyamide terminal amine groups, and the apolar end of the functionalized macromolecule interacts with HDPE by means of Van der Waals forces.
2. The promotion of the *in situ* functionalization of HDPE. This means the promotion of the grafting and compatibilization by reactive extrusion in a single processing step.

The most common compatibilizer for the PA-6/HDPE blend is maleic anhydride grafted polyethylene

(PE-*g*-MA) or with acrylic acid. A low-cost and environmentally interesting alternative to the use of HDPE and PE-*g*-MA is the use of postconsumer polyethylene (PEpc). PEpc possesses polar groups formed by oxidative degradation during its use and disposal. If we consider that PE is among the five most consumed thermoplastics in the world, its application for blends after consumer use creates the possibility of reducing the environmental impact of its disposal.

Presently, polyolefins grafted with maleic anhydride are commercial products used as compatibilizers for blends,[7] including the PA-6/HDPE blend.[8] Maleic anhydride grafting promotes the formation of polar groups in the polyolefin backbone, and this reaction can also be done in a single step during blend extrusion. Figure 1 presents this reaction in a simplified manner; where I represents the initiator (peroxides are frequently used) and R$^\bullet$ represents the free radical formed.

The reaction of the acidic grafted groups of the compatibilizer with the amine terminal groups of the polyamide is shown in Figure 2, where P represents the polyolefin chain and P' represents the polyamide chain.[9] This acid–base reaction generates a covalent bond between the polyolefin and the polyamide.

PE, like other polymers, is exposed to oxidation reactions during its processing and consumer use. These reactions have been thoroughly studied, and in addition to crosslinking, they produce different polar groups, such as carbonyl, carboxyl, lactone, alcohol, and ester groups, attached to the polymer chain.[10] Thus, PEpc contains these polar groups in variable concentrations.

To evaluate the compatibilization effect of the oxidized groups of PEpc, in this study, we compared PA-6/PE blends prepared with this material, blends prepared with pure HDPE, and blends prepared with HDPE and PE-*g*-MA as a compatibilizer. In addition, these blends were processed in single-screw and twin-screw extruders to study the effect of the processing method.

EXPERIMENTAL

Materials

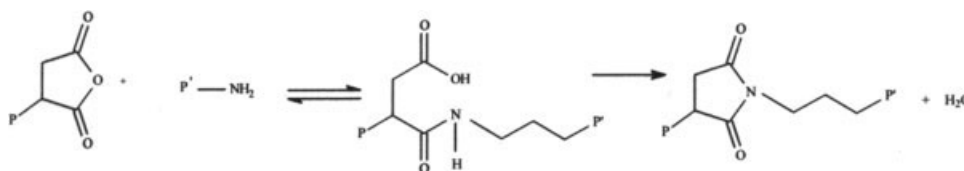For this study, we used PA-6 [melt flow index (MFI) = 24 g/10 min; Zytel, DuPont do Brasil, Paulinia,

Figure 2 Chemical reaction between PE-*g*-MA and PA-6.

Figure 3 Screw profile used in the twin-screw extruder to process the blends.

Brasil], HDPE (MFI = 0.3 g/10 min; HB-0454, Braskem, Triunfo) [Triunfo, Brazil], and PEpc (average MFI = 6.0 g/10 min; Proceplast, Campinas) [Campinas, Brazil]. PE-g-MA was supplied by Megh Industria e Comércio Limitada (São Paulo, Brazil), from two batches (acidities = 40–60 and 100–30 mg of KOH/g). PA-6 was dried in a vacuum oven (Cole Parmer 5053-10) for 6 h at 27 mmHg and 120°C before processing.

PEpc was sorted from collected plastic waste in a recycling plant, milled, and washed to remove contamination from its original use. It was supplied in the form of flakes of different colors. The presence of oxidative degradation was evidenced by Fourier transform infrared spectroscopy, mainly by absorptions in the carbonyl, hydroperoxyl, and hydroxyl wave-number ranges.

