

Polyethylene/Polyamide-6 Blends Containing Mercapto-Modified EVA

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SYNOPSIS

The effect of poly(ethylene-co-vinyl alcohol-co-vinyl mercaptoacetate) (EVASH) on the compatibilization of nylon-6 (PA6)/low-density polyethylene (LDPE) was investigated. EVASH was prepared from hydrolyzed EVA through an esterification reaction with mercaptoacetic acid. Mechanical properties, differential scanning calorimetry, and scanning electron microscopy results are discussed. The mechanical properties were improved with the addition of EVASH. The compatibilizing agent also affects the crystallinity degree of both components of the blend, as indicated by the results obtained from DSC studies. The addition of EVASH results in a reduced dispersed-phase particle size. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyamide-6 is normally blended with polyolefins to improve several important properties such as processability, impact resistance, low moisture absorption, and barrier properties. Since these polymers are inherently incompatible, special blend compatibilizers must be added during melt processing to provide the required interfacial adhesion between the polymer matrix and the dispersed phase and to enhance the dispersion of the incompatible blend component.

Most of the compatibilizing agents employed for these purposes are constituted of polyolefins, thermoplastic elastomers, and elastomers functionalized with maleic anhydride.¹⁻¹⁰ These functional groups react with the amine end groups of the polyamide, giving rise to strong links between the two phases. The introduction of these functional groups along the polymer backbone is normally performed by reacting the polymer with maleic anhydride in the presence of free-radical promoters.¹⁰ This process does not provide an efficient control of func-

tionalization. In addition, by using reactive extrusion, some polymer degradation or crosslinking may occur during the functionalization process in the melt.

Recently, an EVA-based functionalized polymer containing mercapto groups along the backbone was developed in our laboratory.¹¹ The synthesis employed a simple esterification reaction between hydrolyzed EVA and mercaptoacetic acid. This new copolymer, namely, poly(ethylene-co-vinyl alcohol-co-vinyl mercaptoacetate) (EVASH) was employed either as a reactive compatibilizing agent for natural rubber/EVA blends¹² or as a precursor for the graft copolymer to be used as a nonreactive compatibilizing agent.^{11,13,14}

This work deals with the ability of EVASH in enhancing the mechanical properties of low-density polyethylene (LDPE)/polyamide-6 (PA-6) blends. It is believed that the EVA backbone in EVASH has some physical affinity with the LDPE phase because of the high polyolefin character of the EVA used on EVASH synthesis. On the other hand, the polar SH groups along the EVASH backbone are expected to interact with the PA-6 phase in the blend. The compatibilization effect of EVASH on thermal and morphological properties was also investigated.

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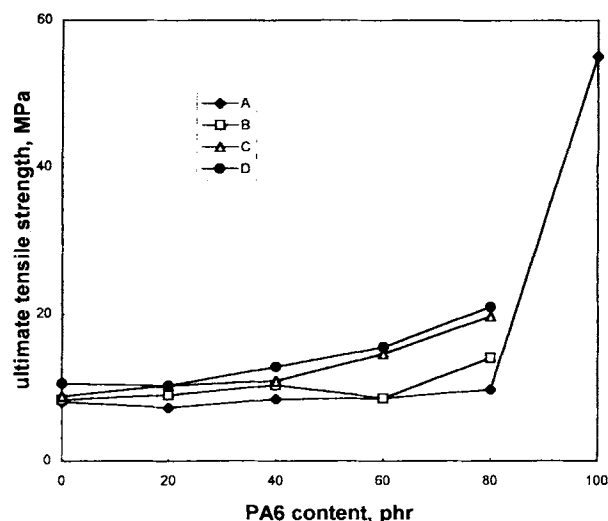


Figure 1 Ultimate tensile strength as a function of blend composition for (A) uncompatibilized PA6/LDPE blends and compatibilized blends with (B) 1%, (C) 5%, and (D) 10% of EVASH.

