

# Blends of Polypropylene with Poly(*cis*-butadiene) Rubber.

## I. Phase Structure and Morphology of Blends

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**ABSTRACT:** Pressed films of blends of polypropylene with poly(*cis*-butadiene) rubbers (PcBR) or grafted copolymer of ethyl acrylate (EA) onto PcBR (PcBR-*g*-EA) was examined by IR spectra, small angle X-ray scattering, small angle laser scattering (SALS), and scanning electron microscopy (SEM). The problem of isomerization on PcBR (or PP/PcBR) is discussed by melt mixing (at a temperature of 180°C) using IR. X-ray scattering from the relation of phase was analyzed using Porod's law and led to the values of the interface layer of the blends. With increasing content of rubber, the interface layer thickness ( $\sigma_b$ ) had a maximum value at 60/40 (PP/PcBR-*g*-EA) for the blends. The invariant ( $Q$ ) was calculated and the relation of  $Q$  with  $\sigma_b$  was calculated using Debye–Buech statistical theory, and the average chord length ( $l$ ) was obtained by Porod's definition of blends. The morphology and structure of the blends were investigated by SEM. The phase separation of the blends was found by SALS. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2265–2272, 1997

**Key words:** polypropylene; poly(*cis*-butadiene) rubber; ethylacrylate

## INTRODUCTION

Most of the widely used thermoplastic materials show marked limitation in their use when toughness and high impact resistance are required.<sup>1</sup> These limitations may be overcome by melt mixing these materials with a rubber polymer. But if two phases in thermoplastic/rubber blends are incompatible, the thermoplastic cannot be modified. Clearly the improvement of the compatibility of the two phases in heterogeneous polymer blends by adding a small amount of grafted or block copolymers is a topic of major practical significance.

Polypropylene (PP) and poly(*cis*-butadiene) rubber (PcBR) are nonpolar, and PP/PcBR is in-

compatible with. But they may become compatible or semicompatible in PP/PcBR-*g*-ethyl acrylate (PcBR-*g*-EA) blends.

In this article the phase structure and morphology of PP/PcBR and PP/PcBR-*g*-EA blends are discussed. The relation of phases in PP/PcBR (or PcBR-*g*-EA) blends was studied by small angle X-ray scattering (SAXS). The interface layer (compatible domain) was calculated using SAXS data. The phase behavior of blends was measured by small angle light scattering (SALS). The morphology of blends was observed by scanning electron microscopy (SEM).

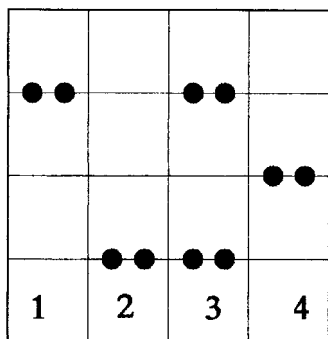
## EXPERIMENTAL

### Materials

Polybutadiene rubber (high *cis*-1,4 content; Mooney viscosity 46) and PP (melt index, MI = 8)

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**Figure 1** The result of TLC. 1, PEA; 2, PcBR; 3, PcBR/PEA; 4, PcBR-*g*-EA.

from Beijing Yanshan Petrochemical Company (China) were used. PEA was synthesized in our laboratory. EA, benzoyl peroxide (BPO), and other chemicals were used as received.

### Synthesis of PcBR-*g*-EA

In a four-necked, round bottom flask under nitrogen, the graft reaction was carried out in anhydrous xylene at 45–60°C. Typical concentrations were 20 g/L, 0.5 mol/L, and 9.0 mmol/L for PcBR, EA, and BPO, respectively. The residual EA and homopolymer of EA was extracted in a Soxhlet extractor with acetone-butane (3 : 1 on volume) for 72 h. The grafting copolymer (PcBR-*g*-EA) was obtained after drying in a vacuum.

