

Compatibilization Efficacy of Poly(isoprene–butyl acrylate) Block Copolymers in Natural/Acrylic Rubber Blends

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ABSTRACT: Poly(isoprene–butyl acrylate) block copolymers with a variety of molecular weights and compositions were prepared via a controlled free-radical polymerization with an iniferter. Subsequently, the block copolymers were used as compatibilizers in natural/acrylic rubber blends. Scanning electron micrographs revealed a cocontinuous morphology in the case of the normal blends with a low natural rubber content (20 wt %), whereas the blends that contained more natural rubber showed a dispersed-particle morphology. When the rubbers were blended with 5 wt % block copolymer, the particle size decreased, and the tensile

strength of the resulted blends increased, regardless of the block copolymer characteristics. For the blend that exhibited a cocontinuous morphology, the most effective compatibilizer was the block copolymer with an average molecular weight of 22,000 g/mol, containing mainly (87%) polyisoprene block. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 921–927, 2003

Key words: blends; block copolymers; radical polymerization; rubber

INTRODUCTION

Natural rubber (NR) has long been used as tire component in the automotive industry because of its unique combination of strength and low cost. However, for some special applications, such as o-rings, gaskets, and seals, the use of NR is not possible because of its nonpolar characteristics and the limited thermal stability of the rubber. In this regard, acrylic rubber (AR), which is characteristically superior in oil and heat resistance, has been the material of choice. AR, however, is relatively weak and expensive compared to NR, and thus, it would be interesting if the advantageous properties of the two rubbers could be combined by blending.

NR has been blended with many synthetic rubbers, including styrene–butadiene copolymer,^{1–3} polybutadiene (BR),^{4,5} *trans*-1,4-polyisoprene (PI),^{6,7} ethylene–propylene–diene copolymer,⁸ ethylene–propylene copolymer,⁹ and nitrile rubber (NBR).^{10,11} In the case of NBR, the blend was immiscible and exhibited poor mechanical properties because of a lack of compatibility between the two polymers. To enhance the compatibility of the blend, Lewan and colleagues¹² used

methyl-methacrylate-grafted NR as a compatibilizer. A decrease in the particle size and an increase in the tensile strength of the blend were observed on the addition of the compatibilizer. Alternatively, some suitable block copolymers have been used as compatibilizers in many polymer blends.^{13,14}

Despite the commercial essence of compatibilized rubber blends and the fact that the compatibilization efficacy of a block copolymer is strongly dependent on its molecular parameters, such as block length and composition,^{15,16} little work concerning the effect of block copolymers on the properties of related rubber blends has been published. In this study, poly(isoprene–butyl acrylate) block copolymers with a variety of chain lengths and compositions were prepared and subsequently used as compatibilizers in NR/AR blends. Our aim was to investigate the effect of the block copolymers on the mechanical properties and morphologies of the blends.

EXPERIMENTAL

Materials

Isoprene (purum grade from Fluka, Buchs, Switzerland) and butyl acrylate (BA; purum grade from Fluka) were purified by the ordinary method.¹⁷ Benzyl diethyldithiocarbamate (BDC) was prepared in accordance with a method described previously.¹⁸ Toluene (AR grade from Fluka), diethyl ether (AR grade from BDH Analar, UK), methanol (commercial grade from Siam Beta Co. Ltd., Bangkok, Thailand), and tetrahy-

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drofuran (THF; HPLC grade from LabScan Asia Co. Ltd., Bangkok, Thailand) were used as received. AR [grade AR-71, Mooney viscosity ML (1+4) 100°C-55, glass-transition temperature (T_g) = -17°C], which contained poly(ethyl acrylate), poly(butyl acrylate) (PBA), and a chlorine cure-site monomer, was supplied by Zeon Advanced Polymix Co. Ltd. (Rayong, Thailand). NR (STR 5L grade rubber, T_g = -64°C) and the curing agents [sulfur, sodium stearate, 2-mercaptobenzothiazole (MBT), zinc oxide, and stearic acid] were supplied by the Hi-Tech Elastomers Co. Ltd. (Bangkok, Thailand).

Synthesis of block copolymers

The block copolymers were prepared with an iniferter technique, which is basically a photopolymerization process suitable for the low-boiling-point isoprene. More details concerning the fundamental concept of iniferters can be found elsewhere.¹⁹ The first step in the preparation of the block copolymers was the homopolymerization of isoprene. The reaction was performed under ultraviolet radiation with a Phillips (HPA-400) ultraviolet lamp (The Netherlands). Two grades of PI with different chain lengths were obtained by adjustment of the reaction conditions (concentrations of isoprene and BDC). After that, the (pseudo)living PI or the macroiniferter were further reacted with BA at various monomer-to-macroiniferter molar ratios. Percentage yield was determined by the weight of the isolated dry product. More details concerning the polymerization procedure are described elsewhere.²⁰

Characterizations

Before characterizations, the crude products were purified by dissolution in selective solvents (acetonitrile and cyclohexane) to remove some possible homopolymer contaminants. Molecular weights [weight-average molecular weight (M_w) and number-average-molecular weight (M_n)] and polydispersity index (M_w/M_n) of both the homopolymer and the block copolymers were determined by gel permeation chromatography with a Hewlett-Packard (series 100) apparatus (Waldbronn, Germany) equipped with Polymer Laboratories (PL) (PL gel, 3 μm , Mixed-E) columns and a Hewlett-Packard (RDI-G1362A) refractive index detector. Polystyrene standards (Polymer Laboratories) were used to generate a calibration curve. THF was used as an eluent at a flow rate of 1.0 mL/min, at 30°C .