MFIs were measured according to ASTM D 1238 with 2.16 kg and temperatures of 235°C for PA-6 and 190°C for PE. The PE samples used in this study had different MFIs because the virgin sample was produced for blow molding, whereas the postconsumer sample came mostly from injection-molded parts; however, the MFI of postconsumer samples could change from batch to batch.

Blend processing

PA-6/PE blends with compositions of 25/75, 50/50, and 75/25 by weight were prepared with HDPE, HDPE with PE-g-MA, and PEpc. The concentration of PE-g-MA was 2 wt % in relation to HDPE. The blend components were previously mixed before they were directly fed into the extruder hopper. The blends were processed by two methods: (1) a single-screw extruder (Wortex; length/diameter = 30, diameter = 32 mm) [Campinas, Brazil] with a Maddock mixing screw, a temperature profile of 230–255°C from feed to dye, and 102 rpm and (2) a twin-screw, corotatory, intermeshing extruder (model MPC/V30, APV [United Kingdom], length/diameter = 13 and diameter = 29 mm) with temperature profile of 230–255°C from feed to dye, a screw rotation of 102 rpm, and a screw profile with an intensive mixing zone followed by a degassing exit (Fig. 3). The extruded strands were milled to pellets and dried for 6 h at 120°C. Stress–strain test samples were injection-molded (Arburg All Rounder, M-250) [Lossburg, Germany] with a temperature profile of 230–255°C, a mold temperature of 20°C, and 30 s of cooling time.

For comparison, pure HDPE, HDPE containing 2 wt % PE-g-MA, and PEpc were subjected to the same processing procedures before characterization.

Thermogravimetry and differential scanning calorimetry (DSC) experiments

The thermal properties of the homopolymers and blends were compared by thermogravimetric analysis (TGA) with a TA Instruments model 2050 thermogravimetric analyzer (New Castle, USA) operating from 30 to 800°C at a heating rate of 10°C/min and under an argon atmosphere (50 mL/min). Phase-transition temperatures and crystallinity degrees were studied by DSC with a TA Instruments model Q-1000 (New Castle, USA) from 0 to 250°C with a heating/cooling rate of 10°C/min under N_2 (50 mL/min).

Stress–strain tests

Stress–strain tests were done according to ASTM D 638 at 50 mm/min with an EMIC MEM-500 apparatus (Curitiba, Brazil). The results are reported as an average of 10 test samples.

Scanning electron microscopy (SEM)

The injection-molded test samples were cryofractured after 15 min of immersion in liquid N_2. The fracture surface was coated with gold and palladium (8:2) with a Bal-Tec Multi Coating System MED020 (Tokyo, Japan). Micrographs were obtained at 20 kV with a Jeol JSM6360LV (Tokyo, Japan) scanning electron microscope. The domain size distribution was evaluated with the software Image Pro Plus, with the measurement of 300 domain diameters for each sample.

