Relation of Chain Constitution with Phase Structure in Blends: Compatibility of Two Phases in Blends of Polyamide with Low-Density Polyethylene and Its Ionomers

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ABSTRACT: Pressed films of binary blends (polyamide with low-density polyethylene or Surlyn) and ternary (polyamide with low-density polyethylene and Surlyn or a graft-copolymer of acrylic acid onto low-density polyethylene) were examined by dynamic mechanical analysis, thermally stimulated current, and small-angle X-ray scattering. The variation of the glass transition temperature for two phases in the blends was studied by dynamic mechanical analysis and thermally stimulated current. X-ray scattering from the relation of the phases was analyzed using Porod's law and led to values of the interface layer in the blends. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 488–494, 2000

Key words: compatibility of polymer–polymer; polymer blend; polyamide blend; polyethylene blend

INTRODUCTION

The mixing of polymers is an excellent way for developing new material with improved properties. The properties of such mixtures depend on the properties of two polymers and the interfacial characteristics. If the two polymers are incompatible, for example, polar polyamide and nonpolar polyethylene (or EPDM) are blended, the interface in this blend is sharp (poor interface adhesion).[1] Clearly, these blends quite often have poor impact properties and a large size of the dispersed phase.[2] However, the relation between the macromolecules in the blends (or alloys) is the key to obtaining a blend of a polymer with improved specific properties such as impact strength. Unfavorable interactions lead to unstable morphology and poor interfacial adhesion, which are the primary causes for the inferior mechanical properties. These limitations can be overcome by compatibilization using modified copolymers or macromolecules such as graft-copolymers that are postulated to act as interfacial agents. Effective compatibilization is the key to successful commercialization of the blends of immiscible polymers. In recent years, reactive compatibilization of polymer blends has been the subject of much interest.[3,4]

In this article, we chose polyamide (Nylon6) and low-density polyethylene (LDPE), Surlyn, and a graft-copolymer of acrylic acid (AA) onto LDPE (LDPE-*g*-AA) as blend components for this study. The miscibility–immiscibility criterion of these blends was evaluated by dynamic mechanical analysis (DMA), thermally stimulated current (TSC), and small-angle X-ray scattering (SAXS).

Table I Relation of σ_b with Compositions in Binary Blends

Compositions	Ratio (wt/wt)	σ_b (NM)
Nylon6/LDPE	40/60	0
Nylon6/Surlyn	80/20	2.196
	60/40	1.116
	40/60	1.282
	20/80	1.612
Nylon6/LDPE/Surlyn	80/10/10	1.877
	60/30/10	1.633
	40/50/10	1.716
	20/70/10	1.597
Nylon6/LDPE/LDPE-g-AA	80/10/10	1.775
	60/30/10	1.517
	40/50/10	1.703
	20/70/10	1.723

Scheme 1

EXPERIMENTAL

Materials

The Nylon6 [T_m = 220°C (DSC), η = 3.5] used was obtained from the Heilongjiang Nylon Factory (China). The LDPE [1F7B, d = 0.923, $\overline{M_w}$ = 2×10^5–3×10^5, T_m = 103°C (DSC)] used was from the Beijing Yanshan Petrochemical Co. (China), and the ionomer Surlyn (the sodium salt of the ethylene/methacrylic acid copolymer, noncrystal) was from the DuPont Co.
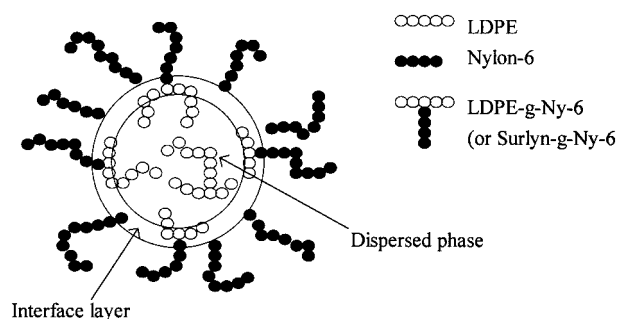
The synthesis of the graft-copolymer of AA onto LDPE [LDPE-g-AA, graft yield 10.44%, T_m = 104°C (DSC)] was made in our laboratory. The grafted product was characterized by IR and XPS analyses in another article.[5]

