Compatibilization of Styrene–Butadiene–Styrene Block Copolymer in Polypropylene/Polystyrene Blends by Analysis of Phase Morphology

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ABSTRACT: Effect of compatibilization of styrene–butadiene–styrene (SBS) block copolymer in polypropylene/polystyrene (PP/PS) blends was studied by means of small angle X-ray scattering (SAXS) and scanning electron microscope (SEM). According to SAXS, a certain amount of SBS was located at the interface in all the analyzed samples, forming the relatively thicker interface layer penetrating into homopolymers, and the thickness of the interface layer was quantified in terms of Porod light scattering theory. The incorporation of SBS into PP/PS blends resulted in a decrease in domain size following an emulsification curve as well as an uniform size distribution, and consequently, a fine dispersion of PP domains in the PS matrix. This effect was more pronounced when the concentration of SBS was higher. A critical concentration of SBS of 15% above which the interface layer approaches to saturation and domain size attains a steady-state was observed. Further, the morphology fluctuation of unetched fracture surface of umcompatibilized and compatibilized blends was analyzed using an integral constant Q based on Debye-Bueche light scattering theories. Variation of Q as a function of the concentration of SBS showed that, due to the penetrating interface layer, adhesion between phases was improved, making it possible for applied stress to transfer between phases and leading to more uniform stress distribution when blends were broken; accordingly, a more complicated morphology fluctuation of fracture surface appeared. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 365–370, 2007

Key words: compatibilization; polypropylene; polystyrene; phase morphology

INTRODUCTION

Blending of polymers is an effective way to obtain new high-performance materials without synthesizing new polymers. However, most polymers are immiscible thermodynamically, which constraints severely the application of polymer blends. A common and effective method is the addition of suitably chosen copolymer. These copolymer having segments at least partially miscible with the particular components of the blend system are located between homopolymers and form the interface layer. The localization of the copolymer at the interface with the block or graft extending into their respective homopolymer phases not only minimizes the contacts between the unlike segments of the copolymer and homopolymer but also displaces the two homopolymer away from the interface, thereby decreases the enthalpy of mixing between homopolymers, which leads to a better compatibility between phases as well as a fine and more stable morphology. Effect of compatibilizers in controlling the domain size in blends can be described as two different mechanisms: coalescence suppression and interfacial tension reduction.[1] Lepers et al.[2] examined the relative role of coalescence and interfacial tension of styrene–ethylene butylene–styrene grafted with maleic anhydride (SEBS-g-MA) in controlling dispersed phase size reduction during the compatibilization of polyethylene terephthalate/polypropylene (PET/PP) blends. According to Lepers, in the PET/PP (99/1) blend, SEBS-g-MA can only reduce the interfacial tension without suppressing the coalescence of dispersed particles, but in the PET/PP (90/10) blend, the addition of the compatibilizer leads to both interfacial tension reduction and coalescence suppression. However, in both cases, a sharp decrease in minor phase size is observed with the addition of small amount of the compatibilizer. This decrease is followed by a leveling-off at high concentration, which can be described by the emulsification curve. Similar result was also found by other researchers.[3–5] Besides, the incorporation of compatibilizer also results in a better adhesion between phases and consequently better properties of the final product. Halimatudahliana et al.[6,7] reported qualitatively the effect of SEBS on the morphology and properties of PS/PP blends. They

found that the addition of SEBS can strengthen the adhesion between PS and PP and has a positive effect on the ductility of PP/PS blends, which can be confirmed by the plastic deformation of the ductile matrix. However, they did not give a quantitative description of the deformation on the fracture surface.

In the present work, the effect of compatiblization of styrene–butadiene–styrene (SBS) on PP/PS blends was studied. Especially, the morphology fluctuation of fracture surface is analyzed quantitatively by means of a simple and effective method based on Deybe-Bueche light scattering theories. It will be found that the addition of SBS strength the adhesion between PP and PS, which results in an uniform stress distribution and consequently a more complicated fracture morphology when blends are broken, which can be well described by an integral constant Q.