The chemical structures and compositions of the copolymer products were determined by $^1\text{H-NMR}$ spectroscopy. $^1\text{H-NMR}$ spectra were recorded by a Bruker (Advance DPX-400) spectrometer (Rheinstetten, Germany) operating at 400 MHz. The polymer

TABLE I
Blending Formulations

Materials	Content (phr)		
	Formula 1	Formula 2	Formula 3
NR	20.0	50.0	80.0
AR	80.0	50.0	20.0
Sulfur	1.5	1.5	1.5
Sodium stearate	7.5	7.5	7.5
MBT	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0
Block copolymer	5.0	5.0	5.0

solution was prepared by dissolution of about 20 mg of the polymer in about 1 mL of deuterated chloroform (CDCl_3).

Blending

The basic formulations for the rubber blends are given in Table I. NR was first masticated in a two-roll mill for 15 min, followed by blending with the AR for 10 min. After that, a block copolymer was incorporated, and the mixing was continued for another 5 min. Finally, zinc oxide, stearic acid, MBT, sodium stearate, and sulfur were sequentially added to the rubber blend, and blending was completed within 15 min.

Vulcanization

The optimum cure time (the time needed to reach 90% of the maximum torque by a curometer) of the compounded NR/AR blends (at a curing temperature of 170°C) was predetermined with an oscillating disk rheometer (Rheo TECH MD+ from Tech Pro, Inc., OH) in accordance with ASTM D 2084. A biconical disk was oscillated through a rotational amplitude of 1° with a standard frequency of 100 cpm (1.7 Hz). The compounded rubber blends were vulcanized to their optimum cure time in a compression mold (2 mm thick) at a curing temperature of 170°C and under a molding pressure of 20 MPa.

Scanning electron microscopy (SEM)

The morphologies of the rubber blends were examined with the SEM technique. Each sample was cut into small pieces and then fractured in its glassy state (with liquid nitrogen). The fracture surface was stained with an osmium tetroxide aqueous solution (2 vol %). The specimen was then coated with carbon before SEM analysis with a vacuum coating unit (Jeol JEE-400, Tokyo, Japan). Finally, the specimen was analyzed with a Jeol (JSM-5800LV) scanning electron microscope at an accelerating voltage of 15 kV. A

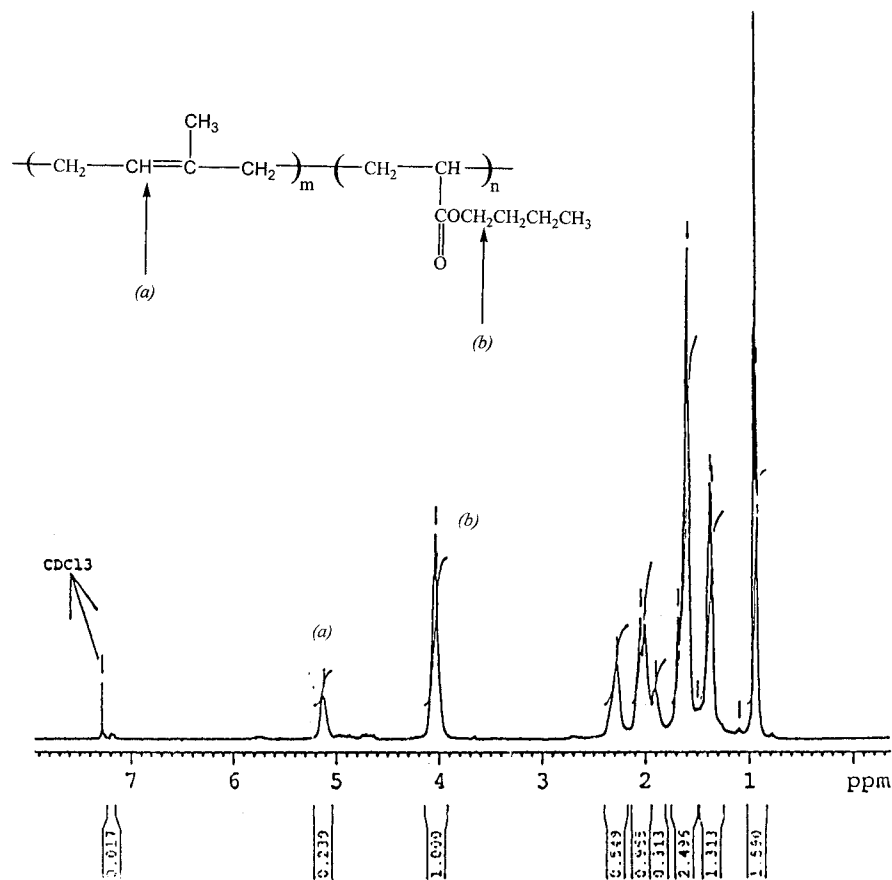


Figure 1 ¹H-NMR spectrum of poly(isoprene-*b*-butyl acrylate).

back-scattering electron detector was used to obtain an electron micrograph with a compositional contrast.