RESULTS AND DISCUSSION

Thermal properties

The thermogravimetric curves and their first derivatives for the pure homopolymers and the 75/25 blends processed in the single-screw extruder are presented in Figure 4. In general, all blend proportions presented similar thermogravimetric curves. The blends prepared without compatibilizer showed an intermediate thermogravimetric response in relation to the pure polymers, which indicated no interaction of the thermal degradation processes of the blend components. Moreover, an initial mass loss at 100°C, due to moisture loss, was observed for pure PA-6 and for the blends prepared without compatibilizer. The onset of mass loss in the TGA curve for the blend prepared with HDPE compatibilized with PE-g-MA shifted to higher temperatures in relation
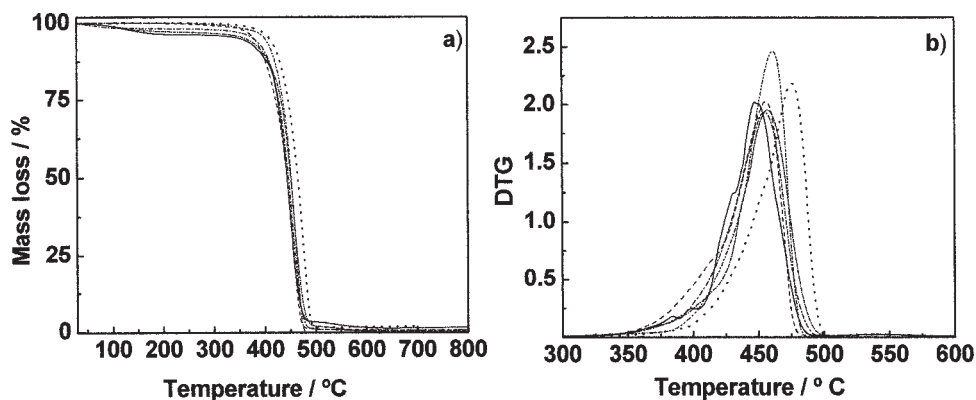
Figure 4 (a) TGA curves under an Ar atmosphere at 10°C/min and (b) first derivatives with respect to temperature for (—) PA-6, (- - -) PEpc, (– · · –) HDPE, (– · ·) 75/25 PA-6/PEpc, (– · –) 75/25 PA-6/HDPE, and (· · ·) 75/25/2 PA-6/HDPE/PE-g-MA (DTG = differential thermogravimetry).

to the corresponding blend without compatibilizer and the pure polymers, which indicated that there was, to a certain extent, a stabilization effect related to the increased interaction between the blend components promoted by the compatibilizer. This was further shown in the first derivative curves [Fig. 4(b)], where a shift of the maximum mass loss rate to higher temperatures was also observed. It is also noteworthy that the first derivative curves showed a single peak for the blends prepared with HDPE, indicating a single thermal degradation reaction for all materials, probably chain scission. In the blend prepared with PEpc, the maximum mass loss rate

also shifted to higher temperatures in relation to PA-6, but it was lower than that of the blend compatibilized with PE-g-MA. In this case, the first derivative curve also showed a shoulder at lower temperatures, which indicated the occurrence of other thermal degradation reactions.

The melting enthalpy (ΔH_m) and melting and crystallization temperatures (T_m and T_c, respectively) were calculated from the DSC curves of all of the blends processed in both extruders and are presented in Table I. Data were collected from the second heating cycle at 10°C/min. From these data, we observed that there was no shift in the T_m (PA-6 = 221°C and

TABLE I
T_m, T_c, and ΔH_m Values Calculated from the DSC Data for the Homopolymers and Blends Prepared in Both Extruders