EXPERIMENTAL

Materials

The basic materials used in this study were a commercial grade polystyrene (PS, 666D) with a density of 1.05 g cm^{-3}, $\overline{M_w}$ of 5.8×10^5 and a glass transition temperature of 111°C; a commercial grade polypropylene (PP, 1300) with a density of 0.91 g cm^{-3}, $\overline{M_w}$ of 5.0×10^5 and a glass transition temperature of 17°C. Linear block copolymer styrene–butadiene–styrene (SBS) was used as the compatibilizer. Detailed characteristics of this copolymer are shown in Table I. All these materials were supplied by Beijing Yanshan Petrochemical. The melt-viscosity of pure materials was determined based on Cox-Merz rule using a Stresstech rheometer in plate–plate configuration. Discs of 25 mm in diameter and 1.0 mm in thickness were obtained by compression molding at 190°C for 5.0 min under a pressure of 20 MPa. These discs were then dried at 50°C under vacuum prior to the rheological measurements. The latter were performed at 190°C at a constant strain of 3%. The frequency was varied from 100 to 1 rad/s. Viscosities of all materials at the shear applied in the mixer are given in Table I.

The blends were prepared in an internal mixer (XXS-30 mixer with rotor diameter of 35 mm, China). Prior to processing, all materials were dried for 12 h

under vacuum at 80°C. Two different mixing procedures were applied: first, PP/SBS blends were blended for 5 min at 190°C and a rotor speed of 45 rpm, which corresponds to a shear rate of 72 S^{-1}. Weight concentrations of SBS ranging from 0 to 20% with respect to the minor phase PP was used. The maximum concentration of the compatibilizer (SBS) used in the present work may lead to an interface saturation.[3] Second, PS was blended with PP/SBS in an 80/20 weight concentration for 10 min under the same processing conditions, i.e., a shear rate of 72 S^{-1} and a mixing temperature of 190°C. This two-step mixing procedure is widely used and proved to be advantages for copolymer to migrant and be located in boundary between phases without forming micelles.[3,8] After the mixing, blends were taken out of the mixer and put into ice-water to freeze the original structure.

Small angle X-ray scattering

Small angle X-ray scattering (SAXS) measurements were performed using an X-ray scattering apparatus (FIGAKU D/MAX 25800V/PC). Flakes of 100 mm in border length and 1.0 mm in thickness were obtained by compression molding for all blends. After cooling to room temperature, these flakes were incised into samples of 10×20 mm^2 for observation in the scattering apparatus. The intensities were taken in the range of the scattering vector $k = (4\pi/\lambda) \sin\frac{\theta}{2}$ from 0.007 to 0.2 Å^{-1} (where θ is the scattering angle and $\lambda = 1.54$ Å is the wave-length of the incident light). The measured intensities were corrected for sample thickness and transmission.

Morphological characterization

A scanning electron microscope (SEM, Philips XL30) operated at an accelerating voltage of 20 kV was used to examine the fracture morphology of blends. The preblended samples were broken in liquid nitrogen and the fracture surface was covered with gold for the observation in the microscope. To make sure the original structure of blends intact, the surface was not etched. The morphology was quantified using self-made software. Contour and mass center of each domain were detected and each domain was scanned by straight lines going through the mass center from different directions, and the span from one side of a domain to the other, which is defined as the chord length Λ in this paper was noted by a computer; therefore, the average domain size can be calculated by averaging these Λ_s. To obtain more reliable data, about 500 particles were considered to calculate these structure parameters for each micrograph. Moreover, the morphology fluctuation of fracture surface can also be analyzed by applying Fou-

TABLE I
Materials Used in This Work

Polymers	$\overline{M_w}$ (g/mol)	Viscosity at 72 S^{-1} (10^2 Pa S)	T_g (°C)	Structure
PP	500,000	5.88	17	Homopolymer
PS	580,000	3.70	111	Homopolymer
SBS	120,000	32.2	–	Linear SBS bound styrene 30% mass

rier transformation to SEM micrographs using this software, which will be discussed in detail later.