Blend Preparation

Nylon6 was dried for 4 h at 110°C prior to blending in order to eliminate the hydrolyzing effect of the absorbed water. Binary blends of Nylon6/LDPE and Nylon6/Surlyn and ternary blends of Nylon6/LDPE/Surlyn and Nylon6/LDPE/LDPE-g-AA were prepared by melt-mixing the polymer in a mixer apparatus (XXS-30 mixer, China) at a temperature of 230°C with a residence time of 5 min at 30 rpm. The compositions of the investigated blends are reported in Table I.
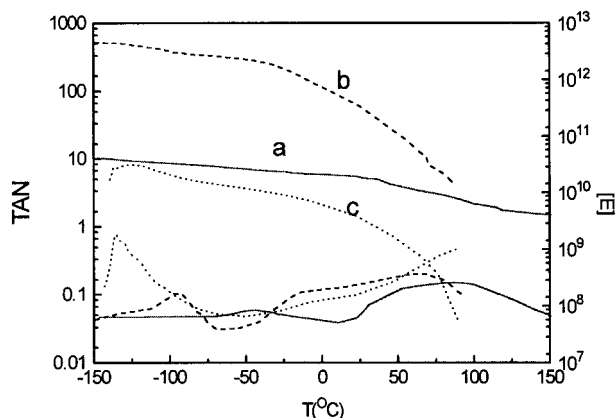
Specimen Preparation

The premixed materials were put in a compression mold to obtain a slab of a thickness of 0.2 or 1 mm at a temperature of 230°C with a residence time of 5 min in a common heated press at 24.5 Mpa, and this slab was quickly moved to a cool press with a residence time of 10 min at room temperature and at 24.5 Mpa. The 0.2-mm-thick slab was cut by cutter ϕ25 films with thin aluminum evaporated at two surfaces of the film as an electrode on which the TSC tests were performed. Another slab of 0.22 thickness was also cut by the cutter to a 5×20-mm specimen on which DMA tests were performed.

Characterization

The compatibility of the two phases in the blends was studied by TSC, DMA, and SAXS. The TSC main instrument was made by the KEHAI Experimental Factory (China). The samples were placed in a shielded cell filled with dry nitrogen. The procedures of polarizing and depolarizing were as follows: (1) Polarize a sample in the electric field E_p = 30 kV/cm at T_p

Figure 1 DMA spectra of Nylon6, LDPE, and Surlyn: (a) Nylon6; (b) LDPE; (c) Surlyn.

