

The Study of Polystyrene Blends: The Relationship of Phases and Structure in Blends of Polystyrene with Ethylene–Propylene Diene Monomer Rubber and Its Grafted Copolymer

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ABSTRACT: Pressed films of blends of polystyrene (PS) with ethylene–propylene diene monomer rubber (EPDM) or grafted copolymer of styrene (St) onto EPDM (EPDM-*g*-St) rubber were examined by small-angle X-ray scattering (SAXS), and scanning electron microscope (SEM). Small-angle X-ray scattering from the relation of phase was analyzed using Porod's Law and led to value of interface layer on blends. The thickness of interface layer (σ_b) had a maximum value at 50/50 (PS–EPDM-*g*-St) on blends. The radius of gyration of dispersed phase (domain) and correlation distances a_c in blends of PS–EPDM-*g*-St were calculated using the data of SAXS. The morphology and structure of blends were investigated by SEM. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 805–810, 1998

Key words: polystyrene blends; ethylene–propylene diene monomer blends; X-ray scattering of polymer blends

INTRODUCTION

Immiscible blends are generally preferred over miscible blends as one can take advantage of the useful properties of each blend component. However, they quite often have poor mechanical properties, relative to their components, and unstable morphology. Unfavorable interaction at the molecular level leads to large interfacial tension in the melt and makes it difficult to disperse the components during mixing. Two phases in the blends of polystyrene (PS) with ethylene–pro-

pylene diene monomer rubber (EPDM) have been incompatible.¹ Unfavorable interaction also 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 graft copolymers that are postulated to act as interfacial agents. Effective compatibilization is the key to successful commercialization of blends of immiscible polymers. The graft copolymer can be obtained by modification of macromolecules is used. If one replaces EPDM with the graft copolymer EPDM-*g*-St on blends (PS–EPDM-*g*-St), the compatible domain has been existed. The properties of PS–EPDM-*g*-St blends have been studied by Shaw et al.^{2–4} The compatibility of two phases in blends of PS–EPDM-*g*-St has been

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studied by thermally stimulated current (TSC) in our other article.¹

In this article, the semicompatibility of two phases in blends of PS-EPDM-*g*-St is examined by small-angle X-ray scattering (SAXS), and the interfacial layer thickness in blends is calculated by Porod's law; the radius of gyration (R_g) and the correlation distance (a_c) are calculated by SAXS data in the blends.

EXPERIMENTAL

Materials

Polystyrene (PS) used in this work was an amorphous polymer with a molecular weight (\overline{Mn}) equal to 1.6×10^5 (density = 1.05 g/cm^3 ; a product by Yanshan Petrochemical Company, Beijing, China). EPDM rubber (Mooney viscosity, 45; \overline{Mn}) = 2.0×10^5 ; density, 0.865 g/cm^3 ; the ratio of ethylene with propylene was 2 : 1; the content of dicyclopentadiene is equal to 0.1%) was from Lanzhou Petrochemical Company, Lanzhou, China.

The synthesis of the graft copolymer of St onto EPDM (EPDM-*g*-St) (grafting yields 32.6%) has been fulfilled in our laboratory. The grafted product is characterized by infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), and chemical analysis in another article.⁵

Preparation of Blends

Binary PS-EPDM and PS-EPDM-*g*-St blends have been prepared by melt mixing polymer in a mixer apparatus (XXS-30 Mixer, China) at a temperature of 180°C with a residence time of 10 min at 30 rpm. The compositions of blends proposed were 70/30, 60/40, 50/50, and 35/65 (v %/v %) PS with either EPDM or EPDM-*g*-St for SEM tests. For SALS tests, the composition of blends used were 90/10, 70/30, 60/40, 50/50, and 40/60 PS with EPDM-*g*-St and 90/10 PS with EPDM. The sample of blends contained only 70, 60, 50, and 40 v % PS; 30, 40, 50, and 60 v % EPDM-*g*-St; 90 v % PS; and 10 v % EPDM for SAXS tests.