EXPERIMENTAL

Materials

Low-density polyethylene (LDPE) (melt flow index = 2.7 g/10 min at 190°C), supplied by PPH/Poli-olefinas, and polyamide-6 (PA6) (melt flow index = 4.1 g/10 min at 235°C), supplied by De Millus S.A., were dried at 80°C under vacuum for 24 h. Poly(ethylene-co-vinyl acetate) (EVA) (melt flow index = 2.1 g/10 min at 180°C; acetate content = 18 wt %), supplied by Petroquímica Triunfo S.A., were employed on EVASH preparation. EVASH samples with different SH content were synthesized from hydrolyzed EVA by esterification with mercaptoacetic acid, according to the literature.¹²

Blend Preparation

The blends were prepared on a Brabender Plastimeter 821100 equipped with a mixing head heated at 250°C. The polymers were added at a rotor speed of 20 rpm for 1 min, following the order PA6/EVASH/LDPE. After melting, the speed was increased to 60 rpm and blending was performed for 4 min. Samples were compression-molded at 250°C for 2 min into sheet of 0.9 mm thickness. The blends are designated as P_{100} , P_{80} , P_{60} , P_{40} , P_{20} , and P_0 , where the subscripts denote the weight % of PA6. Blends with 10 phr of EVASH at the corresponding compositions were designated P'_{100} , P'_{80} , P'_{60} , P'_{40} , P'_{20} , and P'_0 .

Testing and Characterization

Tensile testing was performed on an Instron apparatus 4204 in accordance with ASTM D882-83, using a crosshead speed of 50 mm min⁻¹. All tests were carried out on samples conditioned for 2 days at room conditions (25°C and 60% relative humidity). All results were the average of at least five measurements.

The differential scanning calorimetry (DSC) measurements were carried out under nitrogen with a Perkin-Elmer DSC-7. For this study, the samples were programmed-heated at 10°C/min to 250°C, then cooled at 10°C/min to 25°C and heated again at the same rate for a second time.

For scanning electronic microscopy analysis, the samples were immersed in liquid nitrogen for about 20 min, then fractured and the surface coated by gold vapor. Micrographs were taken by a JEOL 5300 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Mechanical Properties

The effect of EVASH addition on ultimate tensile strength, σ_B , for LDPE/PA6 blends with different compositions is shown in Figure 1. For these studies, an EVASH sample containing 65.4 mmol SH/100 g was employed. Increased ultimate tensile strength with EVASH addition was observed. This effect is more pronounced at higher EVASH concentration

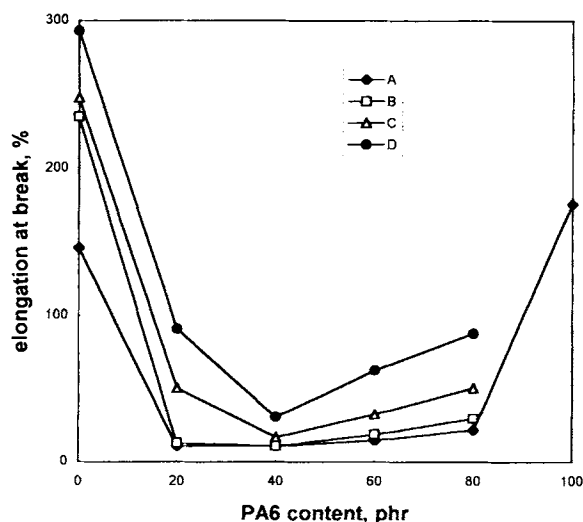


Figure 2 Elongation at break as a function of blend composition for (A) uncompatibilized PA6/LDPE blends and compatibilized blends with (B) 1%, (C) 5%, and (D) 10% of EVASH.