The existence of PcBR-*g*-EA was verified by thin layer chromatography (TLC). The solution sample (xylene as solvent) of 2% PcBR with PEA on filter paper was dripped using iodine-alcohol ethanol solution as developer. Figure 1 shows the TLC results. Crosslinking was not caused in the PcBR-*g*-EA because it was dissolved by anhydrous xylene. The grafted product was characterized by chemical analysis as presented in another article. The graft yield of PcBR-*g*-EA on PP/PcBR-*g*-EA blends was 8.94%.

### Preparation of Blends

Binary PP/PcBR and PP/PcBR-*g*-EA blends were prepared by melt mixing the polymer in a mixing apparatus (XXS-30 Mixer, China) at a temperature of 180°C with a residence time of 15 min at 30 rpm. The compositions of the investigated blends are reported in Table I.

### Specimen Preparation

The premixed material was compression molded to get slabs of 1-mm thickness at 180°C with a residence time of 5 min in a common heated press at 24.5 MPa. The slabs were quickly moved to a cool press with a residence time of 4 min at room temperature and at 2405 MPa. The 1-mm thick slabs were cut by a cutter from a 2 × 4 mm specimen on which SAXS tests were performed. The same slabs were broken in liquid nitrogen in which SEM tests were executed.

### Characterization

The IR spectra of PcBR (or PP/PcBR blends) was measured by a Nicolet-5DX IR spectrometer. The compatibility of the two phases in the blends was studied by SAXS on a Rigaku D/max-rA. The phase behaviors of the blends was measured by SALS on a 2-dimensional laser angles scattering instrument. The morphology of the fracture surface of the blends was observed on a Hitachi X-650 scanning electron microscope.

## RESULTS AND DISCUSSION

### IR Spectrum Studies

Polybutadiene can be formed by a 1,2 addition or a *cis*- or *trans*-1,4 addition. Polybutadiene with high *cis*-1,4 content may cause isomerization at high temperature (about 180°C). It is not hopeful that the isomerization of poly(*cis*-1,4 butadiene) occurred in this work. Manson and Sperlin<sup>2</sup> found that the IR spectrum of the 1,2 structure of polybutadiene is at 910 cm<sup>-1</sup>, the characteristic IR spectrum of the *trans*-1,4 structure of poly(*trans*-1,4-butadiene) is at 967 cm<sup>-1</sup>, and the IR spectrum of the *cis*-1,4 structure of poly(*cis*-1,4-butadiene) is at 738 cm<sup>-1</sup>. Figure 2 indicates the IR spectra of PcBR and PP/PcBR blends. Obviously, the characteristic spectra of the 1,2 Structure and the *trans*-1,4 structure are not found in Figure 2. Therefore, the isomerization of polybutadiene in PP/PcBR blends is not caused by melt mixing.

### SAXS Studies

The relationship between the two phases in the blend may be discussed by SAXS intensity. According to Porod's Law,<sup>2,3</sup> the intensity in the tail

**Table I** Compositions of Blends

Component	Compositions (wt %)								
PP/PcBR	100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80
PP/PcBR-g-EA	100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80