Specimen Preparation

The premixed material is compression-molded to get a slab of a definite thickness (1, 0.2, and 0.15 mm) at 180°C with a residence time of 5 min in a common heated press (24.5 Mpa), and the slab is quickly moved to a cool press with the residence time of 10 min at room temperature and at 24.5

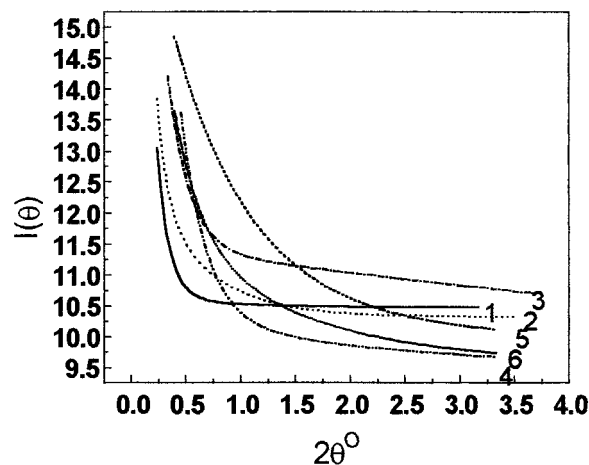


Figure 1 The relation of SAXS intensity (I) with 2θ for blends of PS-EPDM (90/10) and PS-EPDM-*g*-St: (1) PS-EPDM (90/10); (2) PS-EPDM-*g*-St (90/10); (3) PS-EPDM-*g*-St (70/30); (4) PS-EPDM-*g*-St (60/40); (5) PS-EPDM-*g*-St (50/50); (6) PS-EPDM-*g*-St (40/60).

Mpa. A 1-mm thick slab is cut by a cutter in a $5 \times 10 \text{ mm}$ specimen on which the SAXS test was run. The same slab, broken in liquid nitrogen, was the one on which SEM tests are carried out.

Characterization

The compatibility of 2 phases in the blends was studied by SAXS on a Rigaku D/max-rA and dynamic mechanical analysis (DMA) was studied on a Rheovibron DDV-II. The morphology of fracture surface on blends was observed by a HITACHI X-650 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Small-Angle X-ray Scattering Studies

The variation in relative SAXS intensity with 2θ is shown in Figure 1 for blends of PS-EPDM (90/10) and PS-EPDM-*g*-St. According to Porod's Law,^{6,7} the intensity in the tail of a diffraction curve from a two-phase structure with interface layer (compatible domain) in a four-slit system is given by⁸

$$I(s) \cong \frac{K}{S^3} \exp[-38(\sigma_b S)^{1.81}] \quad (1)$$

where $I(s)$ is the intensity of scattering, $S = 2 \sin \theta$, and σ_b is interface layer thickness. A plot of $\ln[I(s) \cdot S^3]$ versus $S^{1.81}$ is used, and these

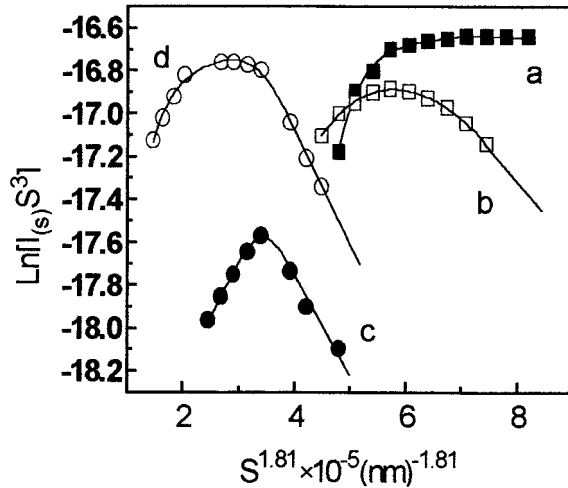


Figure 2 Plot of $\ln[I(s) \cdot S^3]$ against $S^{1.81}$ for blends: (a) PS-EPDM (90/10); (b) PS-EPDM-g-St (70/30); (c) PS-EPDM-g-St (60/40); (d) PS-EPDM-g-St (50/50).

results are shown in Figure 2. The curve is flattened when S increased because a sharp phase boundary exists on the PS-EPDM blend. In other curves, the tail of the curve leads to a reduction when S increased and σ_b may be calculated by the slope of the tail of curve; these results are listed in Table I. The value of σ_b depends on the composition of blends, and it is maximum for PS(50)-EPDM-g-St(50) blends. This result is of the same as previous experimental results.⁸⁻¹⁰ In this system of PS-EPDM-g-St, the branch chains of St on the main chains of EPDM have been joined; as such, the grafted points of St onto EPDM can be regarded as compatible domain (interface layer) in blends of PS-EPDM-g-St (Fig. 3).