a. Nylon6/Surlyn=20/80

b. Nylon6/Surlyn=40/60

c. Nylon6/Surlyn=60/40

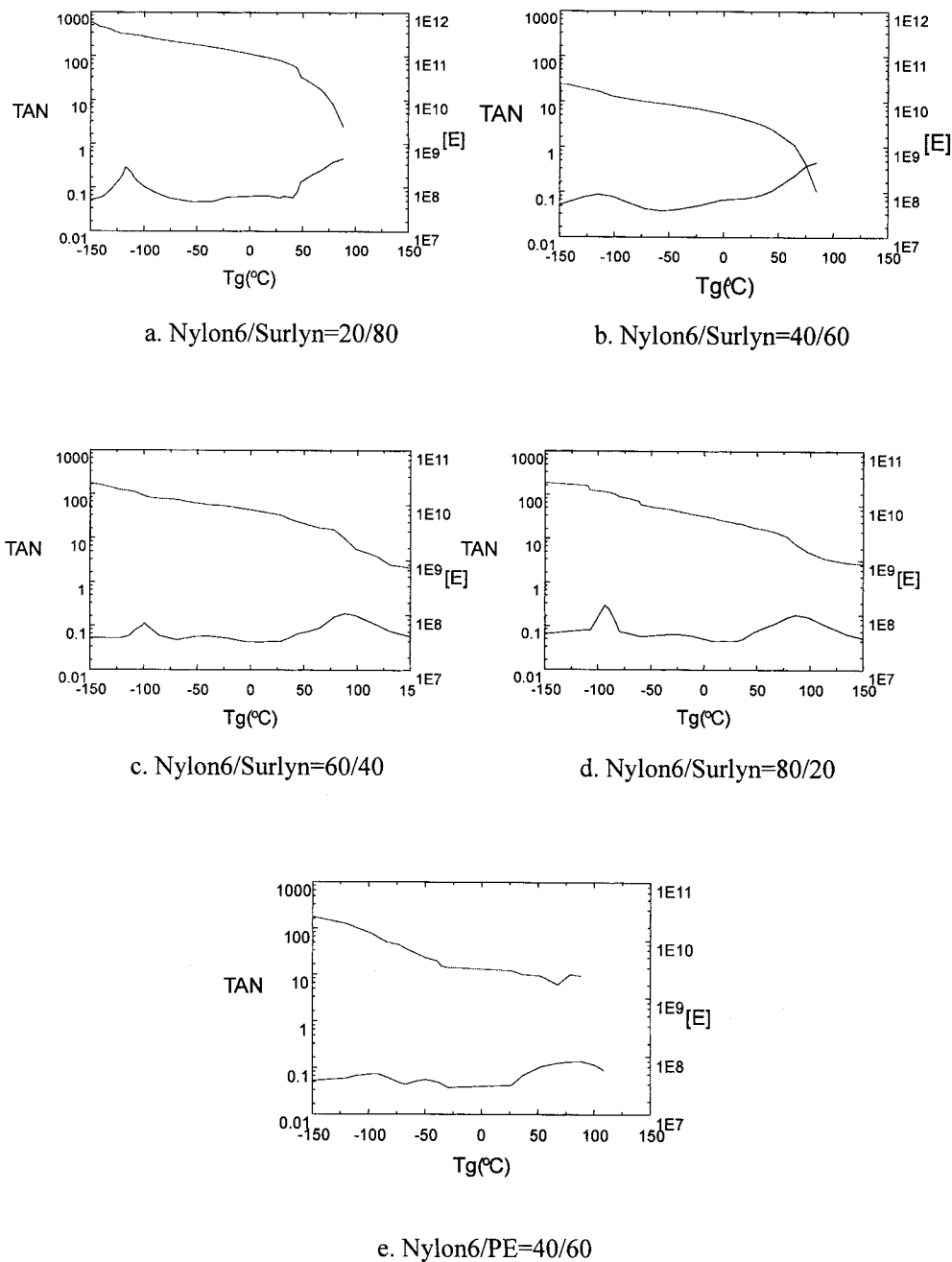d. Nylon6/Surlyn=80/20

e. Nylon6/PE=40/60

Figure 2 DMA spectra of the blends.

= 155°C for 30 min; (2) cool the sample to −160°C rapidly under the same electric field; (3) remove the electric field and keep at this temperature in a short-circuited state for 30 min; and (4) depolarize the sample at a heating rate of 1.6°C/min and record the TSC spectra. The DMA instrument was a DDV-II by RHEOVBRON. The SAXS instrument was a D/max-rA X-ray diffraction by Rigaku.