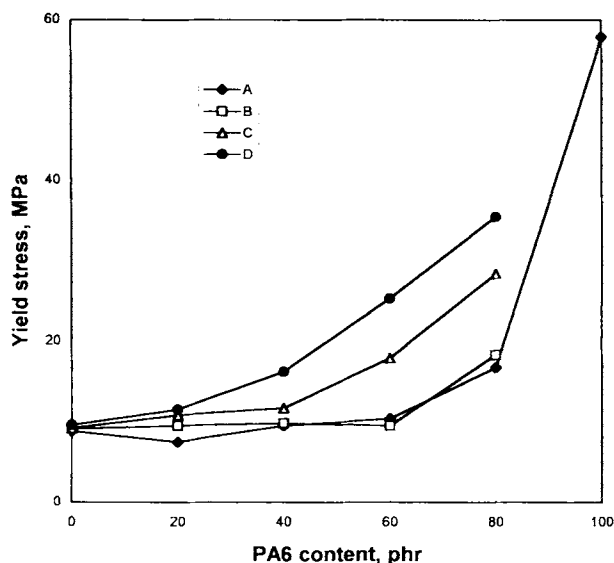


Figure 3 Yield stress as a function of blend composition for (A) uncompatibilized PA6/LDPE blends and compatibilized blends with (B) 1%, (C) 5%, and (D) 10% of EVASH.

and higher PA6 proportion. The presence of EVASH also increases the elongation at break, ϵ_B , as illustrated in Figure 2. These results indicate an increase in toughness, which is defined as the area beneath the stress-strain curve. The increased elongation and ultimate tensile strength suggest an improvement of interfacial interaction promoted by EVASH, as stated in several other compatibilizing systems.^{3,7}

Yield stress and the Young's modulus are plotted as functions of blend composition in Figures 3 and

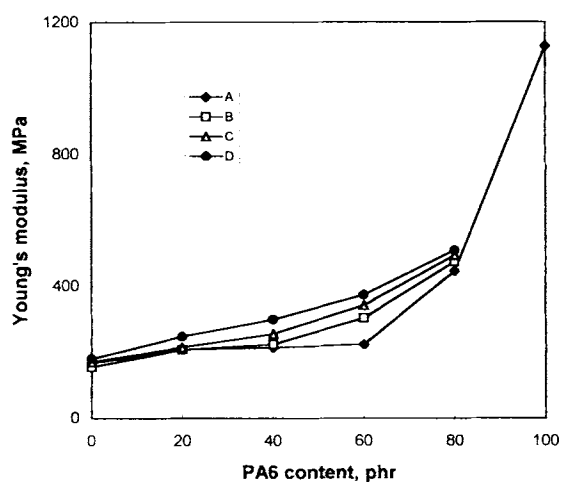


Figure 4 The Young's modulus as a function of blend composition for (A) uncompatibilized PA6/LDPE blends and compatibilized blends with (B) 1%, (C) 5%, and (D) 10% of EVASH.

Table I Effect of SH Content on the EVASH Backbone on Tensile Properties of PA6/LDPE (20 : 80 phr) Blends

EVASH				
phr	[SH] mmol/100 g	σ_B (MPa)	ϵ_B (%)	E^a (MPa)
0	—	7.3 ± 1.6	11 ± 1	207 ± 7
5	0 ^b	9.1 ± 0.5	11 ± 1	182 ± 3
5	13.8	9.8 ± 1.2	15 ± 1	208 ± 1
5	41.7	9.7 ± 0.3	33 ± 1	212 ± 5
5	65.4	10.8 ± 1.4	51 ± 3	215 ± 5

^a Young's modulus values.

^b EVOH with 229 mmol OH/100 g.

4, respectively. In both cases, an improvement of these values was observed with increasing EVASH concentration. A more pronounced difference on the Young's modulus values between compatibilized and uncompatibilized polymer blends was observed for PA6/LDPE (60 : 40 phr) blends. As reported in the literature,¹⁵ this composition is near the phase inversion (cocontinuity). Blends at cocontinuous phase morphology behave as a physical interpenetrating network (IPN).¹⁶ In the presence of a compatibilizing agent, this morphology can be stabilized as a result of interfacial adhesion, increasing the stiffness of the material.