We use a modification of the Debye-Bueche^{6,7} description of scattering from random heterogeneous media, which gives, for spherical symmetrical systems,

$$I_s(\theta) = K\bar{\eta}^2 \int_0^\infty r(r) \frac{\sin(hr)}{hr} r^2 dr \quad (2)$$

where $h = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$. If we regard the blend of polymer as a solid solution, the size of dispersed phase (domain) in the blend can be expressed using the radius of gyration (R_g). The R_g of the whole particles (dispersed phase) is given by⁸

$$\bar{R}_g^2 = \frac{\int_0^\infty r(r)r^4 dr}{2 \int_0^\infty r(r)r^2 dr} \quad (3)$$

$\sin(hr)$ may be expanded as a power series in equation (2), so we have

$$\begin{aligned} I_s(\theta) &= c \int_0^\infty r(r) \frac{\sin(hr)}{hr} r^2 dr \\ &= c \left[\int_0^\infty r(r)r^2 dr - \frac{h^2}{3!} \int_0^\infty r(r)r^4 dr + \dots \right] \\ &= I_s(0) \left[1 - \frac{h^2}{3!} \frac{\int_0^\infty r(r)r^4 dr}{\int_0^\infty r(r)r^2 dr} + \dots \right] \quad (4) \end{aligned}$$

Where equation (3) is substituted into equation (4), one obtains

$$P(\theta) = \frac{I_s(\theta)}{I_s(0)} = 1 - \frac{\bar{R}_g^2}{3} h^2 + \dots \quad (5)$$

A plot of $P(\theta)$ versus h^2 is used, and the curve leads to a straight line for small values of h . The slope of line is equal to $\left(-\frac{\bar{R}_g^2}{3}\right)$, and these results

Table I Interface Layer Thickness (σ_b)

Composition (v %)	PS-EPDM (90/10)	PS-EPDM-g-St			
		70/30	60/40	50/50	40/60
σ_b (nm)	0	2.68	4.73	4.78	3.35

are shown in Figure 4. Clearly, there is a minimum of \overline{R}_g for intermediate concentration of blends of PS-EPDM-*g*-St (50/50), and a corresponding value of σ_b is maximum. But the value of \overline{R}_g of PS-EPDM-*g*-St (60/40) is bigger, and this result may be in close relationship with double phases (Figure 6).

The $r(r)$ in equation (2) is the correlation function. The $r(r)$ is found by the inverse Fourier transform of $I(h)$. For systems not having a clearly defined structure, $r(r)$ often decreases monotonically with r and may be represented by empirical equation, such as

$$r(r) = \exp(-r/a_c) \quad (6)$$

where the parameter a_c is known as the correlation distance and defines the size of heterogeneity. It may be considered as an average wavelength of the $\eta(x)$ fluctuations where $\langle \eta^2 \rangle$ is the mean-square amplitude.⁸ If equation (6) is substituted into equation (2), one obtains

$$I(h) = K_2 \langle \eta^2 \rangle_{av} a_c^3 [1 + h^2 a_c^2]^{-2} \quad (7)$$

Upon rearrangement, this gives

$$I(h)^{-1/2} = [K_2 \langle \eta^2 \rangle_{av} a_c^3]^{-1/2} [1 + h^2 a_c^2] \quad (8)$$

Consequently, a plot of $I(h)^{-1/2}$ against h^2 should lead to a straight line having a ratio of slope to intercept of a_c . Figure 5 shows that the value of a_c is calculated and it is related to composition of blends. The variation of a_c is the same as \overline{R}_g . The dimensions of variation for $\langle \eta^2 \rangle$ are a bigger near the phase inversion region.

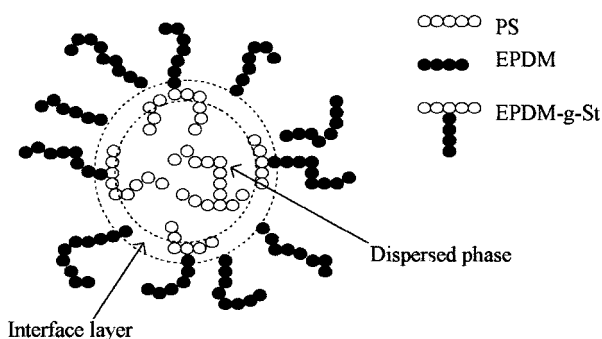


Figure 3 The model of the phase structure in the blends.