RESULTS AND DISCUSSION

Reaction Mechanism for the Action of Nylon6 with Surlyn and LDPE-*g*-AA

If we substitute Surlyn for LDPE in the Nylon6/LDPE blends or on the addition of the Surlyn (or LDPE-*g*-AA) copolymer to the Nylon6/LDPE blends, the following reaction may take place be-
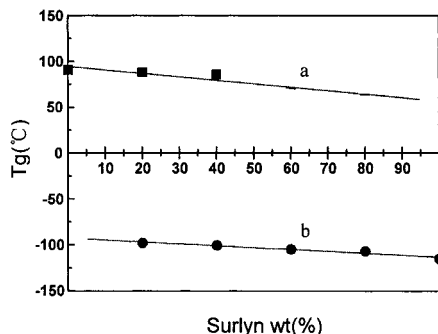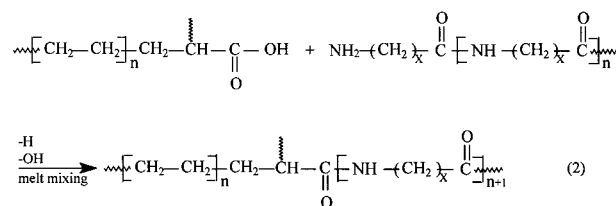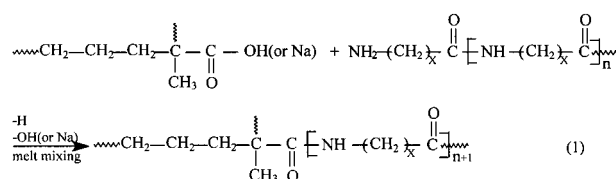
Figure 3 Relation of T_g with compositions in SUR-LYN/Nylon6 by DTA: (a) Nylon6 phase; (b) Surlyn phase.

tween the ester groups of Surlyn or AA in LDPE-*g*-AA and the terminal amino groups of Nylon6 during melt-mixing[6]:

The product Surlyn-*g*-Nylon6 (or LDPE-*g*-AA) acts as an interfacial agent (or a chemical combination is formed) for the Nylon6/LDPE blend system (see Scheme 1).

Relaxation of Nylon6 Blends by DMA

Figure 1 shows the DMA spectra of Nylon6, LDPE, and Surlyn (110 Hz, $b = 2°C/min$, from −150 to 150°C). Nylon6 has two transition peaks at −43.7 and 86.6°C. α-Relaxation is at 86.6°C, which is considered by many authors to be the glass transition of the polymers.[7] Therefore, the glass transition temperature (T_g) of Nylon6 can be shown to be at 86.6°C. β-Relaxation is at −43.7°C. That is the same result as that of Takayanagi.[8] But the γ-relaxation was not found in these tests.

LDPE has three transition peaks at −97.3, −13.7, and 64.6°C, respectively. The argument of what is the glass transition temperature of polyethylene has lasted over 20 years. The glass transition temperature of polyethylene has three regions at 240 ± 20 K ($-30°C$), 195 ± 10 K ($-78°C$), and 145 ± 10 K ($-128°C$).[9] We thought that −97.3°C is the glass temperature (T_g) of LDPE, which is approximate to Boyer's result by the ESR method.[10]

The peaks of −135.3 and −7.3°C are two transition peaks of Surlyn. Due to that Surlyn is the copolymer of ethylene with methacrylic acid, −135.3°C would be the T_g, as compared to LDPE.

Figure 2 shows the DMA spectra of the Nylon6/Surlyn system and the Nylon6/LDPE (40/60) blends. The peaks at −97.7°C are a T_g of LDPE in the Nylon6/LDPE blend, and 88.6°C is a T_g of Nylon6 in this blend. Clearly, the T_g's of Nylon6 and LDPE in the blend did not change as compared with the pure polymers. Therefore, we can deem that the two phases of the blend of Nylon6/LDPE are incompatible. The T_g's of the Nylon6 and Surlyn phases in the blends of Nylon6/Surlyn are shown in Figure 3. The T_g of the Nylon6 component is decreased and the T_g of the Surlyn component increases with the increase of Nylon6 because the reaction can occur between the ionomer Surlyn and Nylon6 [see eq. (1)]; as such, the chemical combination point (compatible domain, see Scheme 1) exists at the interface in the blends of Nylon6/Surlyn.