The compatibilization of PA6/LDPE blends with a styrene-(ethylene-*co*-butylene)-styrene block copolymer functionalized with 2% of maleic anhydride (MA-SEBS) was reported in the literature.⁷ In this system, the authors observed a decreasing modulus and yield stress with MA-SEBS addition, probably because of the elastomeric nature of the compati-

Table II Percentage of Extracted PA6 as a Function of Blend Composition for Uncompatibilized and Compatibilized PA6/LDPE Blends

Blend Composition (phr)		Percentage of Extracted PA6	
PA6	LDPE	Without EVASH	With 5 phr EVASH
80	20	100	90
60	40	75	46
40	60	64	27
20	80	14	12

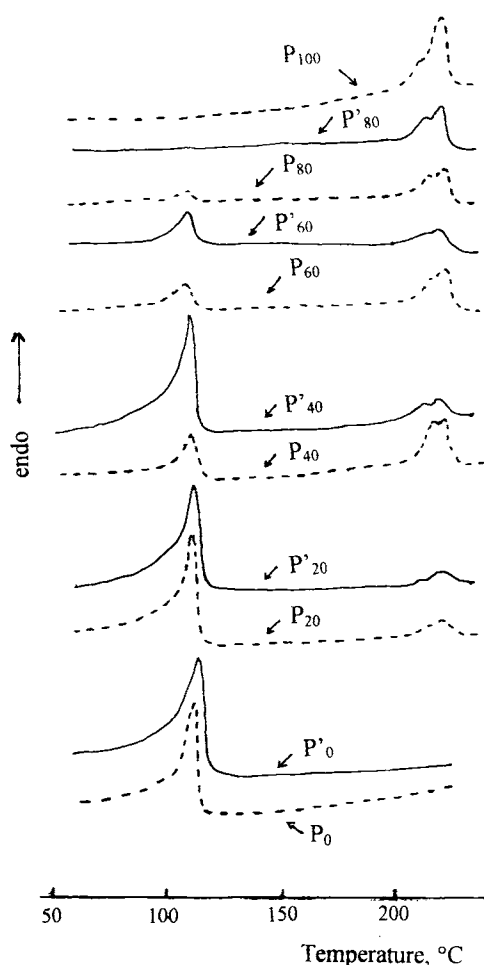


Figure 5 Melting endotherms of uncompatibilized and compatibilized PA6/LDPE blends as a function of blend composition. The code number denotes the proportion of PA6 in the blend (see Experimental part).

bilizing agent. The higher modulus and yield stress values found in our system may be attributed to the semicrystalline nature of the compatibilizing agent that should cocrystallize at the PA6/polyethylene interface. This explanation was suggested by Mülhaupt et al. for the PA6/polypropylene system compatibilized with succinic anhydride-terminated oligopropenes.⁴ In that system, the authors also found a higher Young's modulus and yield stress values with high stereoregular isotactic oligopropenes when compared with the atactic one.

As pointed out at the beginning of this discussion, the EVASH sample employed in this previous study contains 65.4 mmol SH/100 g. Considering that the hydrolyzed EVA (EVOH) employed on its preparation contains 229.0 mmol OH/100 g, the SH content incorporated in this sample corresponds to 30 mol % of the initial OH. It means that the EVASH

used as the compatibilizing agent presents a high nonesterified OH content in the backbone. These groups can also interact with the PA6 phase through hydrogen bonding. To verify the influence of SH groups on compatibilization of PA6/LDPE blends by EVASH, some experiments were performed with EVASH samples with different SH content. For comparison, hydrolyzed EVA (EVOH) was also employed as the compatibilizing agent. Table I presents the results on mechanical properties of PA6/LDPE (20 : 80 phr) blends, containing 5 phr of the compatibilizing agent (EVOH or EVASH). The presence of 5% EVOH brought about an improvement on the ultimate tensile strength, whereas the modulus was decreased. The incorporation of mercaptoacetate groups along the backbone of EVOH does not cause dramatic improvement on ultimate tensile strength, but increases both the Young's modulus and elongation-at-break values of compatibilized PA6/LDPE blends. These last properties were increased with increasing the SH content on the EVASH backbone. The elongation at break is more sensitive to the effect of the chemical structure of the compatibilizing agent.