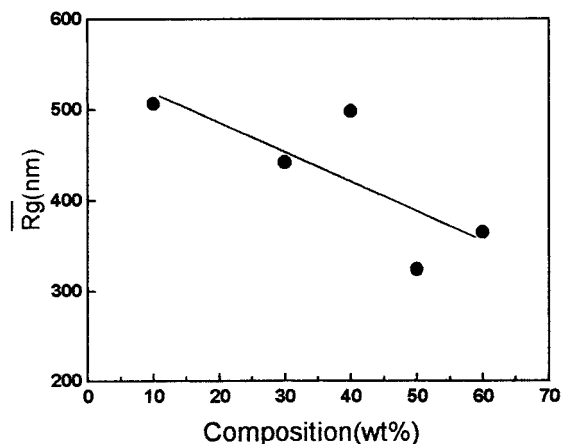


Figure 4 The relation of R_g with composition in blends of PS-EPDM-*g*-St.

Scanning Electron Microscopy Studies

The overall morphology of blends is investigated on surface of specimens broken in liquid nitrogen, and the rubber (EPDM) phase in the fractured surface has been etched in *n*-heptane. SEM micrographs of cryogenically fractured surfaces of PS-EPDM and PS-EPDM-*g*-St blends are shown in Figure 6. As can be seen, such the blend exhibits a hole-like morphology, distributed unevenly throughout the whole sample for blends PS-EPDM; the hole is bigger, and the size of each phases is great. This is a homogeneous distributed for two-phase in blends of PS-EPDM-*g*-St, and the size of each phases is a smaller. The characterization of near-double phases has been shown in blends from compositions of 60/40 (PS-EPDM-*g*-St) to 50/50. PS is dispersed phase at a

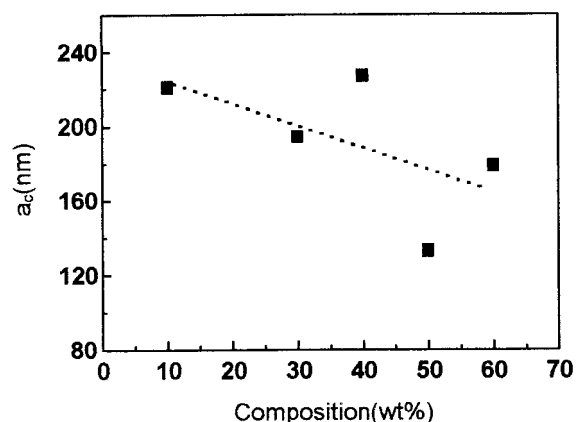
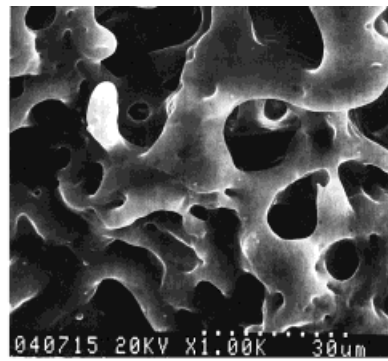
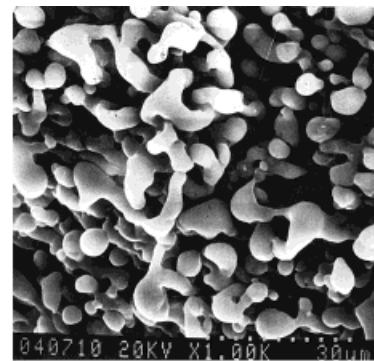


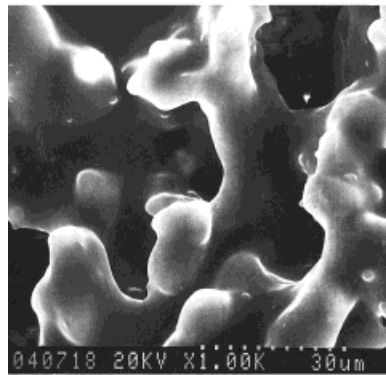
Figure 5 The relation of a_c with composition in the blends of PS-EPDM-*g*-St.



