Study on the Compatibility of BR/CR/SBS Blends by Using Small Amounts of SBS

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ABSTRACT: The structures and properties of BR/CR/SBS blends were studied by using optical, electron microscopy, FTIR methods, etc. Results showed that the addition of a small amount of SBS to the thermodynamically immiscible blends BR/CR could significantly promote fine and homogeneous dispersion of the system, increase crosslink density of vulcanizates and tensile strength, and decrease loss of tan δ of the blends. IR spectra also demonstrated the stronger interaction between SBS and BR, CR. The theoretical prediction of compatibilizing activity of SBS in the BR/CR blends is in excellent agreement with experimental results. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 215–220, 1999

Key words: BR/CR/SS blends; electron microscopy, FTIR

INTRODUCTION

Blending of different polymers, which combines the desired properties of each component, is an important method to produce a new material. Such a blend shows poor mechanical properties due to the inherent incompatibility of most polymer combinations and the poor adhesion between phases; this leads to premature failure during processing and application. In recent years several techniques have been proposed to solve this problem. For instance, suitably chosen block or graft copolymers are recognized as a simple and efficient method of controlling the morphology and mechanical properties of immiscible polymer blends. Many experimental investigations[1–5] have demonstrated that the addition of copolymer could effectively decrease the interfacial tension and the particle size of dispersed phases, provide a finer dispersion of the system, and improve mechanical properties of the material. Owing to strong interfacial activity of copolymer in immiscible polymer blends, these methods can offer a wide modification of polymer blends and has been receiving much attention in this field. In such blends, various factors like blend radio, structure, and molecular weight of the copolymer, processing condition, etc., affect the structures and property of multiphase systems. However, selection of copolymer is the key factor controlling the morphology and improving mechanical properties. So, how to predict the interfacial activity of the copolymer theoretically is a serious subject. In this article, block copolymer SBS was used as a compatibilizer for the BR/CR blends. The effect of SBS on the structure and properties of the BR/CR blends was studied. The compatibilizing activity of SBS has been predicted theoretically, and compared by a series of experimental results.

EXPERIMENTAL

The polymers used in the blends were commercial materials. They were *cis*-polybutadiene (BR)

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Table I Blend Composition and Parameters of the Interfacial Properties

Dispersion Phase Coefficient (1)	Continuous Phase (2)	The Third Component (3)	Interfacial Tension, 10^{-3} N/m, 140°C Spreading				
			Υ_{12}	Υ_{32}	Υ_{13}	Υ_{13}	Υ_{31}
CR[a]	BR[b]	PS[c]	3.8	5.3	0.5		
BR	CR	SBS	3.8	1.1	1.5	−4.2	+1.2
CR	BR	SBS	3.8	1.5	1.1	−3.4	+1.2

[a,b,c] Surface tensions (140°C, 10^{-3} N/m): PS 32.1, BR 24.8, CR 33.2, SBS 28.

(9000,Yan Shan Petrochemical Corp., China), polychloroprene (CR) (Bayerprene 320), and triblock copolymer SBS (YH-791, Ba Ling Petrochemical, Corp., China). The blends were mixed on a laboratory mill at 75 ± 5°C; the systems and their compositions are as follows: for BR, the blend includes sulfur powder 1.0, CZ 2.0, TMTD 1.5, zinc oxide 5, and stearic acid 1.0; for CR the blend includes zinc oxide 5.0, magnesium oxide 4, and stearic acid 1.0. Master batches of the separate individual polymers containing appropriate curative were first prepared, and these master batches were then blended with other components according to the prescribed ratio. The blends were cured at 143°C for 20 min. For simplicity, wt % of the added copolymer was defined with respect to the total weight of blend.

The morphology of the blends was investigated by both optical and scanning electron microscopy (SEM). BR, CR, and SBS well were blended in a mixer and dissolved in toluene. The mixture was kept overnight. Films were cast on a glass plate and dried in vacuum for 24 h. The morphologies of the films were studied by optical microscopy (BH-2). Fracture surfaces of vulcanizates were prepared at the liquid nitrogen temperature and observed by SEM (JEM-10CXII). Thin films were cast on NaCl crystal from solution (the solvent being toluene), and were measured on a Nicolet 20 DXB FTIR spectrometer. For swelling experiments, three pieces, each weighing approximately 30 mg of cured samples of each blend, were cut and immersed in toluene. After 3 days the swollen sheets were weighed, and then dried for 24 h and reweighed. The volume fraction ν_r of elastomer in the network at swelling equilibrium was calculated. Mechanical tests were made on a tester AG-2000A at room temperature at 500 mm/min.