| Sample	T_m (°C)	T_c (°C)	ΔH_m (J/g)
Single-screw extruder			
PA-6	221	187	51
HDPE	131	112	179
HDPE/2PE-g-MA	122	111	156
PEpc	131	115	167
25/75 PA-6/HDPE	221/131	185/112	15/123
50/50 PA-6/HDPE	222/131	185/111	29/90
75/25 PA-6/HDPE	221/131	186/113	36/43
25/75/2 PA-6/HDPE/PE-g-MA	220/133	183/113	15/133
50/50/2 PA-6/HDPE/PE-g-MA	221/132	184/113	27/90
75/25/2 PA-6/HDPE/PE-g-MA	222/132	184/112	38/45
25/75 PA-6/PEpc	221/131	185/113	15/124
50/50 PA-6/PEpc	221/131	186/113	32/65
75/25 PA-6/PEpc	221/130	186/112	43/39
Twin-screw extruder			
PA-6	221	187	66
HDPE	130	0/111	172
25/75 PA-6/HDPE/	221/131	185/111	11/118
50/50 PA-6/HDPE	221/131	185/112	27/84
75/25 PA-6/HDPE	221/131	185/112	40/40
PEpc	131	115	179
25/75 PA-6/PEpc	220/131	185/113	15/146
50/50 PA-6/PEpc	221/130	186/115	28/78
75/25 PA-6/PEpc	221/130	186/113	34/31
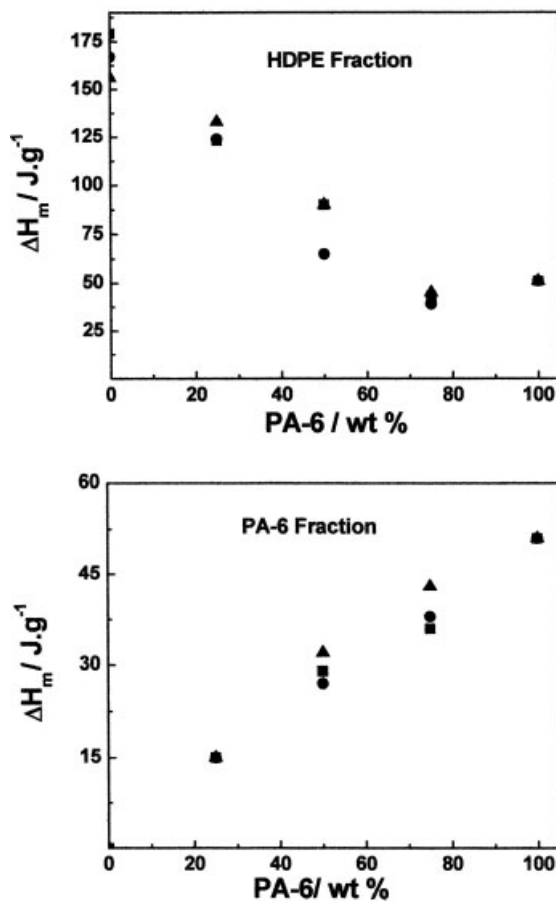
Figure 5 Variation of ΔH_m as a function of the composition for both crystalline phases (HDPE and PA-6) present in the blends: (■) PA-6/HDPE, (●) PA-6/PEpc, and (▲) PA-6/HDPE/PE-g-MA.

HDPE = 131°C) and T_c (PA-6 = 190°C and PE = 119°C) values of the blend components in relation to the pure polymers. This occurred for blends prepared in both extruders with HDPE, HDPE and the compatibilizer PE-g-MA, and PEpc, which confirmed the immiscibility of the blend components.

ΔH_m is directly related to the degree of crystallinity. To quantify the relative variation of this parameter with blend composition, we plotted ΔH_m of the HDPE and PA-6 fractions as a function of blend
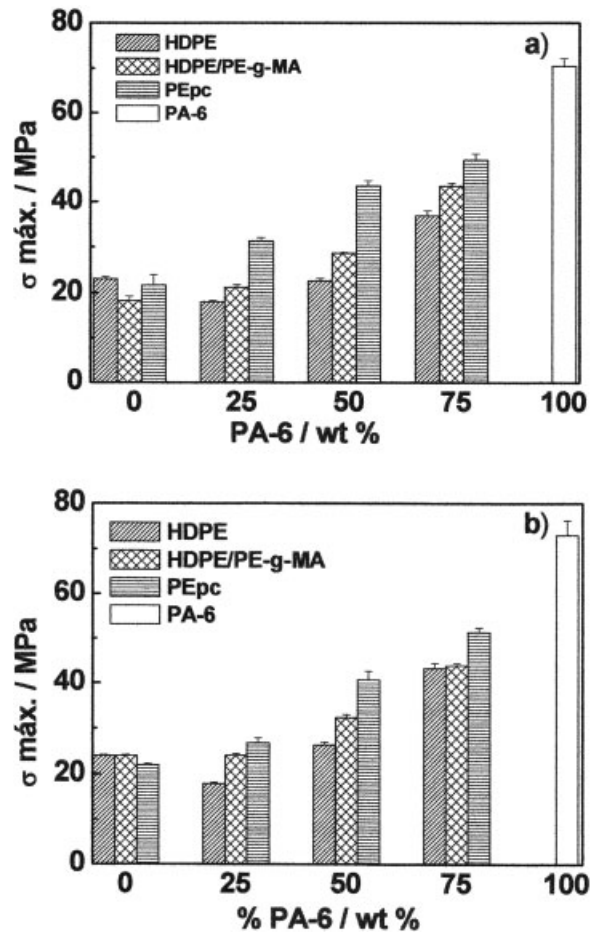

Figure 6 Variation of the maximum yield stress (σ_{max}) as a function of composition for the PA-6/PE blends with HDPE, PEpc, and HDPE compatibilized with PE-g-MA and processed in (a) single-screw and (b) twin-screw extruders.

composition (Fig. 5). In both curves, the data was approximated to a linear correlation, which indicated that one component of the blend did not affect the crystallinity of the other. This result, associated with the nonshifted T_m and T_c, indicated no interaction of the thermal properties of one component of the blend in relation to the other, even in the presence of the compatibilizer.