Relaxation of Nylon6 Blends by TSC

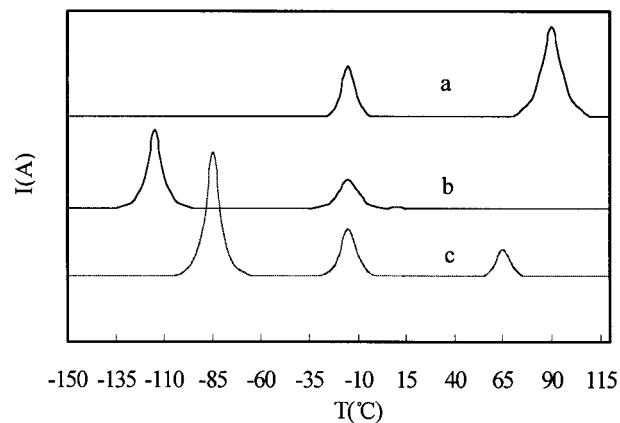Figure 4 shows the TSC spectra of Nylon6, LDPE, and Surlyn. Nylon6 has two depolarization peaks

Figure 4 TSC spectra of Nylon6, Surlyn, and LDPE: (a) Nylon6; (b) Surlyn; (c) LDPE.
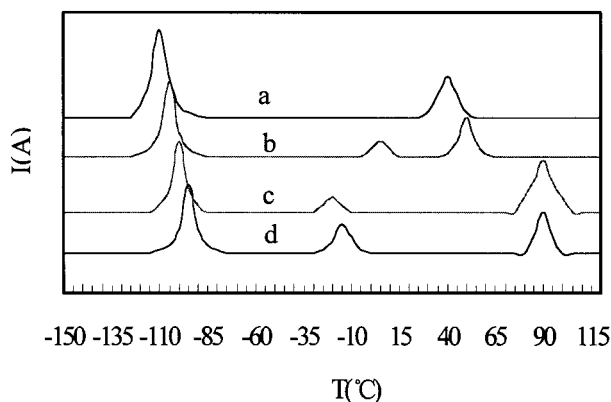
Figure 5 Spectra of TSC for binary blends of Nylon6/Surlyn: (a) Nylon6/Surlyn (80/20); (b) Nylon6/Surlyn (20/80); (c) Nylon6/Surlyn (40/60); (d) Nylon6/Surlyn (60/40).

at 91 and $-16°C$. The 91°C is a T_g of Nylon6. The LDPE has three transition peaks at -84, -16, and 64.6°C. The T_g of LDPE is at $-84°C$. Surlyn has two depolarization peaks at -115 and $-14.5°C$, which is the same result of the DMA.

Figures 5–7 show the TSC spectra of the binary blends of Nylon6/Surlyn and the ternary blends of Nylon6/LDPE/Surlyn and Nylon6/LDPE/LDPE-*g*-AA, respectively. The relation of the glass transition temperature of every phase with the composition in the blends is shown in Figures 8–10. These results are the same as those of DMA and are also incompatible.

SAXS Studies

The relationship between the two phases in the blends can be discussed by the SAXS intensity.
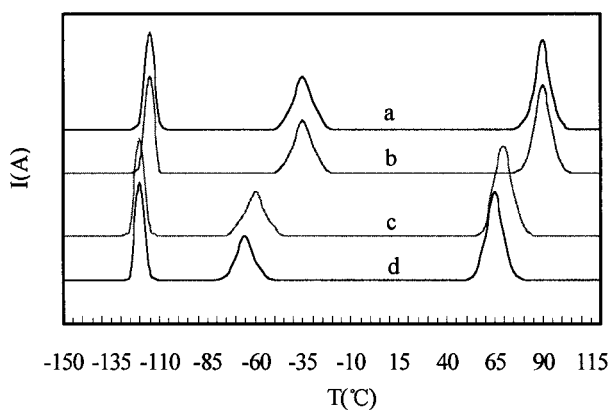