RESULTS AND DISCUSSION

Predicting the Morphology of BR/CR/SBS Blends

Polymers of BR and CR are different in polarization, and form a typically thermodynamically immiscible system. To enhance compatibility of BR and CR, SBS can be used as a compatibilizer; it is of the A-C type. Efficient compatibilizing effects of SBS in several polyolefin systems have been reported.[3, 4] The interfacial activity of SBS in blends composed of differential polar polymers have not yet been reported. In a multiphase system the attempt to predict and analyze the morphology of blends has been carried out. Hobbs[6] reported on the prediction of the morphology of complex polymer blends by means of spreading coefficients, calculated from surface and interfacial tensions of components. By using the Harkin-Hobbs equation, spreading coefficients of blends BR/CR/SBS have been calculated and listed in Table I. It is very well known that SBS is microscopically separated into two phases. The PB of segment SBS possesses a similar chemical structure to BR, which is one component of the blends. Thus, they are miscible and the interfacial tension between PS and CR is very low and far less than that between PS and BR, so it is beneficial to interaction and interpenetration between the segments of CR and PS in SBS. Higher interfacial tension between BR and CR causes their incompatibility. For ternary blend BR/CR/SBS spreading coefficients are $\lambda_{13} < 0$, while $\lambda_{31} > 0$. Thus, according to data listed in the table, analysis and prediction could be made that SBS will preferentially be dispersed at the interface between BR and CR and act as the role of compatibilization.

EXEPERIMENTAL INVESTIGATIONS

The high immiscibilty of BR and CR impedes a fine and homogeneous dispersion at each blend

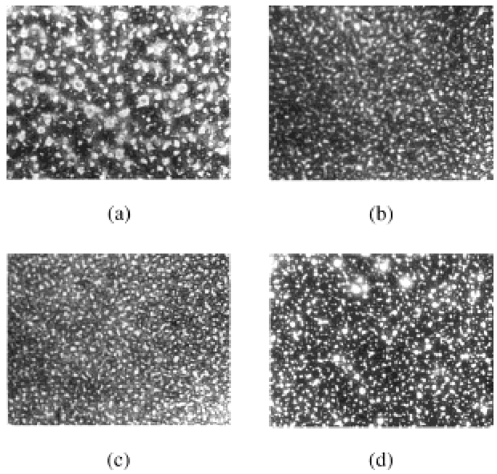

Figure 1 Optical photographs of 70/30 BR/CR blends with variable amounts of block copolymer SBS: (a) 0%; (b) 1%; (c) 5%; (d) 10%.

composition. Large and irregular CR particles are dispersed in the continuous BR phase in the 70/30 BR/CR blends. The addition of SBS can obviously improve dispersion of BR/CR blends. Figure 1 shows the optical photomicrographs of 70/30 BR/CR blends with and without the addition of copolymer. It shows that the addition of 1% SBS greatly reduce and homogenizes the particle size. Rather finer dispersions are obtained when 5% of SBS is added, but the effect of further increase in the additive percentage on the decrease in particle size is relatively small. The particle size finally rise when 10% of SBS is added. This indicates that the addition of more copolymer produces no more effect, because it does not affect the interfacial situation but rather produces micelles of the copolymer dispersed in the homopolymer phases.

IR spectra of CR, SBS, and BR/CR blends are shown in Figure 2.

A comparison of IR spectra in Figure 2 shows that the bending vibration bands of CH_2 and Ar—H of PS in SBS change clearly from 1451 cm^{-1} to 1444 cm^{-1}, and from 757 cm^{-1} to 768 cm^{-1}, respectively. This demonstrates that a strong interaction exists between CR and PS segments in SBS. This interaction may be Van der Waals type bonding (dipole– dipole interaction).[7] For the BR/CR and BR/CR/SBS blends (Fig. 3), when SBS is added to the BR/CR blend, first, there appear new bands at 1600 cm^{-1} and 699 cm^{-1}, which are characteristic bands of benzenering in SBS. Second, the stretching vibration bands of $—CH_2$ in the BR shift from 2941 cm^{-1} and 2853 cm^{-1} to 2931 cm^{-1} and 2850 cm^{-1}, respectively. This also shows that there is interaction between SBS and BR. The bands of IR spectra are consistent with the prediction above.

