

Properties and Morphology of Poly(ethylene terephthalate) and High-Density Polyethylene Blends

CARLOS GUERRERO, TOMÁS LOZANO, VIRGILIO GONZÁLEZ, ELIUD ARROYO

Universidad Autónoma de Nuevo León, FIME, Pedro de Alba S/N, Cd. Universitaria, San Nicolás, N.L., 66450 México

Received 17 July 2000; accepted 11 December 2000

ABSTRACT: Blends of poly(ethylene terephthalate) (PET) and high-density polyethylene (HDPE) with and without a compatibilizing agent were studied. Both materials are widely used in the soft drink bottle industry. The compatibilizing agent was a copolymer of ethylene and methacrylic acid partially neutralized with zinc (Surlyn). The olefinic segment of Surlyn is compatible with HDPE, whereas the Surlyn carboxylic acid groups is affine with the PET carbonyl groups. The effectiveness of the compatibilizing agent was evaluated using different techniques, such as infrared spectroscopy, differential scanning calorimetry, scanning electron microscopy, and mechanical properties. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1382–1390, 2001

Key words: blends; compatibilization; morphology; PET; HDPE; Surlyn

INTRODUCTION

Polymer blends consist of mixtures of homopolymers or copolymers which are, in most cases, thermodynamically immiscible. Usually, the immiscible blends form a two-phase system with a minor phase with poor physical and mechanical properties due to weak adhesion at the interface. Compatibilization is generally needed to improve the adhesion and enhance the properties of polymer blends. Different methods can be employed for achieving such compatibilization. Functionalization of the blend components before blending^{1–4} or the addition of a copolymer during blending^{5–11} promotes, in most cases, compatibilization in multiphase systems. Compatibilization through *in situ* reactions during melt blending is also becoming very important and may result in the formation of copolymers primarily located at the interface.^{12–19}

Blends of polyolefins and poly(ethylene terephthalate) (PET) have attracted considerable research activity,^{3,5,6,11,19,20} probably because they are placed among the most consumed plastics.^{21–23} PET is widely used in the packaging and electronic industries; it presents, among other properties, good tensile and impact strength, stiffness, printability, and a very good gas barrier. On the other hand, high-density polyethylene (HDPE) is a polyolefin widely employed in the packaging and the injection-molding industries. It is a very good moisture barrier and presents very good tensile and impact strength. A blend of these two materials could offer a very attractive balance of mechanical and barrier properties; nevertheless, PET and HDPE are immiscible. Compatibilization of this blend is necessary for commercial applications.

In this work, we studied the effectiveness of a third component acting as a compatibilizing agent. This material would be affine with the components of the immiscible blend. We chose a copolymer of ethylene and 6.5 wt % of methacrylic acid partially neutralized with zinc (Surlyn) because specific interactions between the olefinic segment of Surlyn with the HDPE are expected, whereas the carboxylic acid groups will be affine

Correspondence to: C. Guerrero et al.

Contract grant sponsor: Mexican Science and Technology Council (CONACyT); contract grant number: 28188-U.

Contract grant sponsor: Universidad Autónoma de Nuevo León's Science and Technology Research Program (PAICyT); contract grant number: CA082.

Journal of Applied Polymer Science, Vol. 82, 1382–1390 (2001)
© 2001 John Wiley & Sons, Inc.

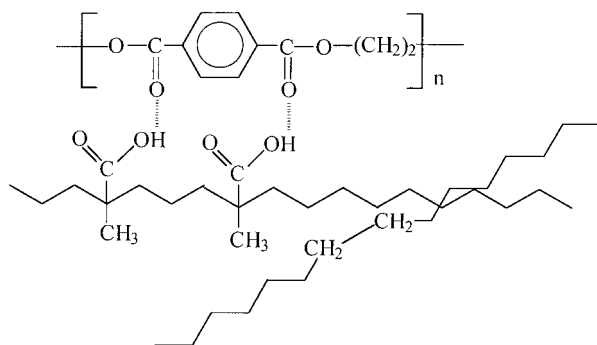


Figure 1 Expected interactions between carbonyl groups of PET and carboxylic acid groups of Surlyn.

with similar PET functional groups. Figure 1 shows the expected interactions. The compatibility of the blend was analyzed using infrared spectroscopy (IR), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The mechanical behavior of the blends was also analyzed.

EXPERIMENTAL

Materials

PET (86N, Artega Specialties, KoSa) and HDPE (PEAD 60120, Petróleos Mexicanos, Mexico D.F., México) were the blend components used in this study. PET is a blow-molding-grade material with a melt flow index (MFI) of 12.3 g/10 min (270°C/2.16 kg), an intrinsic viscosity of 0.81 dL/g, $M_n = 14,155$, and $M_w = 69,039$. HDPE is an injection-molding-grade homopolymer with a wide molecular weight distribution, MFI = 12.0 g/10 min (190°C/2.16 kg), $M_n = 6087$, and $M_w = 73,532$. The compatibilizer agent was a copolymer of ethylene and 6.5 wt % of methacrylic acid partially neutralized with zinc (Surlyn 1652, DuPont, Mexico D.F., México). All the resins were obtained from Mexican Suppliers (Mexico City, Mexico).