RESULTS AND DISCUSSION

Small angle X-ray scattering

According to Porod's law,[9] the intensity in the tail of the scattering curve from a two-phase system with sharp phase boundary is given by

$$\lim_{s \to \infty} I(s) = \frac{C}{s^4} \tag{1}$$

where I(s) is the scattering intensity, $s = 2 \sin \theta / \lambda$, and C is a constant. For system with thicker interface layer, eq. (1) should be modified as

$$\lim_{s \to \infty} I(s) \approx \frac{C}{s^4}(1 - 4\pi^2\sigma_b^2 s^2) \tag{2}$$

where σ_b is the thickness of interface layer. For a four slit system, eq. (2) may be approximated by

$$\lim_{s \to \infty} I(s) \approx \frac{K}{s^3} \exp[-38(\sigma_b\, s)^{1.81}] \tag{3}$$

Plotting a curve of ln $I(s)s^3$ versus $s^{1.81}$ (see Fig. 1), σ_b can be easily obtained. From Figure 1, the curve of a to level s increases because the sharp phase boundary exists in PP/PS blends. In other curves, the tail of the curve decreases when s increases and σ_b is calculated by the slope of the tail of curves; the result is shown in Figure 2 and corresponding values of σ_b are listed in Table II. As can be seen, the value of σ_b depends on the concentration of SBS and shows a maximum around 15% of SBS with respect
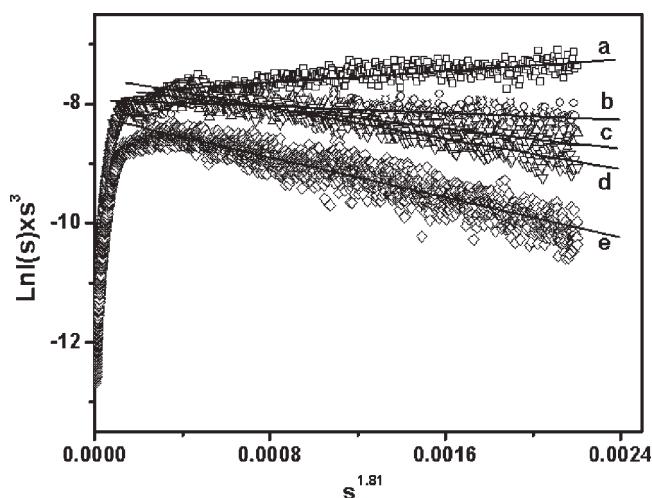

Figure 1 Curves of ln $I(s)s^3$ versus $s^{1.81}$ with different concentration of SBS: (□) SBS = 0%, (○) SBS = 3.75%, (△) SBS = 5%, (▽) SBS = 7.5%, and (◇) SBS = 12.5%.
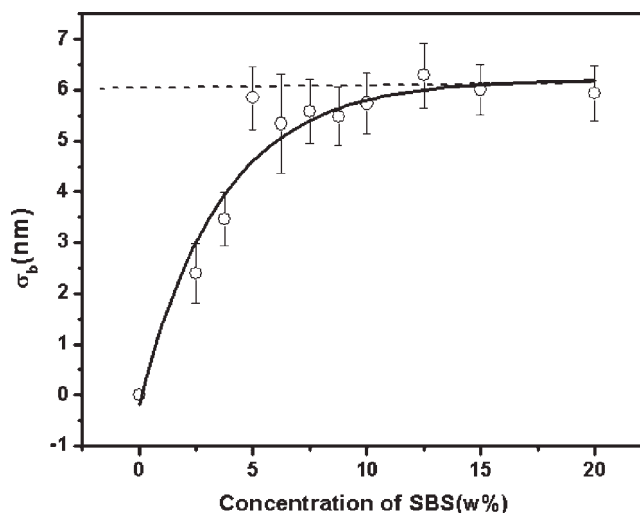

Figure 2 Variation of σ_b as a function of concentration of SBS.

to PP. Above 15%, σ_b levels off, indicating that the interface layer approaches to saturation.