Figure 4 shows that addition of an appropriate amount of SBS results in increasing the volume fraction ν_r, for example, ν_r when 1% of SBS is added. However, ν_r obviously decreases when 10% of SBS is added. In this case, the value of ν_r is similar to that of the blend with 10% of SBS. The increase of the value of ν_r indicates the increase of chemical crosslink density of elastomer. Possible explanation for the increase in the crosslink density of the blend is the compatibilizing activity of SBS so that the finer dispersion is achieved. It is beneficial to promote efficient valcanization and increase the degree of crosslinking. When 10% of SBS is added, the decrease in value ν_r is due to the large amount of copolymer in the blend, which itself expends curing agents. Thus, it leads to decreasing the crosslink density (for each composition of the BR/CR blend the addition of SBS was increased from 0 to 10%, while the amount curing agents was constant). These results are in good agreement with the observations of the microscopy.

The improvements of morphologies of BR/CR blends will be beneficial to improving mechanical properties. Evidence for compatibilizing activity of SBS is also provided by the mechanical test. The effect of SBS on the tensile strength of BR/CR blends is shown in Figure 5. The addition of SBS could significantly increases tensile strength of blends. The effect is clear when only 1% of SBS is added, while when 10% of SBS is added, the tensile strength is decreased to a value similar to that of 1% of SBS additive. This behavior is in agreement with results of microscopic observations and volume fraction examinations. In the case of a higher amount of SBS, lower crosslink density leads to reducing the ability of resisting stress, and tensile strengths were decreased. Therefore, the addition of more copolymer (>10%) is wasteful, because it does not beneficially affect the structures and properties of blends.

The effect of SBS on tan δ of blends is shown in Figure 6, which gives further evidence on the compatibilizing activity of SBS. When 1% of SBS is added, values of tan δ decrease, and the effect is more obvious with the increasing frequency of tension. When 10% of SBS is added, the degree of the decrease in tan δ is the lowest. Because the crosslink density is decreased in the case of higher content of SBS, the ability of resisting alternative stress is decreased. The mechanical