TABLE II
Average Yield Stress for the Homopolymers and PA-6 Blends Prepared with HDPE, PEpc, or HDPE/PE-g-MA in Both Extruders

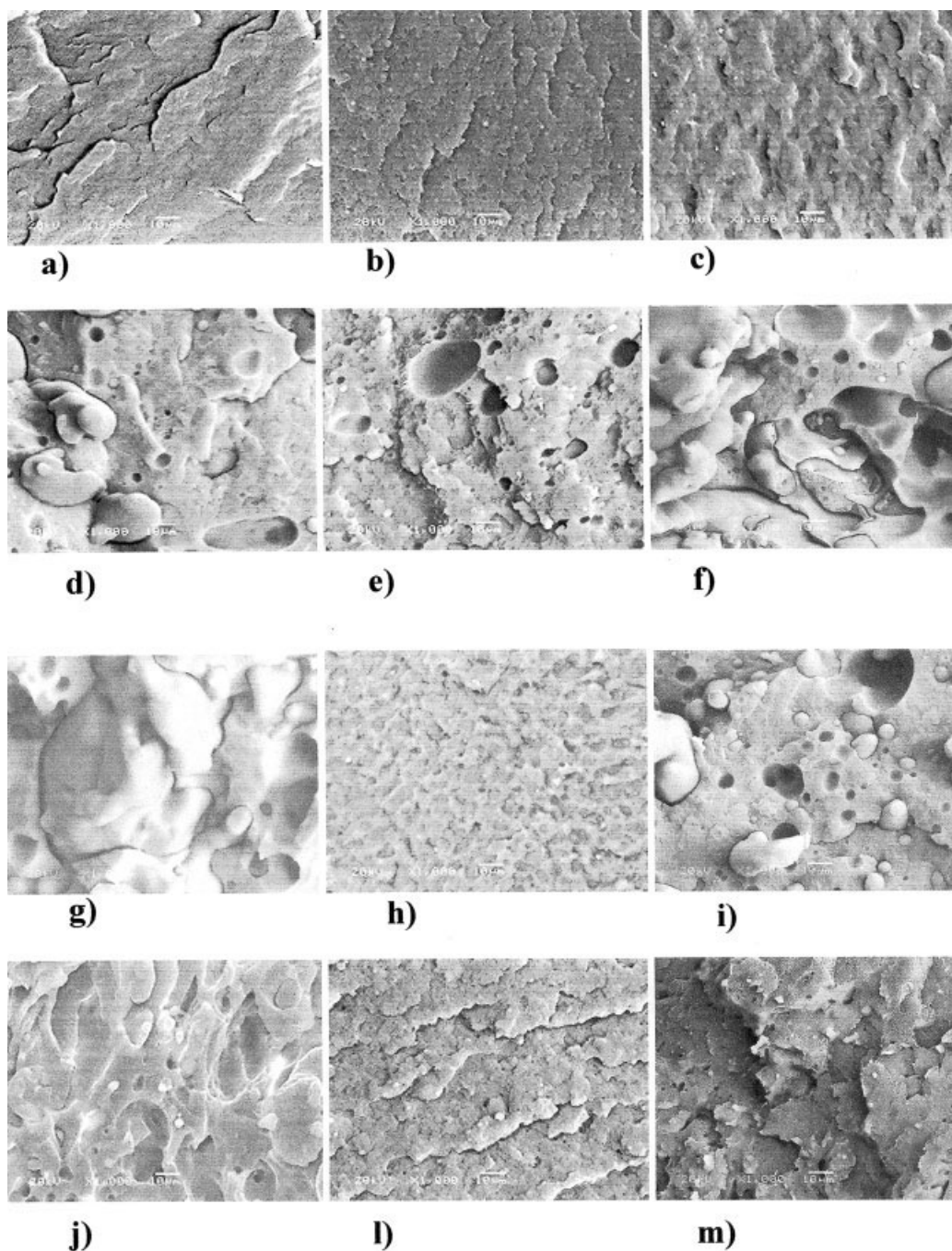|	Average yield stress (MPa)					
	Single-screw extruder			Twin-screw extruder		
PA-6/PE	HDPE	PEpc	PE-g-MA	HDPE	PEpc	PE-g-MA
100/0	65.0 ± 0.2	65.0 ± 0.2	65.0 ± 0.2	73 ± 3	73 ± 3	73 ± 3
75/25	36 ± 10	48 ± 1	43.5 ± 0.6	43 ± 1	51 ± 1	43.8 ± 0.6
50/50	22 ± 0.2	37 ± 1	28.6 ± 0.3	26 ± 1	41 ± 2	32.3 ± 0.7
25/75	17 ± 1	29.5 ± 0.3	21.1 ± 0.7	18 ± 1	27 ± 1	24.0 ± 0.4
0/100	24 ± 2	20.6 ± 0.2	24 ± 2	23 ± 0.1	22.0 ± 0.3	23 ± 0.1