Figure 6 TSC spectra of blends of Nylon6/LDPE/Surlyn: (a) Nylon6/LDPE/Surlyn (80/10/10); (b) Nylon6/LDPE/Surlyn (60/30/10); (c) Nylon6/LDPE/Surlyn (40/50/10); (d) Nylon6/LDPE/Surlyn (20/70/10).
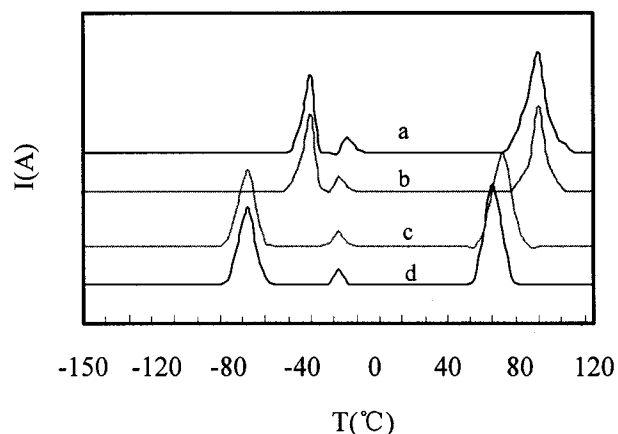

Figure 7 TSC spectra on blends of Nylon6/LDPE/LDPE-*g*-AA: (a) Nylon6/LDPE/LDPE-*g*-AA (80/10/10); (b) Nylon6/LDPE/LDPE-*g*-AA (80/10/10); (c) Nylon6/LDPE/LDPE-*g*-AA (40/50/10); (d) Nylon6/LDPE/LDPE-*g*-AA (20/70/10).

According to Porod's law,[11,12] the intensity in the tail of the diffraction curve from a two-phase structure with sharp phase boundaries is given by

$$\text{Lim} I(S) = C/S^4 \qquad (3)$$

where $I(S)$ is intensity of the scattering and $S = 2 \sin \theta$. If it is assumed that the interface layer (compatible domain) exists, Porod's law is given by

$$I(S) \cong \frac{C}{S^4}(1 - 4\pi^2 \sigma_b S^2) \qquad (4)$$

where σ_b is the interface layer thickness between the two phases in the blends. In a four-slit system, eq. (3) may be approximated by
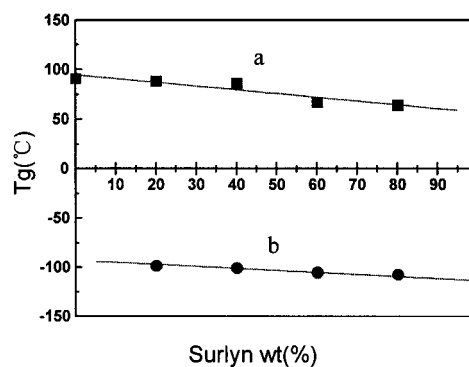

Figure 8 Relation of T_g with compositions of Nylon6/Surlyn by TSC: (a) Nylon6 phase; (b) Surlyn phase.
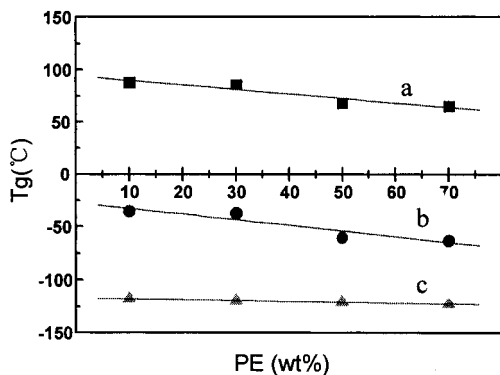
Figure 9 Relation of T_g with compositions in Nylon6/LDPE/Surlyn by TSC: (a) Nylon6 phase; (b) PE phase; (c) Surlyn phase.