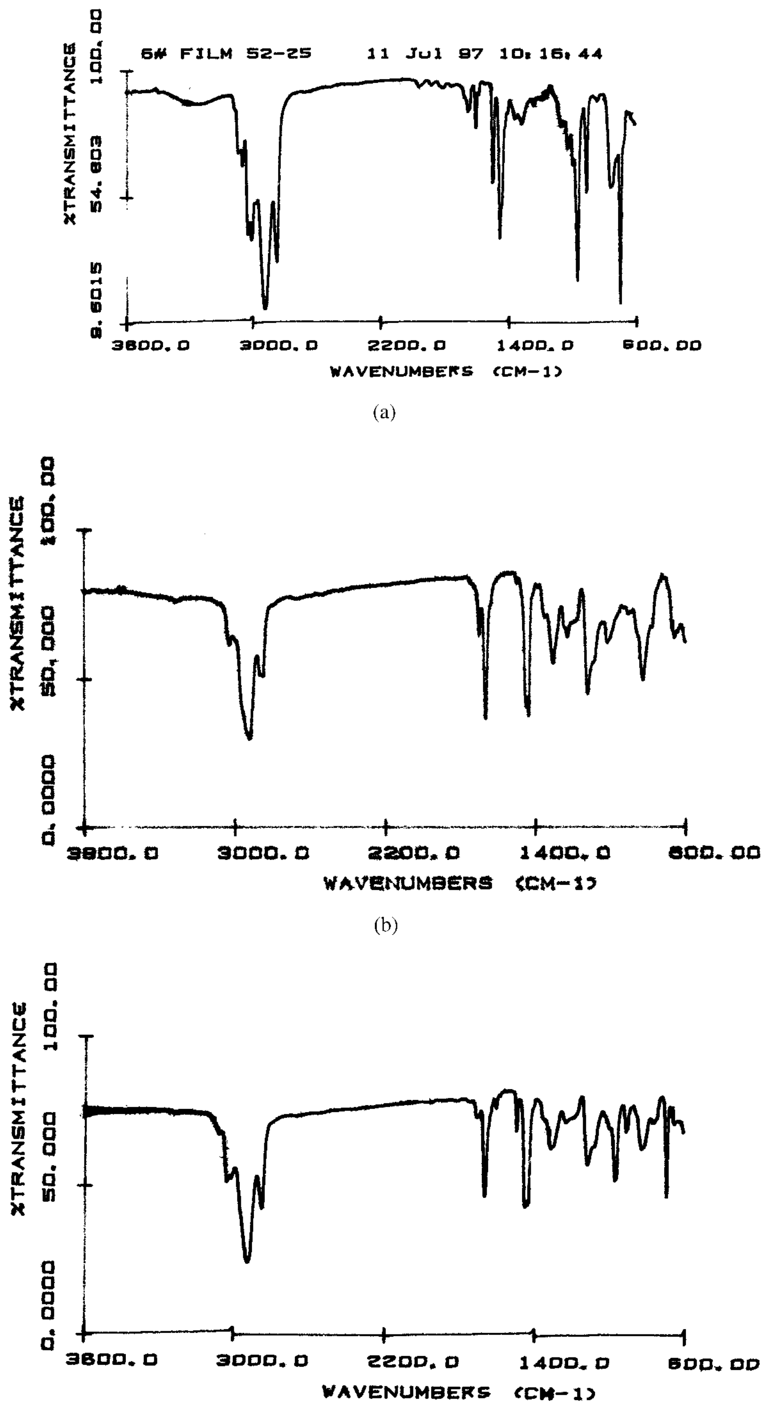

Figure 2 IR spectra of SBS (a), CR (b), and 50/50 SBS/CR blends (c).

properties once again demonstrate that because SBS preferentially disperses in the interfacial region of BR and CR, it rises the dispersity of system and forms wider interphase at the interface between BR and CR, increases the adhesion between the phases, and decreases internal stress, so as to facilitate chain orientation along the side of imposed stress. All of these demonstrate that the blends containing SBS have better mechanical properties.

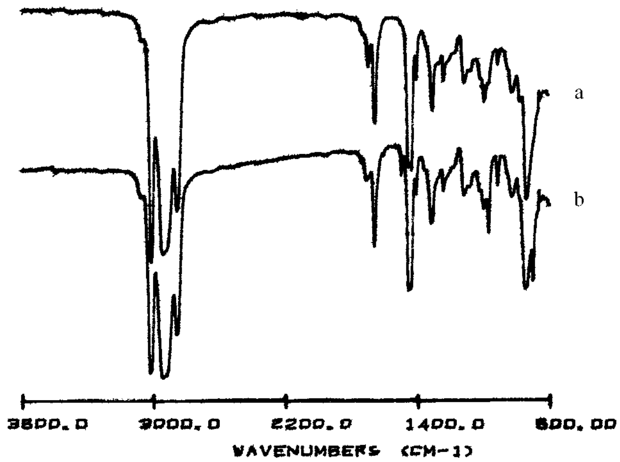

Figure 3 IR spectra 50/50 BR/CR blends with variable amount of block copolymer SBS: (a) 0%; (b) 10%.

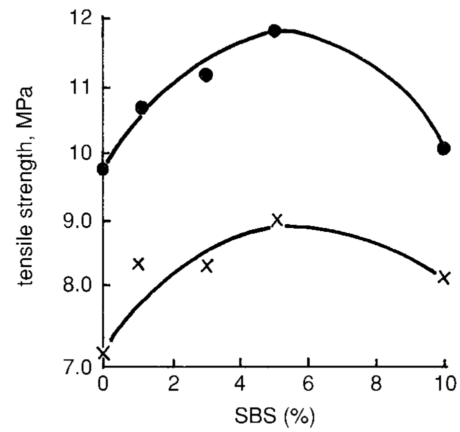

Figure 5 Effect of SBS contents on the tensile strength of blends: --- 30/70 BR/CR; + --- 50/50 BR/CR.