Blend Preparation

Prior to blending, the materials were dried under a vacuum at a temperature of 90°C overnight. Blending of the samples was carried out using a 50-mL Haake chamber. The mixed resin pellets were melt-blended in the chamber using roller blades. A typical blending experiment consists of the following steps: The mixture was fed into the mixing chamber (one-step mixing) initially set at 270°C with the blades turning at 50 rev min⁻¹. Once all the resin was added, the blending pro-

cess was conducted for 300 s, the time necessary to reach a constant torque value. Then, the melt was crushed in a Brabender mill. Preliminary tests were done with 2.5, 5.0, and 7.5 wt % of the compatibilizing agent based on the total weight of the blend. Morphological observations (homogeneity and size of the dispersed phase) of the blends prepared with these Surlyn compositions showed that 7.5 wt % of Surlyn (by 7 net wt %) was sufficient to achieve the desired compatibilization of PET and HDPE. Therefore, on subsequent analysis, the concentration of this blend component was held constant. Table I shows the composition of the different analyzed blends.

IR

IR analyses (Nicolet 710 FTIR) on thin films of components and blends (compression-molded) were carried out at a resolution of 2 cm⁻¹. A minimum of 50 scans were averaged.

DSC

The transition temperatures of the components and blends were determined using a DSC (Perkin-Elmer DCS-7). Two heating scans were performed at a rate of 10°C/min on samples of 10–15 mg. The first heating was made to erase the thermal history of the sample. The measurements correspond to the second melting curve. The crystallinity of the components, PET and HDPE, was calculated from the area under the melting peaks. The values of 120 J/g as the heat of fusion of the 100% crystalline PET²⁴ and 291 J/g for the 100% crystalline HDPE²⁵ were assumed.

SEM

Blend morphologies were examined using an SEM equipment (LEO Stereoscan 440). The samples were fractured in liquid nitrogen and coated with an ultrathin layer of a gold-palladium alloy.

Table I Composition of the Analyzed Blends (wt %)

PET	HDPE	Surlyn
75	25	0
75	25	7.5
50	50	0
50	50	7.5
25	75	0
25	75	7.5

Mechanical Properties

Injection-molded specimens were tested following ASTM standards for tensile properties (D638) and notched Izod impact strength (D256). The reported values for all properties are the average of five measurements. Samples were tested without special conditioning.

RESULTS AND DISCUSSION

Mixing torque data for the blends with and without Surlyn are shown in Figure 2. In all cases, once the equilibrium was reached, the compatibilized blends required a higher mixing torque. It is well known²⁶ that an incompatible blend, characterized by no interaction between phases, fre-

quently exhibits an interlayer slip. This promotes a reduction of the viscosity of the blend. The fact that the torque and, hence, the viscosity had increased indicates that there is less slippage at the interface as a result of the addition of Surlyn. This suggests the existence of specific interactions at the interface between the polymers.^{13,19}

Figure 3 shows FTIR transmittance spectra for compatibilized and uncompatibilized blends. In the ternary blends, attention must be paid to the broadening of the PET carbonyl band at about 1725 cm^{-1} . This is more evident when the PET content is higher [Fig. 3(a)]. Displacements to the lower frequencies of the functional group bands usually with increased intensity and band widening are indicative of hydrogen bonding.²⁷ Thus, the modification of the width at half-height of the