The better efficiency of EVASH on this blend compatibilization may be attributed to the ability of the SH groups in reaching the PA6 phase, compared to OH groups. EVASH at the interface continues to diffuse into the LDPE phase because of the better affinity between both components. The interaction between PA6 and the compatibilizing agent may occur only through either OH or SH groups along the EVASH backbone. The SH groups should be more available for this kind of interaction because of the presence of $-\text{OOCCH}_2-$ groups as spacers between SH groups and the EVASH backbone.

Extraction Experiments

Several reports in the literature suggest that, during melt blending of PA6 with a functionalized polymer with maleic anhydride, a reaction takes place between the amine end group of PA6 and the anhydride group, thus forming an imide bond.⁹ This graft copolymer formed *in situ* is essential for the interfacial adhesion.

The effectiveness of interaction between EVASH and PA6 was also investigated in this report by performing selective extraction experiments with formic acid. This solvent is able to extract only the PA6 phase. Compression-molded samples were submitted to extraction to observe also the phase-inversion composition. This procedure is a well-known

Table III Thermal Properties of PA6/LDPE as a Function of Blend Composition^a

Blend	Without EVASH						With 10 phr EVASH ^b					
	P100	P80	P60	P40	P20	P0	P'80	P'60	P'40	P'20	P'0	
PA6	T_m (°C)											
	α -Form	221	221	221	220	220	220	220	218	217		
	γ -Form	214	214	214	215	213	213	212	211	208		
	ΔH_m (J/g)											
	Exp.	48.4	45.6	42.4	35.5	9.8	49.3	27.3	15.6	7.6		
	Theor.		(39)	(29)	(19)	(9.7)	(39)	(29)	(19)	(9.7)		
	T_c (°C)	182.4	186.0	186.0	189	186.7	186.0	184	188	181		
	ΔH_c (J/g)											
	Exp.	54.1	50.4	47.6	37.7	8.5	54.3	23.9	2.5	5.4		
	Theor.		(43.3)	(32.5)	(21.6)	(10.8)	(43.3)	(32.5)	(21.6)	(10.8)		
LDPE	T_m (°C)		110.2	110.0	110	111	111	—	110	110	111	112
	ΔH_m (J/g)											
	Exp.		9.1	22.0	24.0	65.2	81.7	—	29.5	70.0	71.3	79.7
	Theor.		(16.3)	(32.7)	(49)	(65.3)			(32.7)	(32.7)	(49)	(81.7)
	T_c (°C)		96.0	95.0	96.0	96.6	95.0	—	96.5	96.4	96.3	95.9
	ΔH_c (J/g)											
	Exp.		7.2	20.0	25.0	64	78.5	—	28.8	64.2	64.2	77.7
	Theor.		(15.7)	(31.4)	(47.1)	(63)			(31.4)	(47.1)	(63)	(78.5)

^a The number of the blend code corresponds to the proportion of PA6 in the blend; EVASH with 65.4 mmol SH/100 g; T_m = melting temperature; ΔH_m = heat of fusion; T_c = crystallization temperature; ΔH_c = heat of crystallization.

^b Thermal properties of EVASH: T_m = 112°C; ΔH_m = 86.75 J/g; T_c = 99.6; ΔH_c = 82.4 J/g.

method for determining dual-phase continuity.¹⁷ Table II presents the percentage of extracted PA6 phase as functions of blend composition. The specimens constituted by PA6/LDPE (80 : 20 phr) blends were completely destroyed under formic acid, indicating a morphology in which LDPE are dispersed into the PA6 matrix. The other compositions kept their original shapes after 1 week extraction, indicating continuity of the LDPE phase. For the PA6/LDPE (60 : 40 phr) blend without EVASH, a high amount of PA6 was extracted without losing its dimensional stability. As pointed out in several reports,¹⁷ this behavior suggests a morphology near the dual-phase continuity. This morphology may be responsible for the greater difference on the Young's modulus observed in compatibilized and uncompatibilized PA6/LDPE blend at this composition.