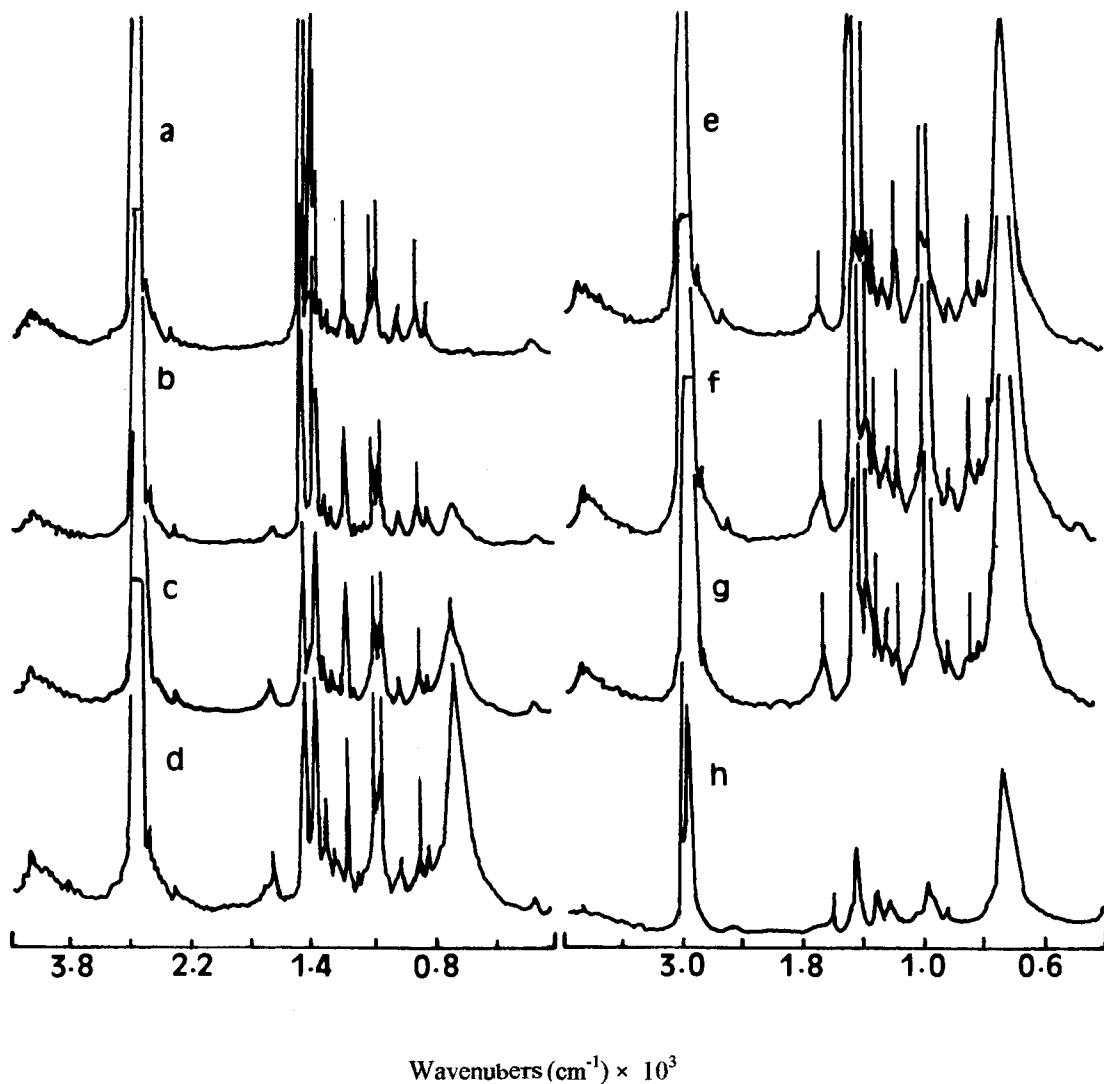
of a diffraction curve from a two-phase structure with sharp phase boundaries is given by

$$\lim I(s) = C/s^4 \quad (1)$$

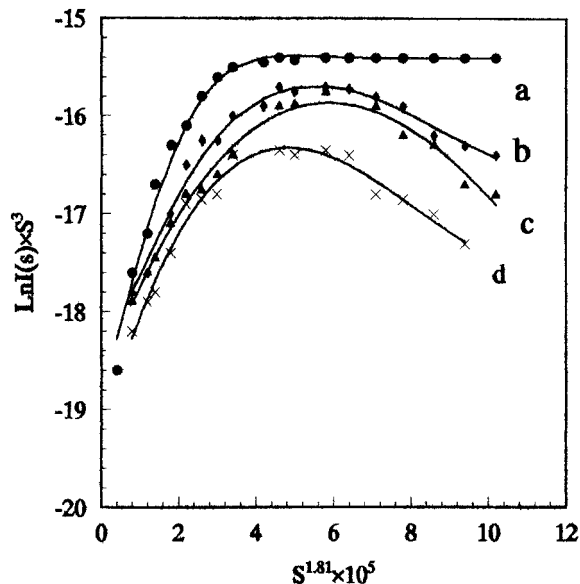
where  $I(s)$  is the intensity of scattering,  $s = 2 \sin$

$\theta$ . It is assumed that the interface layer (compatible domain) exists. The Porod's law is given by

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



**Figure 2** The IR spectra of PP, PcBR, and PP/PcBR blends. (a) PP, (b) PP/PcBR10, (c) PP/PcBR20, (d) PP/PcBR30, (e) PP/PcBR40, (f) PP/PcBR50, (g) PP/PcBR60, (h) PcBR.