SEM studies

Figure 3 shows the fracture morphology of PP/PS blends compatibilized with various content of copolymer SBS. A domain dispersion morphology type can be observed, that is, PP is distributed in the matrix in the form of spherites, forming the dispersed phase and PS is the continuous phase. In Figure 4, the domain size and size distribution as a function of concentration of SBS are shown (Calculation concerning size distribution has been discussed detailedly in our previous work[10]). Since the deviation of average chord length Λ_m has been listed in Table II, it is not represented in Figure 4 for the purpose of showing the typical variation of Λ_m clearly. As can be seen, when SBS is added, the dispersed phase dimension decreases with a typical dependence of the "emulsification curve" described previously by Favis and coworkers.[11–13] The addition of the interfacial modifiers leads to a decrease in domain size up to a critical concentration, C_{crit} (15%). Above this concentration, the interface layer is saturated and the domain size attains a steady-state value. This typical variation of domain size has been studied by other researchers.[2] According to previous studies, the decrease in domain size before C_{crit} can be ascribed to the coalescence suppression and interfacial tension reduction by partial emulsification. It is well known that, when a suitably chosen copolymer is added to uncompatible polymer blends, it will anchor its molecular segments in homopolymers, decrease the enthalpy of mixing and, consequently, reduce the interfacial tension; further, it is reported that the interfacial tension decreases linearly with the increase of copolymer concentration when this

TABLE II
Variation of Structure Parameter with Content of SBS

Content of SBS %	Λ_m (μm)	σ_b (nm)	Distribution width of Λ
0	2.87 ± 2.43	0	0.349 ± 0.012
2.5	2.71 ± 2.33	2.39 ± 0.59	0.273 ± 0.014
3.75	2.64 ± 2.30	3.46 ± 0.53	0.252 ± 0.011
5	2.59 ± 2.13	5.95 ± 0.62	0.237 ± 0.009
6.25	2.57 ± 2.09	5.34 ± 0.97	0.210 ± 0.012
7.5	2.53 ± 2.05	5.58 ± 0.63	0.212 ± 0.008
8.75	2.50 ± 1.91	5.48 ± 0.58	0.215 ± 0.004
10	2.45 ± 1.67	5.74 ± 0.59	0.210 ± 0.006
12.5	2.43 ± 1.61	6.29 ± 0.64	0.184 ± 0.009
15	2.40 ± 1.44	6.01 ± 0.50	0.181 ± 0.006
20	2.41 ± 1.39	5.94 ± 0.55	0.177 ± 0.008

concentration is lower than C_{crit}. Tang and Huang,[14] and Noolandi and Hong[15,16] developed theories based on statistical thermodynamics that can be used to describe the emulsifying effect of a copolymer interfacial modifier on polymer blends. According to them, the decrease in interfacial tension can be reduced to the following expression:

$$\Delta\sigma_{12} = d\phi_c\left\{\frac{1}{2}\chi + \frac{1}{Z_c} - \frac{1}{Z_c}\exp\frac{Z_c\chi}{2}\right\} \tag{4}$$

where d is the width at the half-height of the copolymer profile in units of b, χ is the Flory-Huggins interaction parameter, Z_c is the degree of polymerization of the copolymer, and ϕ_c is the volume fraction of the copolymer. As shown by eq. (4) a linear dependence of the interfacial tension reduction on the copolymer volume fraction is predicted. Further, the minimum obtainable domain diameter in polymer blends can be estimated from the critical capillary number, as in follows[17,18]

$$(Ca)_{crit} = \frac{\eta_m\gamma D_n}{2\sigma_{12}} = \frac{16\,p + 16}{2(19\,p + 16)} \tag{5}$$

and

$$(Ca)_{crit} = \frac{\eta_m\gamma D_n}{2\sigma_{12}} = 4\left(\frac{\eta_d}{\eta_m}\right)^{\pm 0.81} \tag{6}$$