$$I(S) \cong \frac{K}{S^3}\exp[\,-38(\sigma_b S)^{1.81}] \qquad (5)$$

A plot of in $[I(S)S^2]$ versus $S^{1.81}$ is used and the results are shown in Figures 11–13. Curve a (in Fig. 11) is flattened when S increases because the sharp phase boundary exists on the Nylon6/LDPE blend. In the other curves, the tail of the curve decreases when S increases and σ_b may be calculated by the slope of the tail of the curve, and the results are listed in Table I. The value of σ_b depends on the composition of the blends and it is maximum for Nylon6 of 80% (wt) in the blends. Thereby, the existence of Surlyn-g-Nylon6 is proved.

CONCLUSIONS

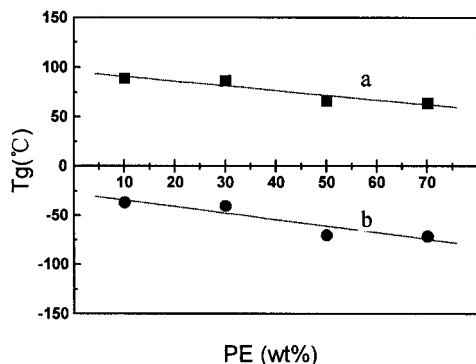The relaxation spectra of the Nylon6, LDPE, and Surlyn binary and ternary blends for Nylon6/

Figure 10 Relation of T_g with composition of Nylon6/LDPE/LDPE-g-AA: (a) Nylon6 phase; (b) PE(LDPE-g-AA) phase.
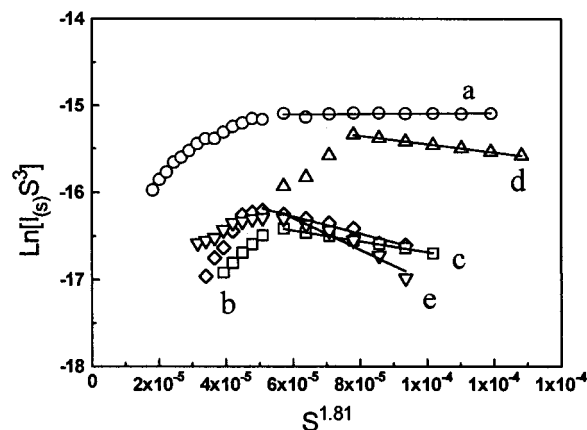

Figure 11 Plot of $S^3 I(s)$ against $S^{1.81}$ on blends of Nylon6/Surlyn: (a) Nylon6/LDPE; (b) Nylon6/Surlyn (20/80); (c) Nylon6/Surlyn (40/60); (d) Nylon6/Surlyn (60/40); (e) Nylon6/Surlyn (80/20).

LDPE, Nylon6/Surlyn, Nylon6/LDPE/Surlyn, and Nylon6/LDPE/LDPE-g-AA were measured by DMA and TSC. Also, the glass transition temperatures of Nylon-6, Surlyn, and LDPE in the blends were obtained. The T_g of Nylon6 and LDPE in the blend of Nylon6/LDPE did not change, as compared with the pure components. Thereby, the Nylon6 and LDPE in this binary blend are incompatible. The glass transition temperatures of Nylon-6, Surlyn (or LDPE-g-AA), and LDPE in the binary or ternary blends of Nylon6/Surlyn, Nylon6/LDPE/Surlyn, or Nylon6/
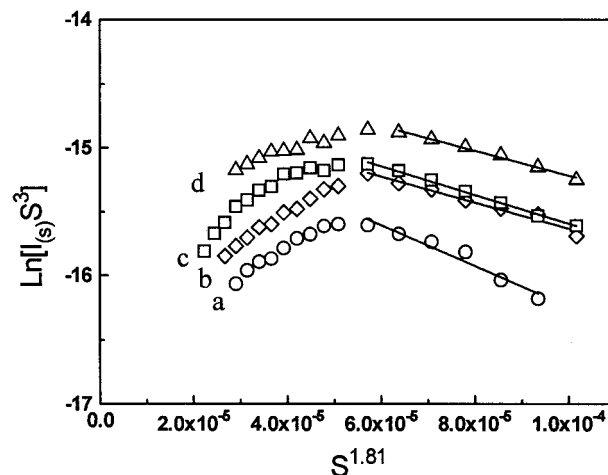