As also indicated in Table II, the EVASH addition decreases the percentage of the PA6-extracted phase for the same blend composition. In addition, the formic acid layer presented as a white colloidal suspension in experiments performed with PA6-richer blends containing EVASH. According to the literature, this behavior is an indication that some grafting reaction has taken place.⁹ These results suggest a chemical reaction rather than hydrogen bonding between PA6 and EVASH.

Thermal Analysis

All the components of polymer blends studied in this work exhibit a semicrystalline feature. For crystalline/crystalline polymer blends, a mutual effect of crystallization behavior between the two components may exist. Thus, it is important to observe the effect of EVASH on melting and cooling behaviors of both components. The melting and cooling characteristics of the blends and the pure components were recorded using differential scanning calorimetry. Figure 5 compares the heating scan of compatibilized and uncompatibilized PA6/LDPE blends as a function of blend composition. LDPE and PA6 exhibit two separate melting endotherms around 110 and 220°C, respectively. The positions of the peaks are not affected by the blend composition. The melting endotherm of pure PA6 appears as a main peak at 220°C and a shoulder at 214°C, corresponding to α - and γ -form crystals, respectively.¹⁸ The shoulder peak is more distinctive in the blends. The presence of EVASH does not change the position of the main melting peak of PA6 at 220°C for PA6-richer blends, but slightly decreases the intensity of the shoulder peak. In addition, there is a broadening of the overall melting peak and a displacement of the position of the shoulder peak toward lower temperature. These effects are more significant in blends with a higher proportion of

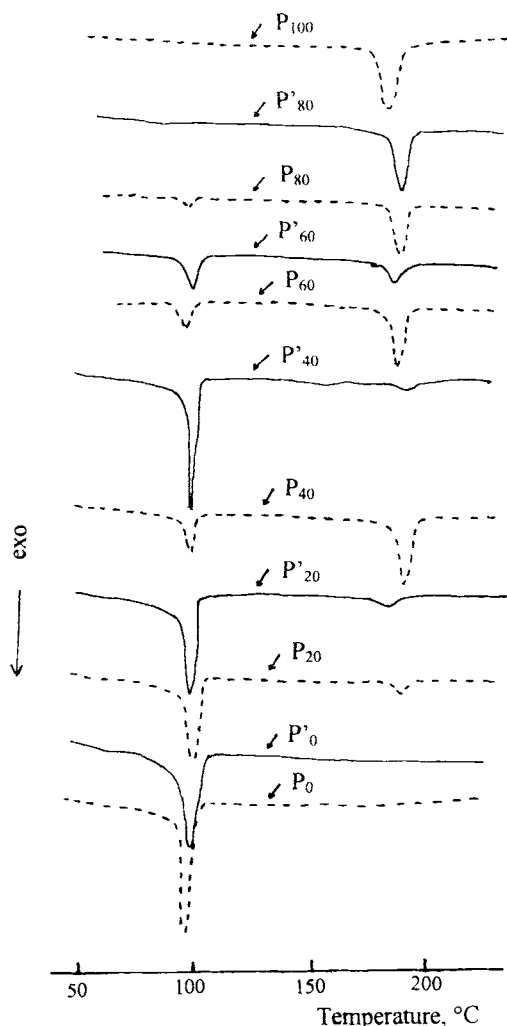


Figure 6 Crystallization exotherms of uncompatibilized and compatibilized PA6/LDPE blends as a function of blend composition. The code number denotes the proportion of PA6 in the blend (see Experimental part).

LDPE, as presented in Table III. At these compositions, a slight decrease on the main peak melting temperature is also observed.

The most striking results have been found with the heat of fusion, ΔH_m . Except for the PA6/LDPE (20 : 80 phr) blend, the PA6 component in uncompatibilized blends presents higher ΔH_m values than does the theoretical one, which means a higher crystallinity degree. On the other hand, the LDPE component exhibits a decreasing crystallinity degree, except for the blend with a higher LDPE proportion. The addition of EVASH results in a decreased ΔH_m of the PA6 phase and an increased ΔH_m of the LDPE phase, except for PA6/LDPE (80 : 20 phr).