**Figure 3** Plot of  $S^3 I(s)$  against  $S^{1.81}$  for PP/PcBR-*g*-EA blends: (a) 70/30/0, (b) 70/0/30, (c) 50/0/50, (d) 30/0/70.

where  $\sigma_b$  is the interface layer thickness between the two phases of the blend. In a four slit system eq. (1) may be approximated by

$$I(s) \cong \frac{K}{s^4} \exp[-38(\sigma_b s)^{1.81}]. \quad (3)$$

A plot of  $[I(s) \cdot s]$  versus  $s^{1.81}$  was used and the results are shown in Figure 3. The curve of *a* to level *s* increased because the sharp phase boundary existed in the PP/PcBR blend. In other curves the tail of the curve decreased when *s* increased and  $\sigma_b$  was calculated by the slope of the tail of curve. The results are listed in Table II. The value of  $\sigma_b$  depends on the composition of the blends and it is maximum for the PP(60)/PcBR-*g*-EA blend. Clearly, the model<sup>4</sup> of the phase structure

may be designed as PP/PcBR-*g*-EA blends and it is shown in Figure 4.

Additional information may be obtained from Debye–Bueche<sup>5</sup> analysis or better yet from the invariant defined by<sup>6</sup>

$$Q = \int_0^\infty I(s) s^2 ds \quad (4)$$

where  $Q = \langle \eta^2 \rangle_{av} / c'$ ,  $c'$  is constant. The  $\langle \eta^2 \rangle_{av}$  is the mean square melted; if it is equal to zero, the scattering system is homogeneous.  $I(s)$  is the scattering intensity.  $Q$  may be calculated by data of  $I(s)$  with  $s$  from the SAXS for blends from eq. (4). Figure 5 depicts the relation of  $Q$  with the composition of the blends. As might have been expected,  $Q$  passed through a minimum for an intermediate concentration of PcBR-*g*-EA and the corresponding value of  $\sigma_b$  was maximum. Therefore, the homogeneity of the blend at PcBR-*g*-EA = 40 wt % was better with other compositions of PP/PcBR-*g*-EA blends.

Presently we use a modification of the Debye–Bueche<sup>3,5</sup> description of scattering from random heterogeneous media, which for spherical symmetrical systems gives

$$I(h) = K \langle \eta^2 \rangle_{av} \int_0^\infty \gamma(r) \frac{\sinh r}{hr} r^2 dr \quad (5)$$

where  $K_2$  is a proportionality constant and  $h = (4\pi/\lambda) \sin \theta$ ;  $\gamma(r)$  is the correlation function. The correlation function may be obtained by Fourier inversion of  $I(h)$ . For systems not having a clearly defined structure,  $\gamma(r)$  often decreases monotonically with  $r$  and may be represented by an empirical equation such as

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

where the parameter  $a_c$  is known as a correlation distance and defines the size of heterogeneity. For dilute discrete particles,  $a_c$  is related to the parti-

**Table II** Interface Layer Thickness ( $\sigma_b$ )

Compositions (wt %)	PP/PcBR/PcBR- <i>g</i> -EA								
	70/30/0	90/0/10	80/0/20	70/0/30	60/0/40	50/0/50	40/0/60	30/0/70	20/0/80
$\sigma_b$ (Å)	0.000	2.4188	2.5456	5.5754	7.6940	4.8969	5.8538	4.2496	2.7771