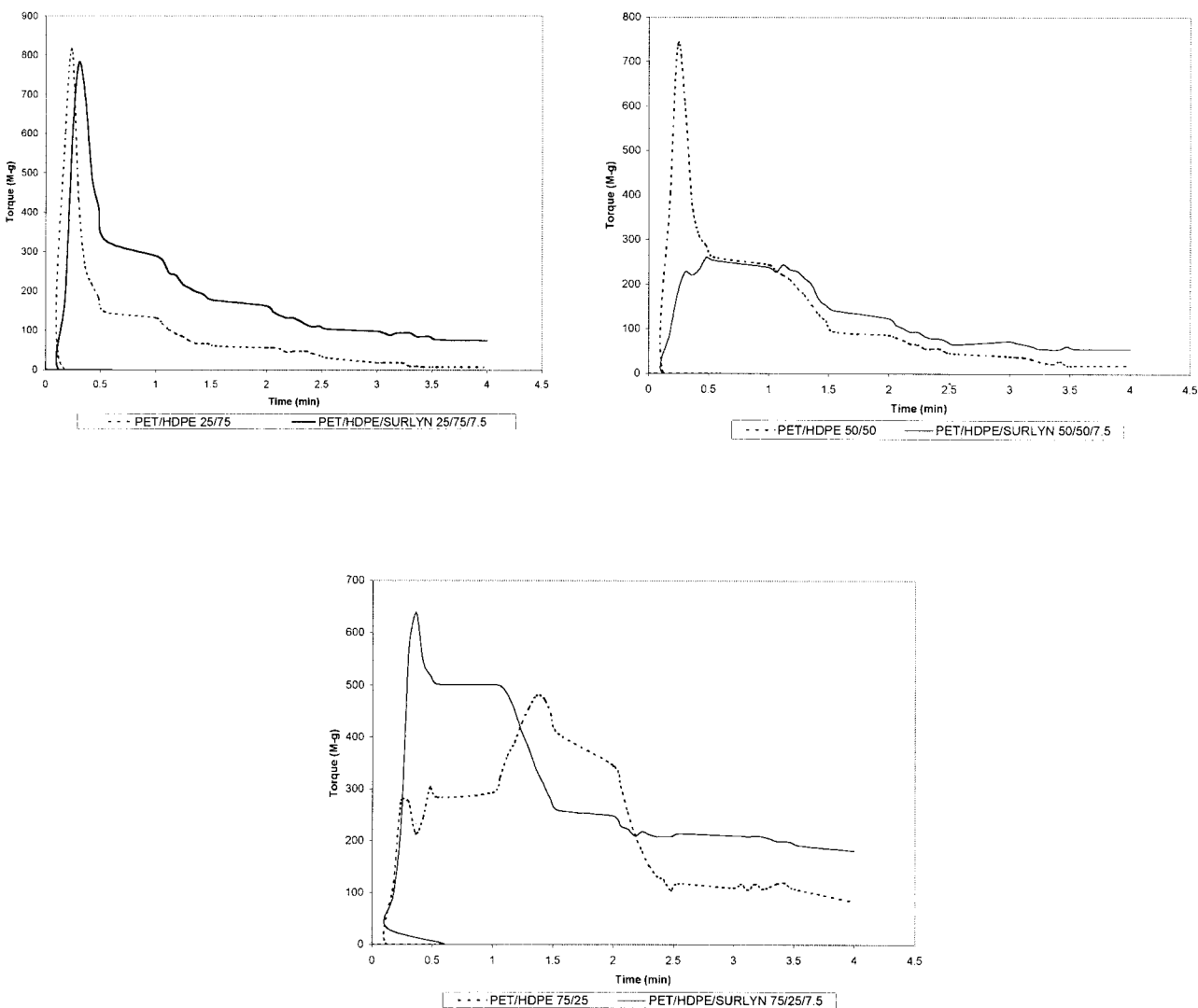


Figure 2 Measured mixing torque for compatibilized and uncompatibilized blends.