Figure 7 SEM micrographs for the PA-6/PE blends processed in the single-screw extruder: (a) HDPE, (b) PEpc, (c) 1/2 HDPE/PE-*g*-MA, (d) 75/25 PA-6/HDPE, (e) 75/25 PA-6/PEpc, (f) 75/25/2 PA-6/HDPE/PE-*g*-MA, (g) 50/50 PA-6/ HDPE, (h) 50/50 PA-6/PEpc, (i) 50/50/2 PA-6/HDPE/PE-*g*-MA, (j) 25/75 PA-6/HDPE, (l) 25/75 PA-6/PEpc, and (m) 25/75/2 PA-6/HDPE/PE-*g*-MA.

Mechanical properties

The calculated average values of yield stress for the injection-molded test samples from the pure polymers and blends processed in the single-screw and twin-screw extruders are presented in Table II. These data are better analyzed in the bar plots of Figure 6, which show the yield stress variation and separate blends prepared with HDPE, HDPE compatibilized

with PE-*g*-MA, and PEpc processed in the single-screw and twin-screw extruders.

As shown in Figure 6, the use of the compatibilizer improved the yield stress for all of the blend compositions in relation to the blends prepared without this agent. This was indirect evidence for its localization at the blend–component interfaces, which increased their mutual adhesion. We also observed that in both processing methods, the use of
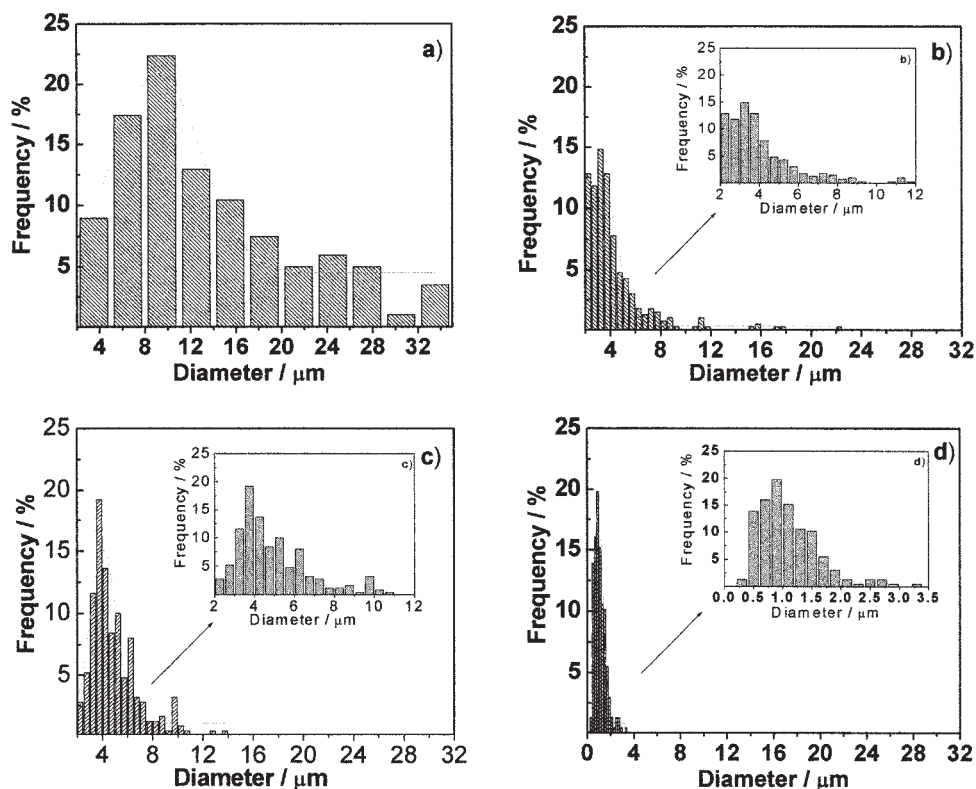
Figure 8 Domain size distributions for the PA-6/PE blends processed in the single-screw extruder: (a) 75/25 PA-6/HDPE, (b) 75/25 PA-6/PEpc, (c) 25/75 PA-6/HDPE, and (d) 25/75 PA-6/PEpc. The insets present the same data on an expanded scale.

PEpc produced better mechanical properties, which indicated a more efficient compatibilization in relation to HDPE containing PE-*g*-MA. For the 75/25 blends processed in the single-screw extruder, there was a 100% improvement in yield stress in relation to pure HDPE for the blend with PEpc and 80% for the blend with PE-*g*-MA [Fig. 6(a)]. For those blends processed in the twin-screw extruder [Fig. 6(b)], the same tendency was observed: PEpc produced a 120% improvement, and PE-*g*-MA produced a 90% improvement. In this case, the best results obtained for the blends processed in the twin-screw extruder were assigned to the better dispersion of the compatibilizer due to the higher shear of the screw.