Similar results were reported in the literature for PA12/polypropylene (1/3 w/w) blends compatibil-

ized with a graft copolymer of PP-MA and poly(ethylene oxide).⁵ The authors suggested an increase on nucleation of PP by the polyamide with the compatibilization. In our system, this phenomenon could be also explained by the crystalline characteristic of the compatibilizing agent.

For blends where PA6 forms the matrix, there is conflicting behavior: The crystallinity degree of PA6 increases with the compatibilization while the crystalline endotherm of LDPE phase is completely suppressed. Similar blends reported in the literature present a decreasing crystallinity degree of both phases after compatibilization with MA-SEBS.⁷ The authors studied PA6/LDPE blends with a high amount of PA6 (PA6/LDPE = 75 : 25%).⁷ The higher crystallinity degree of the PA6 phase on the compatibilized (PA6/LDPE = 80 : 20 phr) blend found in our experiments may also be attributed to the influence of the crystalline characteristic of the compatibilizing agent. The ΔH_m value of EVASH is higher than the corresponding ΔH_m values of both blend components, as indicated in Table III. It is suggested that EVASH promotes a better LDPE phase dispersion, decreasing the ability of LDPE crystallization.

The cooling scans are illustrated in Figure 6. The crystallization exotherm of the LDPE phase appears at around 95°C and seems to be independent of both blend composition and the presence of EVASH. The peak crystallization temperature of pure PA6 appears at 182°C. Uncompatibilized PA6/LDPE blends present crystallization exotherms of the PA6 phase shifted to higher temperatures around 188°C. The increasing of T_c of PA6 in uncompatibilized blends was also reported in the literature for PA6/high-density polyethylene⁸ and PA6/polypropylene.¹⁹ The addition of EVASH decreases the crystallization temperature of the PA6 phase as a result of strong interaction between the EVASH and the PA6 phase. These interactions retard the crystallization rate of PA6 and decrease also ΔH_c , as indicated in Table III. The LDPE phase presents higher ΔH_c values, related to uncompatibilized blends, as an indication of the nucleation effect on this phase promoted by the compatibilization. This behavior was also related by Moon and co-workers in PA6/polypropylene compatibilized blends.¹⁹

Concerning PA6-richer blends (PA6/LDPE = 80 : 20 phr), the effect of EVASH addition on the crystallization behavior of both LDPE and PA6 phases is different. The LDPE phase presents a strong decreasing of ΔH_c , probably because of a better dispersion of this phase in PA6 matrix. On the other