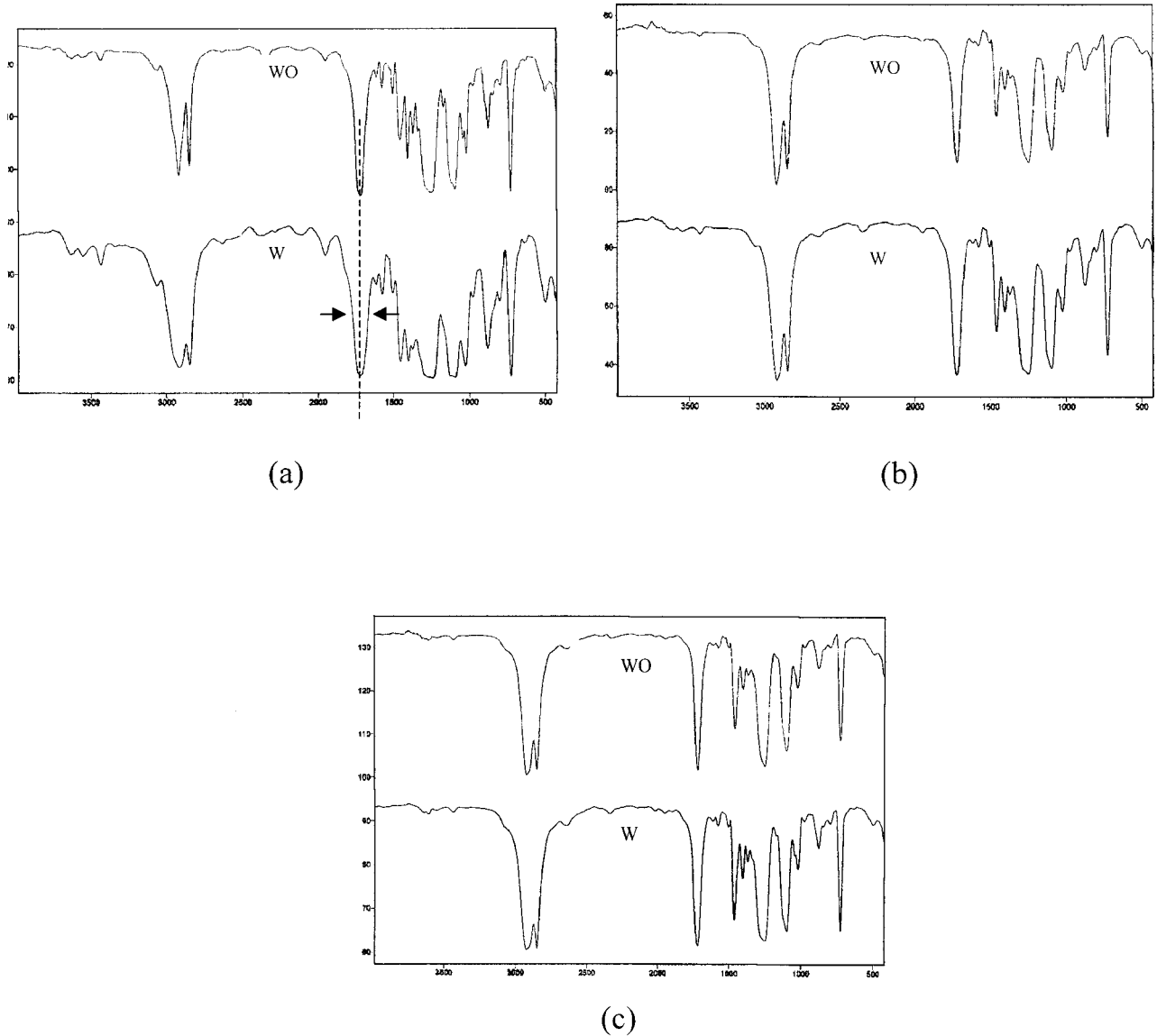


Figure 3 FTIR spectra for the blends: (a) 75 PET/25 HDPE; (b) 50 PET/50 HDPE; (c) 25 PET/75 HDPE. WO, without Surlyn; W, with 7.5% Surlyn.

PET carbonyl band with the addition of Surlyn could be attributed to the hydrogen bonding between this functional group and the OH from the carboxylic acid of Surlyn. Then, it is expected that decrements in the PET content translates to a diminution of interactions because there will be fewer carbonyl groups to interact. In fact, Figure 3(c) (25% of PET) practically did not exhibit any change in the width of the PET carbonyl band.

Melting curves of different blends are shown in Figure 4. Each melting trace is characterized by two peaks: one peak around 130°C corresponding to HDPE and the other at higher temperature, around 247°C, corresponding to PET. It can be

seen that the compatibilized blends present displacements to the lower temperatures in PET and HDPE melting points (see Table II). Notice the displacement of around 3°C for a PET content to 50% and around 2.6°C for an HDPE content to 50%. This behavior is indicative of the compatibility between components.²⁸ The degree of crystallinity ($1 - \lambda$), for each component of the blend evaluated as the ratio of their measured enthalpy of fusion, normalized with respect to the weight fraction of each crystalline material, divided by the enthalpy of fusion of the 100% crystalline component, undergoes a reduction for PET, whereas, for HDPE, there is an increment at a