where η_m represents the matrix viscosity, γ is the shear rate, D_n is the average domain diameter, σ_{12} is the interfacial tension, and p is the viscosity ratio η_d/η_m with η_d being the viscosity of the dispersed phase. On the basis of eqs. (4)–(6) in both cases, the domain size should decrease linearly with increase of concentration of SBS. However, this utopian linear decrease was not observed, even in the case of low concentration of SBS. This result can be ascribed to the coalescence between domains, which is not accounted for in eqs. (5) and (6). Fortelny and
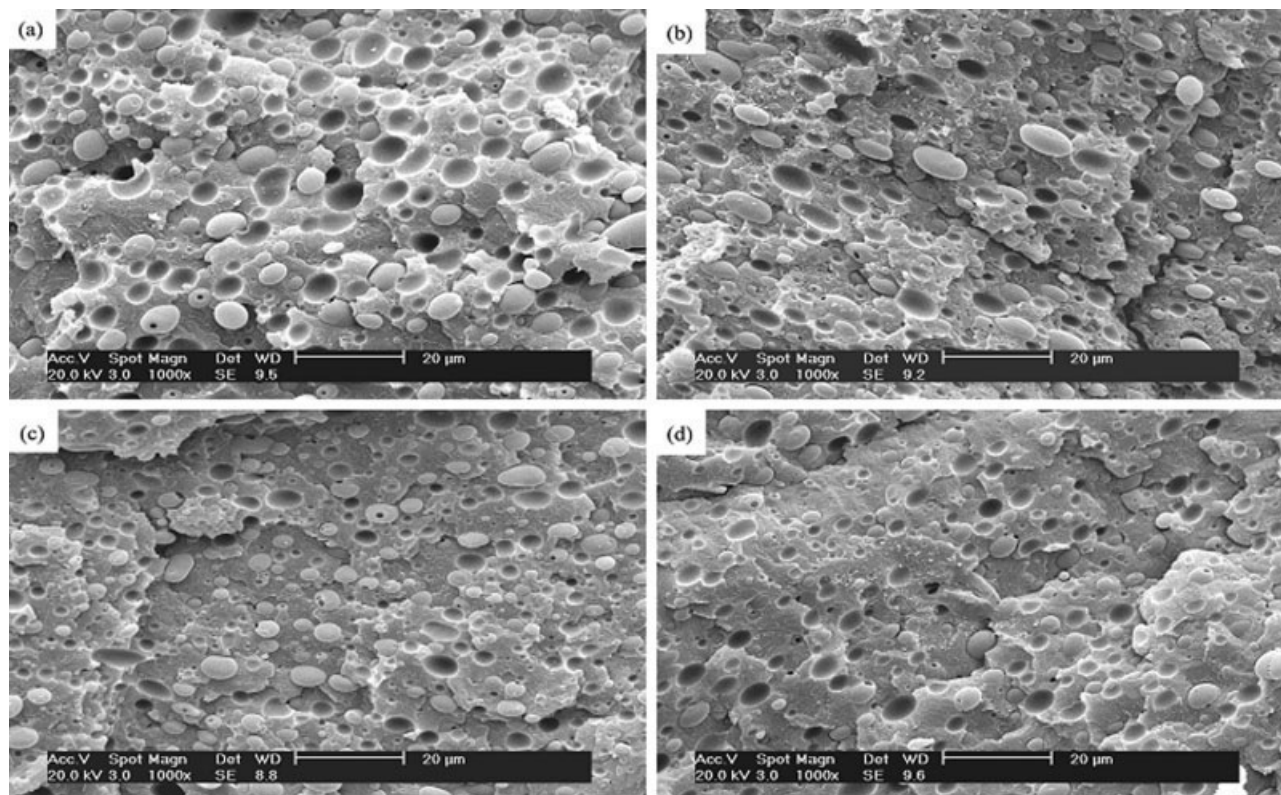

Figure 3 Morphology of PP/PS/SBS blends with different concentration of SBS with respect to PP: (a) 0%, (b) 3.75%, (c) 15%, and (d) 20%.
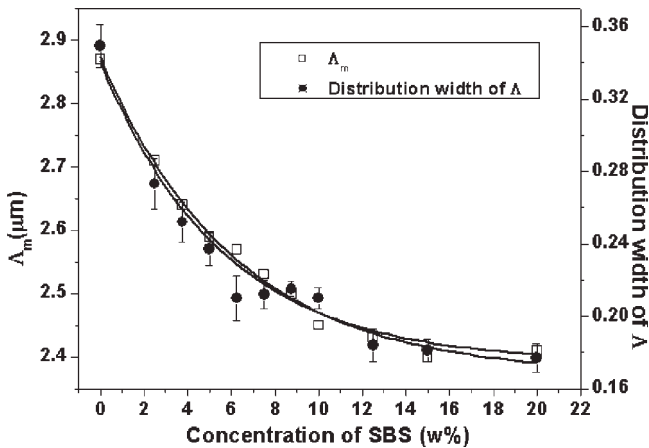
Figure 4 Variation of Λ_m and distribution of Λ as a function of concentration of SBS.