Yield stress is a limiting property; thus, it is proportional to the degree of adhesion in the blend interface. The results presented in Table II and Figure 6 confirm that PEpc promoted a better interfacial adhesion in relation to PE-*g*-MA.

Blend morphologies

The blend morphologies were evaluated by means of SEM of the fractures of injection-molded test samples of the pure polymers and the blends. The micrographs presented in Figure 7 correspond to the materials processed in the single-screw extruder.

For the blends with 25 and 75 wt % HDPE (second and fourth rows from the top in Fig. 7), we observed a continuous phase for the polymer in higher concentrations and a globular phase for the other component, which was independent of the presence of the compatibilizer. For the blends with 50 wt % HDPE (third row from the top in Fig. 7), we observed a cocontinuous morphology. For all blends prepared with HDPE and no compatibilizer (first column on the left in Fig. 7), we observed a low adhesion between the phases and a higher dispersion of globular domain size, which showed the low compatibility between HDPE and PA-6.

The phase morphology in immiscible blends depends strongly on the processing method and is frequently unstable to external disturbances because it may be not in thermodynamic equilibrium. Thus, a second thermomechanical processing may favor the coalescence of droplets to form larger domains. This instability affects the use of the blend in a finished product because its properties may change with time. In our case, the test samples of the blends were exposed to two processing methods (extrusion and injection molding) and to drying in an oven; thus, the morphology studied by SEM corresponded to a state of thermodynamic equilibrium and would be the same as in a finished product.

The SEM micrographs of the blends prepared in the twin-screw extruder are not shown as they presented the same tendencies.