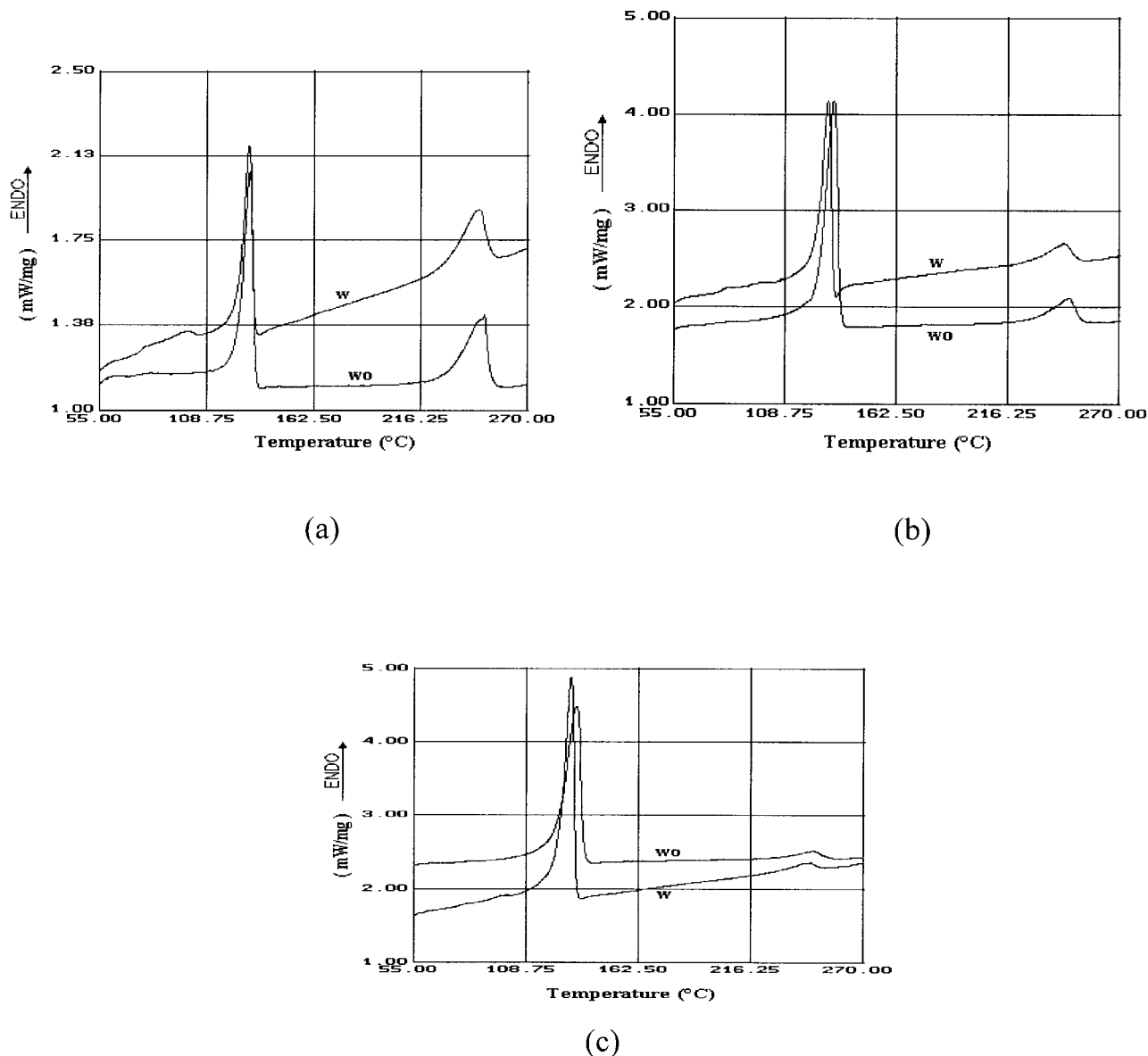


Figure 4 DSC curves for the blends: (a) 75 PET/25 HDPE; (b) 50 PET/50 HDPE; (c) 25 PET/75 HDPE. WO, without Surlyn; W, with 7.5% Surlyn.

content up to 50% (see Table II). This behavior could be indicative that the crystallization of PET is impeded by the presence of Surlyn in the blend. Indeed, this occurs only with a high content of PET in the blend, suggesting that the strongest interactions exist mainly between PET and Surlyn, confirming the FTIR results. At a higher HDPE content, there is a drastic reduction of their degree of crystallinity, also due probably to some kind of interaction between polyolefins, but, at the operating conditions employed, this interaction was not detected by FTIR. The increment in the degree of crystallinity at an HDPE content

Table II Thermal Behavior of PET/HDPE Blends

Blend Composition	$\Delta T = (T_{m,WO} - T_{m,W})$ (°C)		$\Delta\lambda = (1 - \lambda)_{WO} - (1 - \lambda)_W$ (%)	
	PET	HDPE	PET	HDPE
75/25	2.93	0.29	3.42	10.22
50/50	3.05	2.80	-0.54	-1.92
25/75	1.31	2.66	1.05	-2.27

WO, without Surlyn; W, with 7.5% Surlyn.

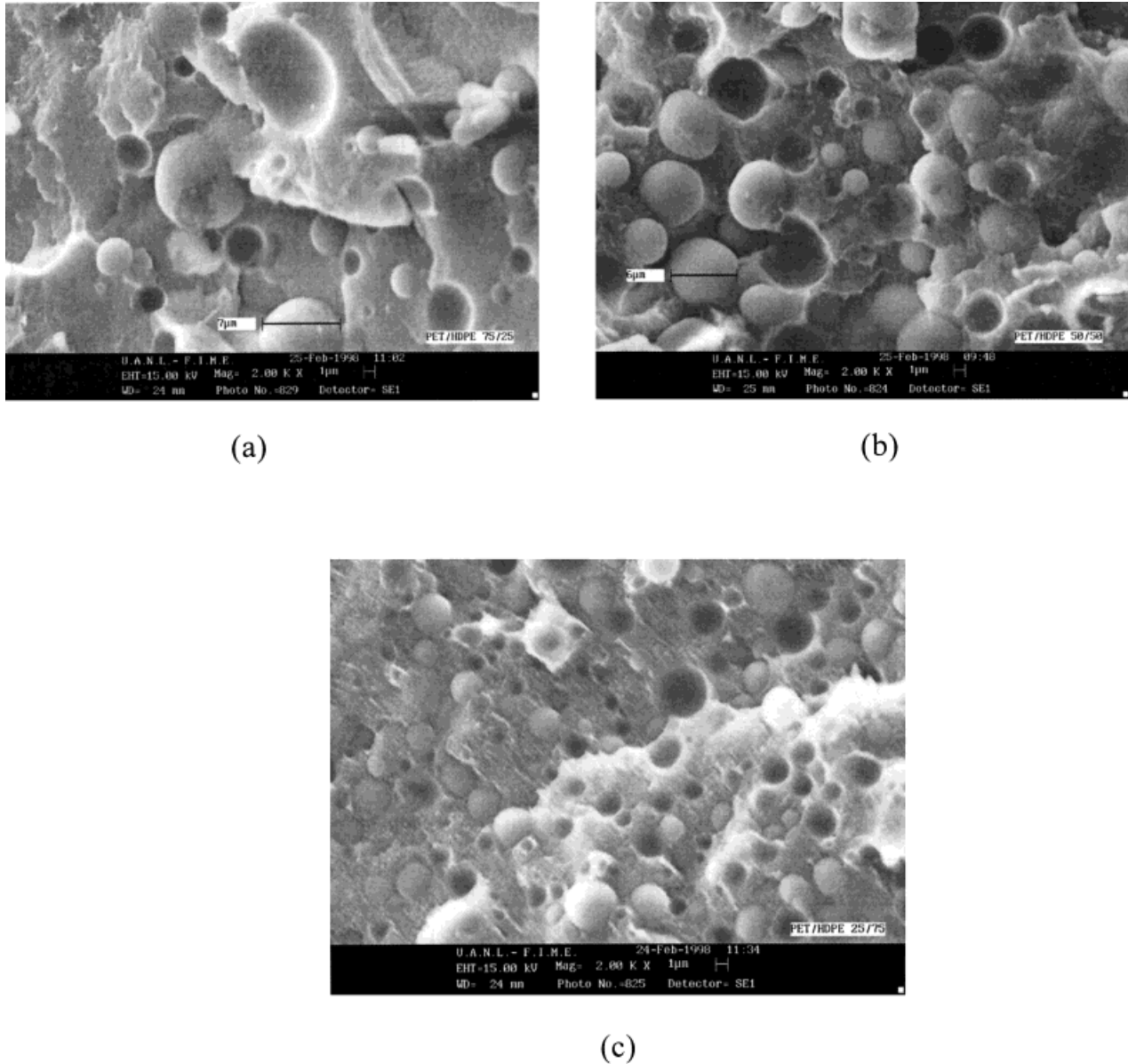


Figure 5 SEM micrographs of uncompatibilized blends: 75% PET/25% HDPE; (b) 50% PET/50% HDPE; (c) 25% PET/75% HDPE.