Kovar[19] proposed an equation taking into account both domain break-up and coalescence to predict the final blend morphology equation

$$r = r_{crit} + \left(\frac{\sigma_{12}}{\eta_m} \frac{\alpha}{f_1} \right) \phi \qquad (7)$$

where r_{crit} represents the critical domain radius as calculated from $(Ca)_{crit}$, α is the probability that domain will coalesce after collision, f_1 is the slope of a function describing the frequency of domain break-up at $(Ca)_{crit}$, and ϕ is the volume fraction of the dispersed phase. Despite that eq. (7) still contains several parameters that can not easily be quantified for the blending of viscoelastic polymers, it might be used to explain the nonlinear relation between domain size and concentration of SBS.

According to SAXS results, besides the significant role of copolymer compatibilizer in reducing domain sizes, the introduction of copolymer also promotes the formation of relatively thicker interface layer, permitting applied stress to transfer between phases and leading to an uniform stress distribution when blends are broken. In the following section, the effect of compatibilization of SBS on PP/PS blends will be further discussed by analyzing the morphology fluctuation of fracture surface of PP/PS blends, which is related to the stress distribution.

It is reported in the experiment section that the fracture surface was not etched to ensure it to be intact. In this case, the fluctuation of gray level of different pixels on these SEM images can be regarded as a true reflection of the morphology of fracture surface. Besides, as reported by Wang et al.,[20] this morphology fluctuation has a significant relation with compatibility between phases in blends, that is, the more complicated the morphology fluctuation, the better the compatibility. Consequently, it is effective to study the effect of compatibilization by analysis of the fluctuation of gray level. For

this purpose, an integral constant Q, which is often used to study the composition fluctuation and density fluctuation in light scattering performance, is introduced in terms of theories of light scattering as follows.

According to Debye–Bueche,[21] description of scattering from random heterogeneous media, for spherically symmetric system, the scattering intensity is given as

$$I(k) = K\overline{\eta^2} \int_0^{+\infty} \gamma(r) \frac{\sin(kr)}{kr} r^2 \, dr \qquad (8)$$

where $k = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}$, $\overline{\eta^2}$ is the mean square fluctuation of density, $\overline{\eta^2} = < \eta(\overline{rj})\eta (\overline{rm}) >_{r_{mj}}$, and $\gamma(r)$ is the density correlation function and can be obtained by the inverse Fourier transformation[22]

$$\gamma(r) = \frac{C}{\overline{\eta^2}} \int_0^{\infty} I(k) \frac{\sin(kr)}{(kr)} k^2 \, dk \qquad (9)$$

if $r = 0$, the correlation function has a value of 1, i.e.,

$$\gamma(0) = \frac{C}{\overline{\eta^2}} \int_0^{\infty} I(k)k^2 \, dk = 1 \qquad (10)$$