SEM investigations provide further evidence of compatibilizing activity of SBS in BR/CR blends (Fig. 7). SEM of fracture surfaces shows that morphology of 70/30 BR/CR [Fig. 7(a)] blend is layer shaped; the particle size is large and irregular. However, when SBS is added, the reduce of the particle size is observed and the particle features change in shape and size and it becomes spherical, which is an important reason for improving tensile strength. The fracture surfaces of 30/70 BR/CR blend differ from those of blend 70/30, because in a blend without SBS the surfaces show an irregular hillock-shaped feature (protrusions) [Fig. 7(a′)]. These hillocks are less uniformly distributed, exposing the smooth surfaces. When 5% of SBS is added, protrusions remain small, and fibrils can be seen on the fracture surface. This provides further evidence of the compatibilizing activity of SBS in blends.

CONCLUSION

From this investigation, it can be concluded that SBS has an effective compatibilizing activity in the BR/CR blend, as predicted by theoretical analysis and as examinated by experimental investigations. Experimental results show that a fine and homogeneous dispersion is observed when the block copolymer SBS is added to the BR/CR blends, and mechanical properties are obviously improved, such as the increase in the tensile strength and the decrease in the loss tan δ are achieved. The fracture surfaces of vulcanizates

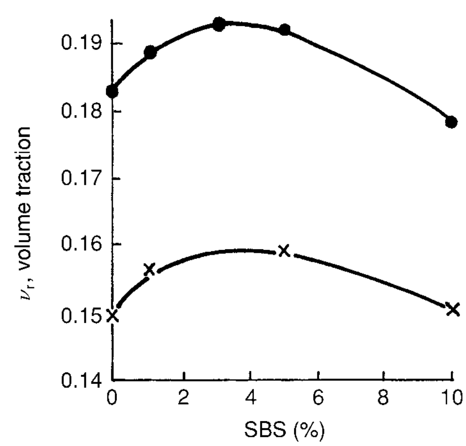

Figure 4 Effect of SBS content on the volume fraction: --- 70/30 BR/CR; + --- 30/70 BR/CR.

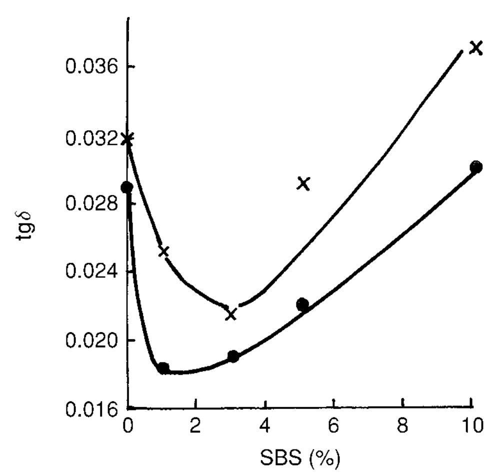

Figure 6 Effect of SBS contents on the dynamic property: --- 70/30 BR/CR; + --- 30/70 BR/CR.

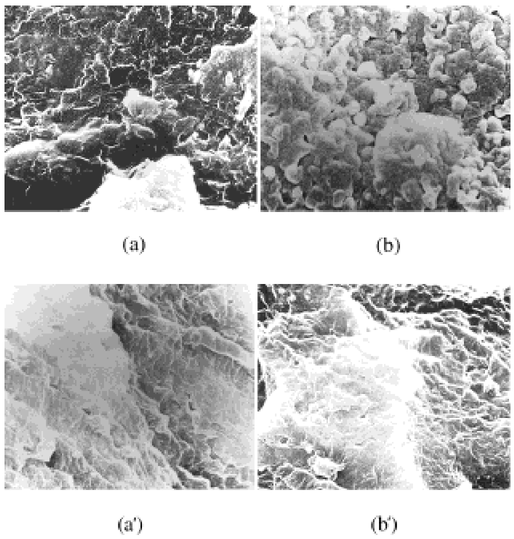

Figure 7 Microphotographs of fracture surface of 70/30 BR/CR (a, b) and 30/70 BR/CR (a′, b′) with variable amounts of block copolymer SBS: (a, a′) 0%; (b) 10%; (b′) 5%.

are mordified. The surface is characterized by brittleness fracture without SBS, while toughness characteristic is displayed with SBS. IR spectra also demonstrate that the interaction between SBS and BR, CR exits. These experimental results are in excellent agreement with the prediction of theoretical analysis based on the spreading coefficients, that is, SBS preferentially disperses in the interfacial region between BR and CR and acts as compatibilizing agent.

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