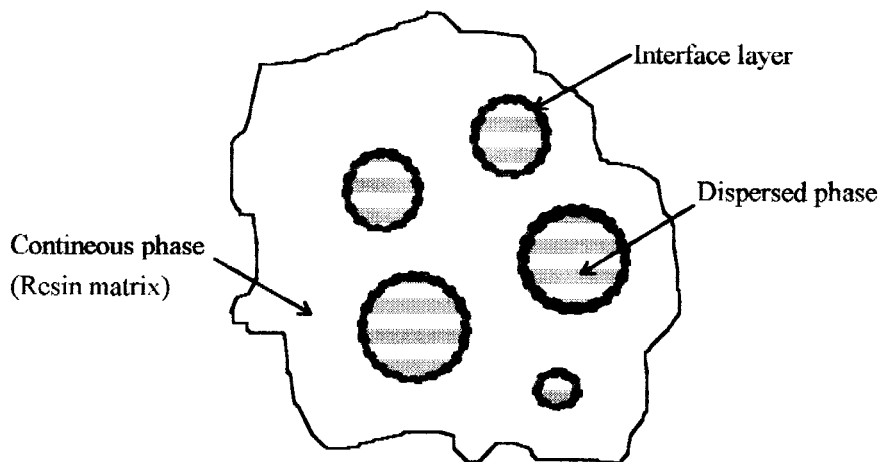


Figure 4 The model of the phase structure of blends.

cle size. Thus, for spheres,  $a_c$  is  $(4/3)R$ . For more concentrated systems,  $a_c$  is not simply related to the size of the structural unit but depends upon the interparticle and intraparticle distances. It may be considered as an average wavelength of the  $\eta(x)$  fluctuations whereas  $\langle \eta^2 \rangle$  is a mean square amplitude.

If eq. (6) is substituted into eq. (5) one obtains

$$I(h) = K_3 \langle \eta^2 \rangle_{av} a_c^3 [l + h^2 a_c^2]^2 \quad (7)$$

Upon rearrangement, this gives

$$I(h)^{-1/2} = [K_3 \langle \eta^2 \rangle_{av} a_c^3]^{-1/2} [l + h^2 a_c^2]. \quad (8)$$

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  $a_c^2$ . Figure 6 shows that the value of  $a_c^2$  is calculated and relates to the composition of the blends. The variation of  $a_c$  is the same as the interface layer.

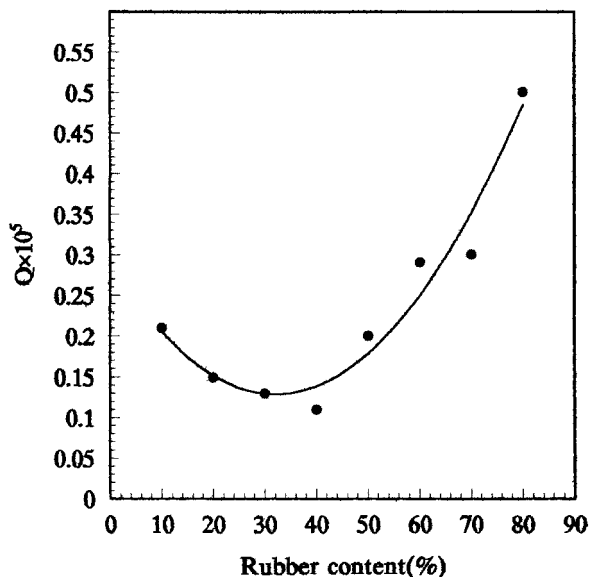


Figure 5 The relation of  $Q$  with composition of blends.