Figure 12 Plot of $S^3 I(s)$ against $S^{1.81}$ on blends of Nylon6/LDPE/Surlyn: (a) Nylon6/LDPE/Surlyn (80/10/10); (b) Nylon6/LDPE/Surlyn (60/30/10); (c) Nylon6/LDPE/Surlyn (40/50/10); (d) Nylon6/LDPE/Surlyn (20/70/10).
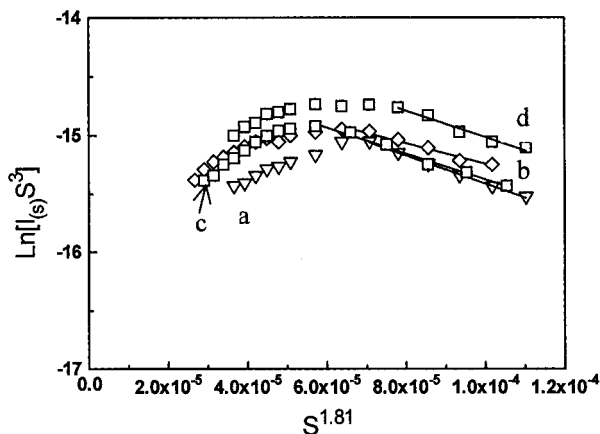
Figure 13 Plot of $S^3I(s)$ against $S^{1.81}$ on blends of Nylon6/LDPE/LDPE-*g*-AA: (a) Nylon6/LDPE/LDPE-*g*-AA (80/10/10); (b) Nylon6/LDPE/LDPE-*g*-AA (60/30/10); (c) Nylon6/LDPE/LDPE-*g*-AA (40/50/10); (d) Nylon6/LDPE/LDPE-*g*-AA (20/70/10).

LDPE/LDPE-*g*-AA change with their composition, indicating that the binary blends of Nylon6/Surlyn and the ternary blends of Nylon6/LDPE/Surlyn and Nylon6/LDPE/LDPE-*g*-AA are semi-compatible. Clearly, the reaction may take place between the ester groups of the ionomer Surlyn (or AA in LDPE-*g*-AA) and the terminal amino groups of Nylon6 during melt-mixing have been proved at the interface range in the binary blends of Nylon6/Surlyn and ternary blends of Nylon6/LDPE/Surlyn and Nylon6/LDPE/LDPE-*g*-AA.

The Fox[12] rule is given by

$$1/T_g = W_a/T_{g_a} + W_b/T_{g_b}$$

where W_a and W_b and T_{g_A} and T_{g_B} are the respective weight fractions and glass transition temperatures of polymers A and B. Our results do not satisfy the Fox equation, because there are two T_g's [T_g's of the Nylon6 and Surlyn (or LDPE) components] and the relation of the T_g for the Nylon6 and Surlyn (or LDPE) components with composition is semi-compatible. The interface layer thickness σ_b of the two phases in the blends of Nylon6/Surlyn, Nylon6/LDPE/Surlyn, and Nylon6/LDPE/LDPE-*g*-AA was calculated by SAXS; the existence of a compatible domain has also been proved.

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