above 50% could be explained considering that Surlyn accelerates the crystallization of polyethylene and that it possibly acts as a nucleating agent.

The addition of the Surlyn to blends of PET/HDPE during one-step mixing resulted in remarkable changes in the morphology of these blends. The freeze-fractured surface of the binary blends are shown in Figure 5. In all cases, the dispersed polymer domains are spherical in shape. There is no evidence of adhesion between the minor phase and the matrix, since the surfaces of the dispersed particles are perfectly

clean. The voids occurring where the particles were located show that they were attached only by mechanical adherence, which is weak. The fractured surfaces of ternary blends are shown in Figure 6. It can be seen that the dimension of the dispersed particles have decreased to a certain size so that the surface appearance is now homogeneous. This is also true if either HDPE or PET is the dispersed phase. This behavior is in perfect agreement with the results of the degree of crystallinity. In conclusion, it is evident that the presence of Surlyn improved the adhesion between the two phases. To identify the dispersed phase,

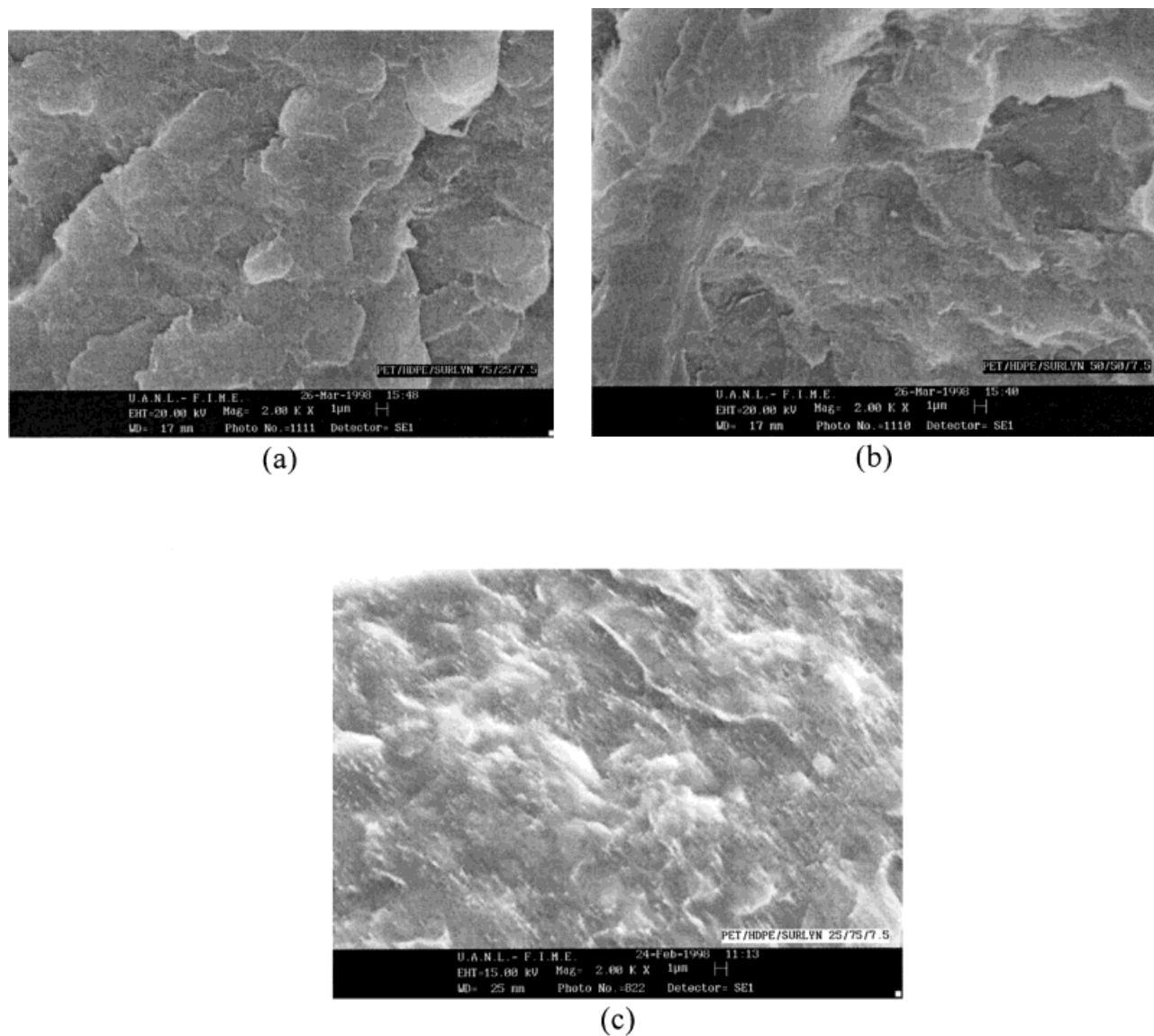
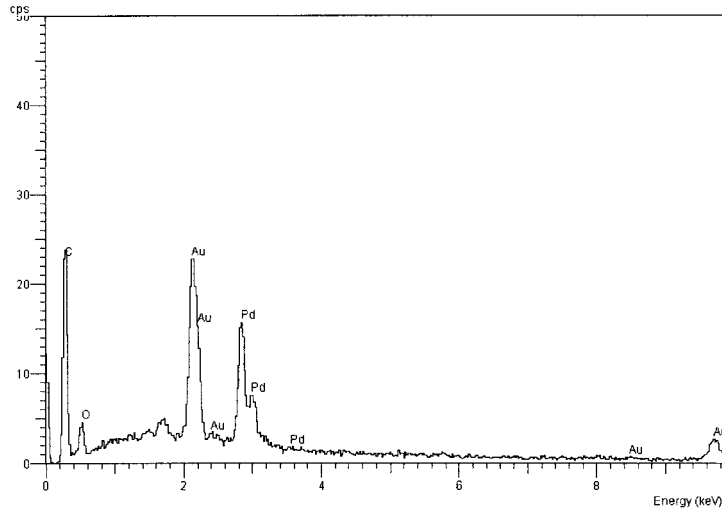