$$\frac{\overline{\eta^2}}{C} = \int_0^{\infty} I(k)k^2 \, dk = Q \qquad (11)$$

From eq. (11), Q is related to the fluctuation of density. In general, Q could also be used to describe fluctuations of different parameters such as pressure, dielectric coefficient, composition, etc., and certainly, is effective to examine the fluctuation of gray level of SEM images. For this purpose, the Fourier transformation is applied to different regions on SEM images to obtain the power spectrum images equivalent to the light scattering images,[23] then, Q can be easily calculated from the variation of $I(k)$ with k
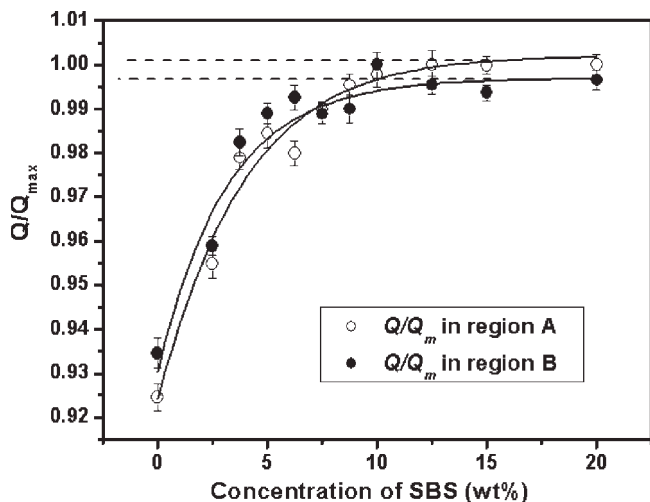

Figure 5 Typical variation of Q as a function of concentration of SBS.

(details concerning the Fourier transformation is discussed in our previous work[24]). Prior to the transformation, the whole SEM image was classified into two different regions: region included within the contour of each domain signed as region A and region outside of but close contour signed as region B. The Fourier transformation was employed for the two different regions, respectively. In Figure 5, the variation of the dimensionless integral constant Q/Q_{max} in both regions is shown. As can be seen, Q/Q_{max} increases with the concentration of SBS, indicating that the fluctuation is becoming more complicated due to the effect of compatibilization. Influence of compatibilizer on the morphology of fracture surface was also studied by Halimatudahliana et al.[6] Comparing the phase morphology of PP/PS compatibilized blends with that of uncompatibilized blends, they found a level of plastic deformation on the fracture surface of compatibilized blends, suggesting that part of the source of plastic deformation is the presence of stretched and broken fibrils material, which is due to the compatibilizer (SEBS) appearing to span the interfaces between regions of PP/PS. However, in our present work, no distinct deformation of the matrix can be found. This can be ascribed to the strong brittleness of PS matrix. Because of the relatively higher glass transition temperature and the super low temperature at which blends were broken, it is impossible for molecular segments of PS to move, leading to the absence of ductile deformation. To our knowledge, it may be more considerate to regard this fracture surface as a rigid surface composed of stress-yielding points. In this case, the morphology fluctuation reflects the stress distribution when blends were broken. In other words, a uniform stress distribution often leads to a more complicated morphology fluctuation of fracture surface. For PP/PS blends in this work, the supplementary SBS copolymer staying mainly between phases anchors its styrene group in PS phase and butadiene group in PP phase, forming a thicker and penetrating interface layer between homopolymers that can transfer applied stress from the matrix to the dispersed phase, especially when the concentration is higher, in this way, the stress distribution is more uniform and stress-yielding points appear more randomly. Consequently, the fracture surface fluctuation is more complicated, indicating a desired compatibilization.

From above, the fluctuation of surface can be used to study the effect of compatibilization to some extend; further, it has a significant relation with phase adhesion and stress distribution. Consequently, it is valuable to correlate the morphology fluctuation and mechanical properties of materials, this is being studied by our research group and detailed results will be discussed in another paper.

CONCLUSIONS

Influence of compatibilizer SBS on phase morphology of PP/PS blends was studied by analysis of domain size and morphology fluctuation of fracture surface. The results show that domain size of the dispersed phase decreases with the concentration of SBS with a typical dependence of the ''emulsification curve,'' accompanied by a more and more uniform size distribution, indicating that the addition of SBS leads to a fine phase morphology. A critical concentration of SBS of 15% above which the interfacial layer approaches to saturation and domain size attains a steady-state is observed. The effect of compatibilization was also studied by analyzing the morphology fluctuation of fracture surface: SAXS measurement shows that SBS is located between phases and forms the interface layer that penetrates into homopolymers and improves the adhesion between phases. This leads to a more uniform stress distribution at the interface; consequently, a complicated morphology fluctuation of fracture surface appears, confirming the desired effect of compatibilization on the improvement of phase morphology and mechanical properties of blends as well as the validity of using morphology fluctuation of fracture surface to describe the compatibilization.

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