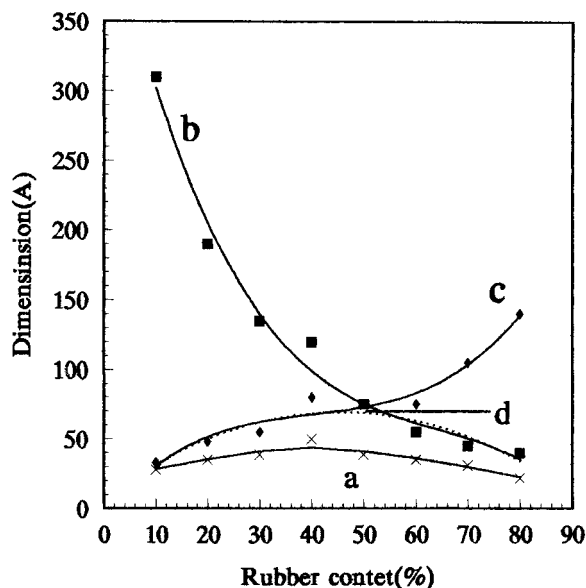
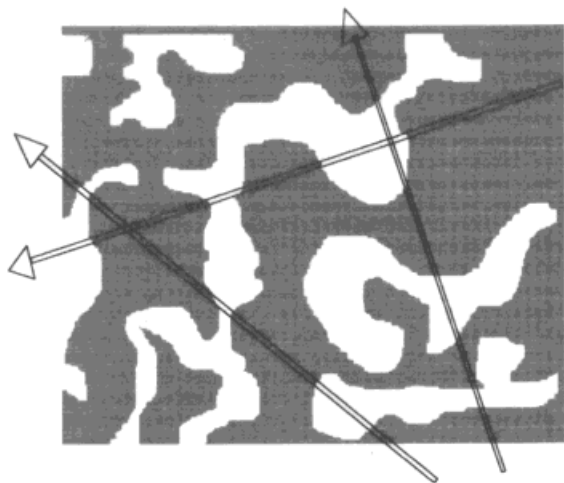


Figure 6 The relation of  $a_c$  and chord length with composition of blends: (a)  $a_c$ , (b)  $l_{PP}$ , (c)  $l_{PcBR-g-EA}$ , (d) average size of disperse phase.



**Figure 7** Chord lengths of a random two phases system.<sup>8</sup>

An analysis may be made using the approach of Debye et al.<sup>7</sup> for a random depression of two phases of volume fractions,  $\varphi_1$  and  $\varphi_2$ , and definite compression for which the ratio of the interphase surface,  $S$ , to the volume,  $V$ , is related to the correlation distance by

$$S/V = 4\varphi_1\varphi_2/a_c. \quad (9)$$

Kralky<sup>8</sup> and Stein<sup>9</sup> defined the average chord lengths  $l_1$  and  $l_2$  that are illustrated in Figure 7. If lines are randomly drawn through the system in these dimensions,  $l_1$  represents, for example, the mean length of the line segments through regions of phase 1.

$$l_1 = \Delta\varphi_1/(S/V) \quad (10)$$

and

$$l_2 = \Delta\varphi_2/(S/V), \quad (11)$$

from which it follows that

$$l_1 = a_c/\varphi_2 \quad (12)$$

and

$$l_2 = a_c/\varphi_1. \quad (13)$$

The values for  $l_{PP}$  and  $l_{PcBR-g-EA}$  are calculated using eqs. (12) and (13) and assuming that the two phases consist of pure components. Results are in-

clude in Figure 6. With increasing concentration of a component, its persistence lengths become greater. The value of  $l_{PcBR-g-EA}$  for 10% PcBR-*g*-EA blend is of the order of 30.84 Å, which is about the size of an isolated PcBR-*g*-EA molecule. And the value of  $l_{PP}$  is 40.0 Å for 10% PP blend. Therefore, this suggests that dilute dispersion of PcBR-*g*-EA or PP in the blends is molecularly distributed. The distribution of the size of the disperse phase may be shown using curve d (see Figure 6).