Figure 6 SEM micrographs of compatibilized blends (7.5% Surlyn): (a) 75% PET/25% HDPE; (b) 50% PET/50% HDPE; (c) 25% PET/75% HDPE.

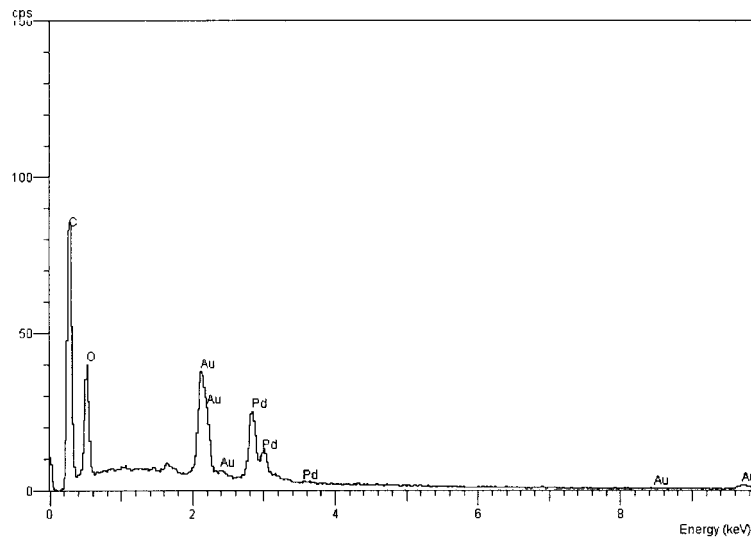
X-ray spectroscopy for both phases was applied to evaluate the oxygen-to-carbon ratio. Figure 7 shows the 50/50 PET/HDPE X-ray spectra of continuous [Fig. 7(a)] and dispersed [Fig. 7(b)] phases. For the former, the O_2/C ratio is 0.19, and for the latter, 0.47. PET contains oxygen in its chemical structure, whereas HDPE does not; therefore, the dispersed phase must be PET. The same procedure was applied for the other different compositions of PET/HDPE blends, obtaining O_2/C ratios of 0.5 and 0.11 for the continuous and dispersed phases, respectively, for the 75/25 PET/HDPE blend, and 0.28 and 0.53, respectively, for the 25/75 PET/HDPE blend. Then, for the former, the dispersed phase is HDPE, whereas this ma-

terial is the continuous phase for the 25/75 PET/HDPE blend.

The mechanical properties of injection-molded specimens are reported in Table III for the 75% PET/25% HDPE blend. It is readily observed that blending the two components causes the break in elongation to fall to very low values. The pronounced fragility of the blend is clearly due to the lack of interface adhesion. The tensile strength of the uncompatibilized blend, on the contrary, is intermediate between those of the pure components. The addition of 7.5% of Surlyn significantly improves the elongation at break of the blend, passing from 2.6 to 41.5%, double of the neat PET value; this allows the blend to have a high capa-



(a)



(b)

Figure 7 X-ray spectra of 50% PET/50% HDPE blend of (a) continuous phase and (b) dispersed phase.