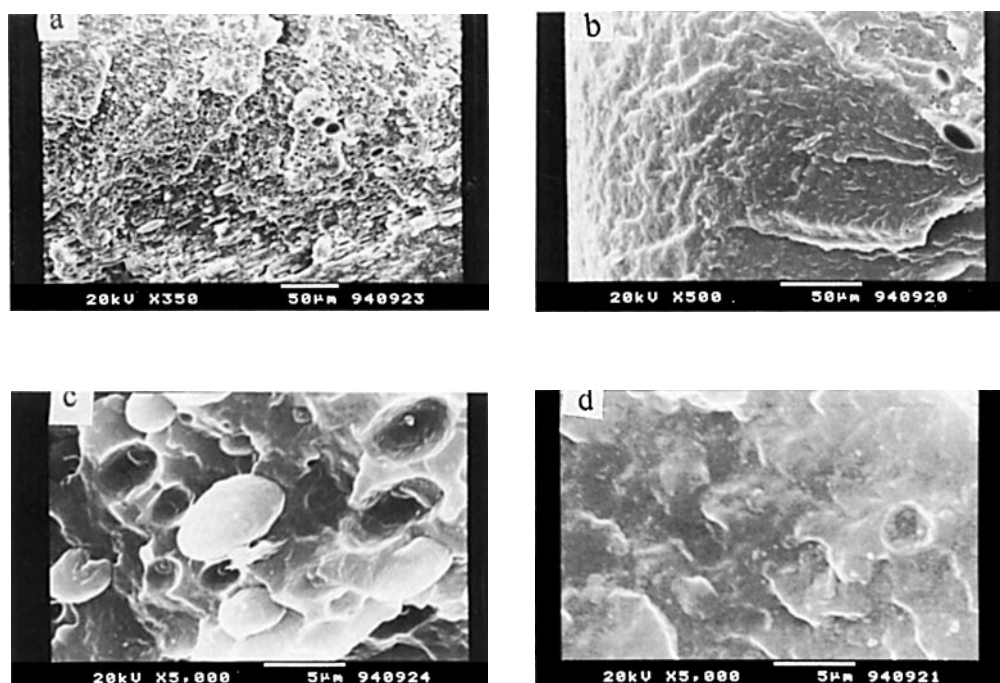


Figure 7 Scanning electronic microscopy of LDPE/PA6 (20 : 80 phr) blends (a,c) pure and (b,d) with 5% of EVASH ($[SH] = 65.4$ mmol/100 g).

hand, the ΔH_c of the PA6 phase increases. At this blend composition, the minor component, LDPE, or the compatibilizing agent, EVASH, acts as a nucleating agent for the PA6 phase. As heterogeneous nucleation is a surface behavior, the addition of the compatibilizing agent decreases the size of dispersed phase (LDPE) and increases the interface area, which promotes the crystallization of PA6.

SEM of the Blend Morphology

Figure 7 illustrates the difference in sample morphology with the addition of EVASH to PA6/LDPE (80 : 20 phr) blends. The freeze-fractured surface of the uncompatibilized blend [Fig. 7(a)] presents holes, indicating lack of adhesion between the two phases. The addition of EVASH improves the dispersion of both phases, as noted in Figure 7(b). Indeed, the fracture surface of the compatibilized blend, after 10 times magnification [Fig. 7(d)], shows no discernible domains, indicating compatibility at this scale.

CONCLUSIONS

EVASH exerts a strong influence on the mechanical properties of PA6/LDPE blends. The compatibilizing effect increases with increasing the EVASH

concentration. Both the Young's modulus and yield stress increase with the compatibilization. These phenomena are more pronounced at PA6-richer blends. The compatibilization effect of EVASH was also confirmed by scanning electronic microscopy of the freeze-fractured surface of PA6/LDPE (80 : 20 phr) blends. Thus, the increasing of the Young's modulus and yield stress may be attributed to the crystalline nature of the compatibilizing agent. Indeed, the DSC studies indicate an increasing crystallinity degree of the PA6 phase with the addition of EVASH for the PA6/LDPE (80 : 20 phr) blend. In addition, the DSC results suggest a better dispersion of the LDPE phase promoted by the compatibilizing agent. Due to the poor affinity between the PA6 phase and EVASH, the interactions should happen through the polar groups of the compatibilizing agent situated at the interface. The crystals of the compatibilizing agent at the interface may be acting as a nucleating agent for the PA6 phase, increasing the heat of crystallization of this phase. This phenomenon does not cause an increasing on crystallization temperature of the PA6 phase, probably because of the lower crystallization temperature of EVASH, compared to PA6.

When PA6 becomes the dispersed phase, the crystallization temperature and crystallinity of PA6 decrease with EVASH addition as a result of a better phase dispersion. On the other hand, the LDPE

phase presents increased crystallinity. It is worth pointing out the crystalline feature of the compatibilizing agent. In addition, the melting scan of the LDPE/EVASH (100 : 10 phr) blend presented in Figure 5 shows only one endotherm peak, suggesting cocrystallization between these components. Thus, increased LDPE crystallinity may be explained by a nucleating effect of the PA6/EVASH system on the LDPE phase and a cocrystallization phenomenon between EVASH and LDPE.

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