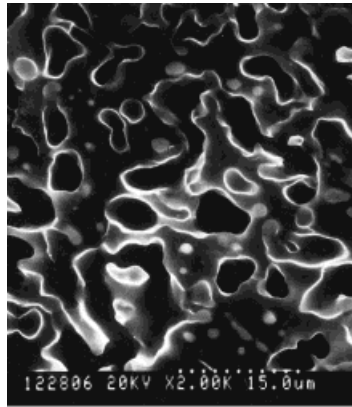
### SEM Studies

The overall morphology of blends was investigated on the surface of specimens broken in liquid nitrogen. SEM micrographs of cryogenically fractured surfaces of the PP/PcBR blend are shown in Figure 8. As can be seen, such a blend exhibits a holelike morphology uniformly distributed throughout the whole sample. The careful fracture surface of the PP/PcBR-*g*-EA blends shows no evidence of holelike morphology (Fig. 8), but the two phases are separate too. The phase interface is clearly different between PP/PcBR-*g*-EA and PP/PcBR blends because of the existence of an interface layer on PP/PcBR-*g*-EA. Figure 9 shows that the mean size of the dispersed phase in the calculated phase was calculated using the micrographic treatment technique.

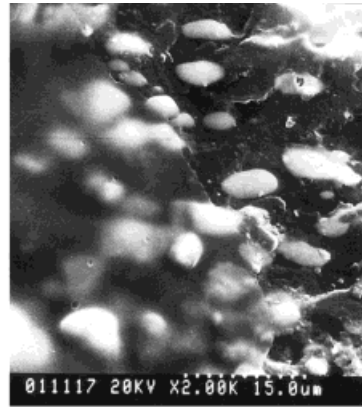
The mean size of the dispersed phase of PP/PcBR-*g*-EA blends was smaller than in the PP/PcBR blends because of the existence of an interface layer on PP/PcBR-*g*-EA. The valuation of the mean size of the dispersed phase with the component was similar to the results of the correlation distance  $a_c$  and average size of disperse phase [see Fig. 6(a and d)].

### Light Scattering Studies Phase Separation

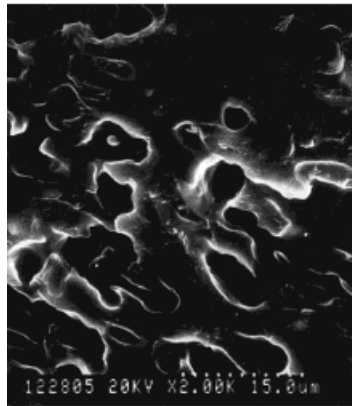
Equation (5) is similarly suitable for light scattering. Therefore, it is the same in physics that  $a_c^*$ ,  $l_{PP}^*$ , and  $l_{PcBR-g-EA}^*$  are calculated by light scattering for SAXS results, but the size range is different. Clearly the degree of phase separation of the blends may be characterized by the variation of the value of the correlation distance and average chord length with time of heat treatment at 80°C. Results are included in Figure 10, the  $a_c^*$ ,  $l_{PP}^*$ , and  $l_{PcBR-g-EA}^*$  values are linearly increased with heat treatment time increase. Thereby, the degree of phase separation in the blends is increased.



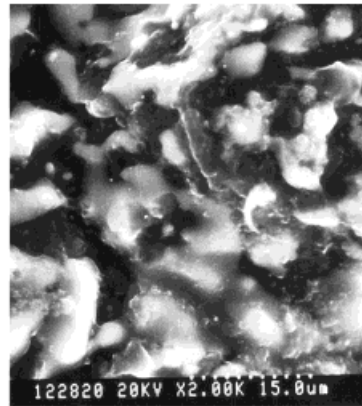
PP/PcBR(80/20)



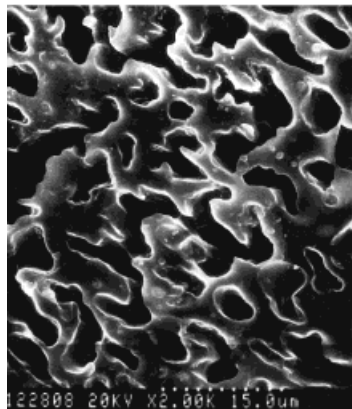
PP/PcBR-g-EA(80/20)