Table III Effect of the Addition of 7.5% of Surlyn on the Mechanical Properties of Injection-molded Specimens of 75/25 PET/HDPE Blends

Composition	Elastic Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Izod Impact Strength (J/m)
PET	2406 ± 192	57.8 ± 0.2	20 ± 1.6	29.1 ± 1.9
HDPE	1307 ± 46	24.5 ± 0.4	628 ± 102	31.2 ± 1.6
PET/HDPE	2122 ± 189	47.2 ± 1.6	2.6 ± 0.2	27.2 ± 1.6
PET/HDPE/Surlyn	1722 ± 80	42.7 ± 0.5	41.5 ± 1.8	49.3 ± 3.1

bility for plastic deformation. In consequence, the Izod impact strength is affected in the same direction; the addition of the third component almost doubles the impact strength of the blend and it is still higher than those of the components. The tensile strength slightly decreases when Surlyn is added, with the elastic modulus following the same behavior. This could be explained considering that the concentration of the compatibilizing agent surpassed the optimum, being, in consequence, the interface between the saturated phases. This fact could lead to the reverse effect observed in the mechanical properties.^{7,14,29} The mechanical results, and, in particular, the behavior of the toughness (elongation and impact properties), confirm the compatibilizing role of Surlyn for the PET/HDPE blend.

CONCLUSIONS

The FTIR results presented a broadening of the carbonyl band of PET on the compatibilized blends, attributed to strong hydrogen bonds between this functional group and the carboxylic acid group of Surlyn. The displacements of the PET and HDPE melting points on the ternary blends suggest interactions of not only PET–Surlyn but also of HDPE–Surlyn. The micrographs of the compatibilized blends show a more homogeneous morphology than do those of the uncompatibilized ones. Finally, the increase in elongation at break and impact strength in the ternary blends leads to the conclusion that Surlyn really acts as a compatibilizing agent between PET and HDPE.

The authors express their gratitude to the Mexican Science and Technology Council (CONACyT) and to the Universidad Autónoma de Nuevo León's Science and Technology Research Program (PAICyT) for their financial assistance (Projects 28188-U and CA082, respectively). The authors are also grateful to KoSa for providing the PET resin.

REFERENCES

- Chen, J. C.; Harrison, I. R. *Polym Eng Sci* 1998, 38, 371.
- Chapleau, N.; Favis, B. D.; Carreau, P. J. *Society of Plastics Engineers Annual Technical Conference Proceedings*, Toronto, Canada, 1997.
- Macaúbas, P. E. P.; Demarquette, N. R. *Society of Plastics Engineers Annual Technical Conference Proceedings*, New York, 1999.
- Ning, P.; Ko, T. *Polym Eng Sci* 1997, 37, 1226.
- Lozano, T.; Guerrero, C. *Society of Plastics Engineers Annual Technical Conference Proceedings*, New York, 1999.
- McLoughlin, K. M.; Elliott, S. J.; Townsend IV, E. B. *Society of Plastics Engineers Annual Technical Conference Proceedings*, New York, 1999.
- Sciamanna, R.; Albano, C.; Arribas, G. *Society of Plastics Engineers Annual Technical Conference Proceedings*, New York, 1999.
- La Mantia, F. P.; Scaffaro, R.; Magagnini, P. L.; Paci, M.; Chiezzi, C.; Sek, D.; Minkova, L. I.; Miteva, T. S. *Polym Eng Sci* 1997, 37, 1164.
- Matos, M. E.; Rosales, C.; Muller, A. J.; Favis, B. D. *Society of Plastics Engineers Annual Technical Conference Proceedings*, Toronto, Canada, 1997.
- Cigana, P.; Favis, B. D.; Jerome, R. *J Polym Sci Polym Phys Ed B* 1996, 34, 1691.
- Márquez, L.; Gambus, D. E.; Romero-Rato, M. P.; Sabino, M.A. *Society of Plastics Engineers Annual Technical Conference Proceedings*, New York, 1999.
- Lacroix, C.; Bousmina, M.; Carreau, P. J.; Favis, B. D. *Polymer* 1996, 37, 2939.
- Dagli, S. S.; Kamdar, K. M. *Polym Eng Sci* 1994, 34, 1709.
- Willis, J. M.; Caldas, V.; Favis, B. D. *J Mater Sci* 1991, 26, 4742.
- Willis, J. M.; Favis, B. D.; Lavallé, C. *J Mater Sci* 1993, 28, 1749.
- Favis, B. D. *Polym Commun* 1994, 35, 1552.
- Legros, A.; Carreau, P. J.; Favis, B. D.; Michel, A. *Polymer* 1997, 38, 5085.
- Tremblay, A.; Tremblay, S.; Favis, B. D.; Selmani, A.; L'Espérance, G. *Macromolecules* 1995, 28, 4771.
- Yao, L.; Beatty, C. *Society of Plastics Engineers Annual Technical Conference Proceedings*, Toronto, Canada, 1997.
- Sambaru, P.; Jabarin, S. A. *Polym Eng Sci* 1993, 33, 827.
- APME, *Rev Plast Mod* 1996, 72, 673.
- Vargas, L. *Rev Plast Mod* 1996, 72, 290.
- Colvin, R.; Moore, S.; O'Neill, M. *Mod Plast* 1998, 75, 51.
- Ar'ev, A. M.; Sotnikov, A. V. *Vysokomol Soedin A* 1970, 12, 1799 (translated in *Polym Sci USSR* 1970, 12, 2040).
- Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley: New York, 1975.
- Willis, J. M.; Favis, B. D. *Polym Eng Sci* 1988, 28, 1416.
- Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1998.
- Utracki, L. A. *Polymer Alloys and Blends*; Hanser: Munich, 1989.
- Horák, Z.; Fort, V.; Hlavatá, D.; Lednichý, F.; Vecerka, F. *Polymer* 1996, 37, 65.