The morphological characteristics of an immiscible blend, such as the domain size of the disperse phase and interfacial adhesion, are important features for determining and explaining the mechanical properties of a blend.[11] In Figure 8, we present the domain size distributions of blends having a phase disperse in a continuous phase to quantify the effects caused by the use of PEpc. To facilitate the comparison, all plots in Figure 8 are presented with the same scale on the domain size axis.

For blends with PA-6 as a matrix [Fig. 8(a)], the globular HDPE domains presented domain size distributions between 4 and 35 μm, with a peak at 10 μm. When PEpc was used [Fig. 8(b)], the domain size distributions were strongly shifted to lower values, ranging from 1 to 12 μm and peaking at 3 μm. Similar behavior was observed when PA-6 was the disperse phase [Fig. 8(c,d)]; with HDPE, the domain size ranged from 1.5 to 11 μm, and with PEpc, the domain size shifted to 0.25 to 2.5 μm and peaked at 1.0 μm. Shifts to lower sizes were more pronounced in the second case (PA-6 domains), and this was assigned to the different viscosities of the blend components. PA-6 was less viscous in comparison to HDPE, and there was a larger tendency to break the droplets in the dispersed phase during melt processing.

The mechanical properties and morphology of the blends could be explained in terms of the ratio of MFI and surface tension among the blend components. A detailed report of the rheological study of these blends will be published elsewhere.

CONCLUSIONS

The properties of PA-6/HDPE blends were studied, and the effects of two processing methods and of the use of PE-*g*-MA as a compatibilizer or the substitution of HDPE with PEpc were evaluated. The use of PE-*g*-MA or PEpc did not affect ΔH_m of the blend. However, the thermal stability was improved when PE-*g*-MA was used. The compatibilizer improved the mechanical properties, whereas the use of PEpc further extended the improvement. This is an advantage because PEpc has a low cost in comparison to the compatibilizer and to virgin HDPE. In general, processing of the blends in the twin-screw extruder promoted an improvement of mechanical properties.

With regard to the morphology of the blends, the use of a compatibilizer reduced the domain size of the disperse phase and increased the interfacial adhesion. When PEpc was used, the same effect was observed because the oxidative degradation products present in this material may have reacted with the terminal amine groups of PA-6 to improve the phase interaction.

Finally, PEpc could be used to make blends with PA-6, and the final properties of this blend represented an improvement in the relation of blends of PA-6 with HDPE prepared with a compatibilizer. This is an important result because it stimulates the use of postconsumer PE in a high-value product such as this blend and may promote a reduction in plastic waste deposition.

References

1. Mark, F.; Bikales, N. T. M.; Berger, C. G. O.; Merges, G. Encyclopedia of Polymer Science and Engineering, 2nd ed.; Wiley: New York, 1989; Vol. 12, p 399.
2. Jiang, C.; Filippi, S.; Magagnini, P. Polymer 2003, 44, 2411.
3. Scafaro, R.; Mistreta, M. C.; La Mantia, F. P. Macromol Chem Phys 2006, 21, 1986.
4. Rezende, C. A.; Schuchardt, U. F.; Gonçalves, M. C. J Appl Polym Sci 2006, 102, 2142.
5. Vallim, M. R.; De Paoli, M. A. Anais Reunião Anual Soc. Brás. Quím. Poços de Caldas, Brazil, 1998, 21, 120.
6. Kudva, R. A.; Keskkuda, H.; Paul, D. R. Polymer 1999, 41, 225.
7. Valenza, A.; Geuskens, G.; Spadaro, G. Polymer 1997, 33, 957.
8. Jurkowski, B.; Kelar, K.; Ciesielska, D. J Appl Polym Sci 1998, 69, 719.
9. Chiono, V.; Filippi, S.; Yordanov, H.; Minkova, L.; Magagninni, P. Polymer 2003, 44, 2426.
10. Billingham, N. C.; Calvert, P. D. In: Degradation and Stabilization of Polyolefins; Allen, N. S., Ed.; Applied Science: London, 1983; Chapter 1.
11. Armat, R.; Moet, A. Polymer 1993, 34, 977.