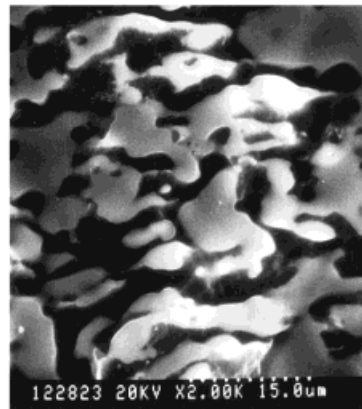
PP/PcBR(60/40)



PP/PcBR-g-EA(60/40)



PP/PcBR(40/60)



PP/PcBR-g-EA(40/60)

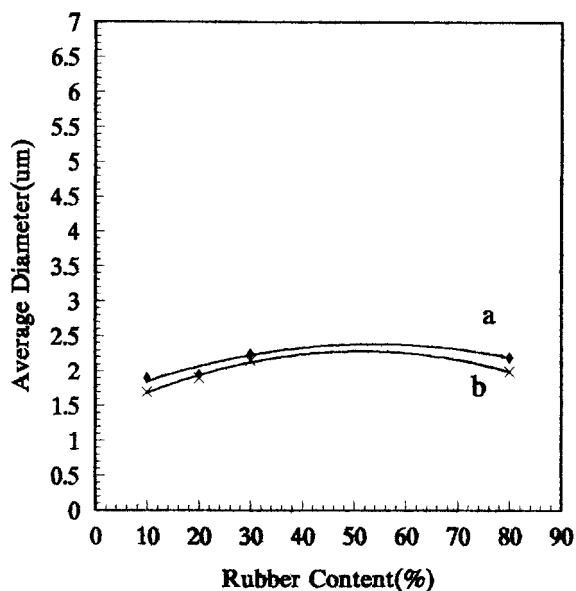
**Figure 8** SEM micrographers if blends.

## CONCLUSIONS

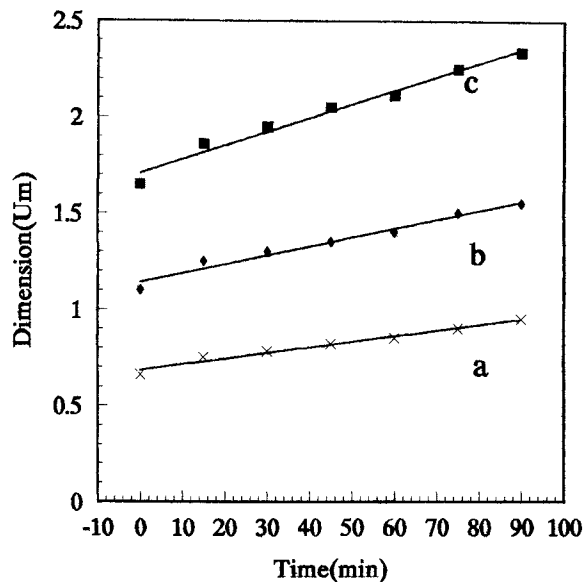
The semicompatible blends of PP with PcBR-*g*-EA was proved by SAXS and the interface layer thickness was calculated, which depends upon the concentrations of the blends. The model of two phase structures consisting of interface layers (interphase) was separate on the blends.

Quantitative SAXS and SEM measurements on blends of PP with PcBR-*g*-EA were consistent with the structure of the phase consisting of the phase size. The mean size of the dispersed phase in blends of PP with PcBR-*g*-EA was smaller than in blends of PP with PcBR.

The kinetics of phase separation in blends of PP with PcBR-*g*-EA was studied using correlation distance and average chord lengths from SALS. The correlation distance and average chord lengths ( $l_1$  and  $l_2$ ) linearly increased at 80°C, so the degree of phase separation in the blends increased.



**Figure 9** Mean size of dispersed phase of blend: (a) PP/PcBR, (b) PP/PcBR-*g*-EA.



**Figure 10** The relation of correlation distance and chord lengths with time at 80°C on PP/PcBR-*g*-EA blends: (a)  $a_c^*$ , (b)  $l_{PP}^*$ , (c)  $l_{PcBR-g-EA}^*$ .

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