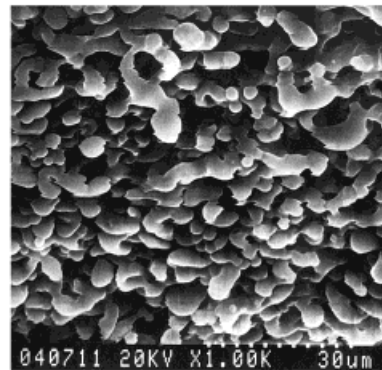
PS/EPDM(70/30)



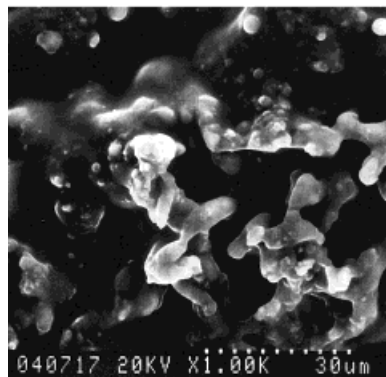
PS/EPDM-g-St(70/30)



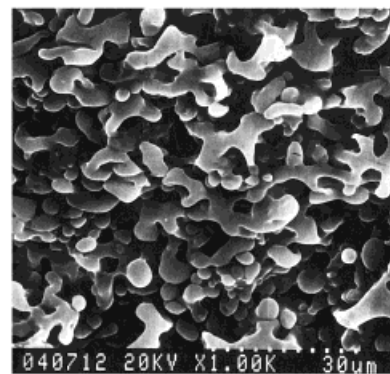
PS/EPDM(60/40)



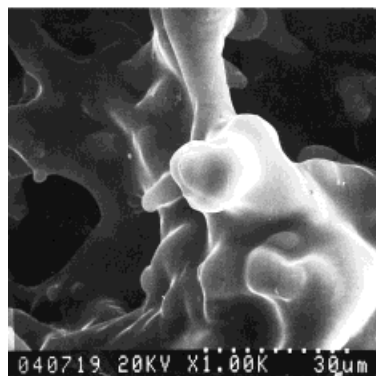
PS/EPDM-g-St(60/40)



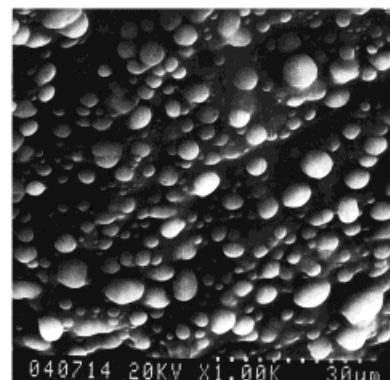
PS/EPDM(50/50)



PS/EPDM-g-St(50/50)



PS/EPDM(35/65)



PS/EPDM-g-St(35/65)

Figure 6 SEM micrographs of blends.

composition of 35/65, then it is a spherical for the PS phase. The phase inversion may be occurred at 50/50 to 35/65 (PS-EPDM-*g*-St). The results are shown because of the existence of the interface layer on PS-EPDM-*g*-St, but the interface layer on PS-EPDM does not exist.

CONCLUSION

The immiscibility of the polymer blends of PS with EPDM is proved by SAXS. The semi-miscibility of blends of PS with EPDM-*g*-St is shown by SAXS and the interface layer thickness (σ_b) is calculated, which depends upon the concentration of blends.

The \bar{R}_g of dispersed phase in blends of PS-EPDM-*g*-St is calculated by SALS, which depends upon the concentration of blends. A minimum value of \bar{R}_g corresponds to the value of σ_b maximum. The fluctuations of \bar{R}_g after the concentration of PS-EPDM-*g*-St (60/40) occurred, which may be near the phase inversion region in blends.

The variation of a_c is the same as \bar{R}_g , and the variation of dimension for $\langle \eta^2 \rangle$ is a bigger as the near-phase inversion region in blends.

The homogeneity of system for PS-EPDM-*g*-St blend has been proved by SEM. The size of phase in PS-EPDM-*g*-St is smaller than it is on blends of PS-EPDM.

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