Tensile testing

The cured rubber sheet was punched into a dumbbell-shaped specimen in accordance with an ASTM D 412. The tensile properties were determined with a Shimadzu (AGS 500D) universal testing machine (Tokyo, Japan) at a crosshead speed of 500 mm/min and at room temperature. Five specimens were tested for each blend, and the average values were reported.

RESULTS AND DISCUSSION

The chemical structure of the synthesized copolymer was confirmed by the ¹H-NMR spectrum (Fig. 1). Several characteristic peaks corresponding to the protons in the PBA and PI molecules could be observed. These include the peaks at 0.9 ppm (CH₃ in PBA), 1.3 ppm (CH₂ in PBA), 2.3 ppm (CH< in PBA), 4.0 ppm (O—CH₂ in PBA), and 5.2 ppm (>C=CH— in PI). To determine the copolymer composition, we used the integrated areas under the ¹H-NMR peaks at 4.0 and 5.2 ppm for calculation.

TABLE II
Molecular Weights and Compositions of Various Block Copolymers

No.	M_w of PI macroiniferter	PI/BA molar ratio	M_w of block copolymers	M_w/M_n	% PI from ¹ H-NMR
1	10,000	1/100	22,000	2.9	87
2	10,000	1/300	29,100	3.8	50
3	10,000	1/500	61,900	1.2	32
4	17,000	1/170	29,500	2.8	80
5	17,000	1/510	33,400	4.3	50
6	17,000	1/850	52,400	1.2	34

Block copolymerization time = 6 h.

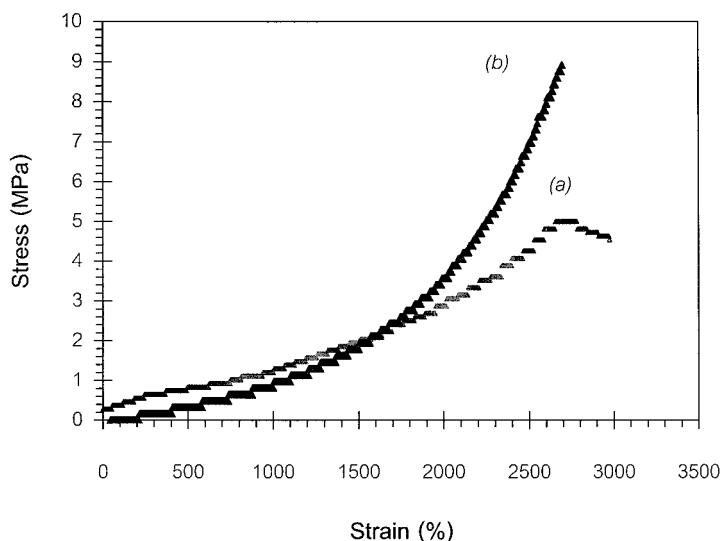


Figure 2 Stress-strain curves of the NR/AR blends (80/20 w/w NR/AR): (a) the normal blend and (b) the blend containing block copolymer 2.

According to our previous studies, the T_g 's of PI and PBA polymerized with the iniferter were very close (-48 and -43°C , respectively).^{16,21} Therefore, differential scanning calorimetry could not be used to demonstrate the "blockiness" of the copolymer, whereas that of the poly(isoprene-ethyl acrylate) block copolymer could be illustrated.²² Nevertheless, control experiments were conducted in this study, and the results indicate that the self-polymerization and grafting reactions of BA were negligible.

Table II summarizes the relationships between the polymerization parameters and block copolymer characteristics (chain length and composition) obtained from the experiments. From gravimetric analysis of both crude product and purified product, we found

that the percentage conversion of BA ranged between 12 and 45%, depending on the reaction conditions. This means that weight ratio of PI to PBA should not be calculated with the PI/BA molar ratio (Table II) and the molecular weight of BA (128 g/mol).

As shown in Table II, block copolymers with a variety of chain lengths and compositions were prepared. M_w/M_n 's of the copolymers ranged between 1.2 and 4.3, which were similar to the literature values.^{17,20} The values were greater than unity, which might be attributed to bimolecular terminations of some propagating chains during the polymerization. This means that the products might have been a combination of diblock and triblock copolymers. Therefore, the percentage PI determined from $^1\text{H-NMR}$

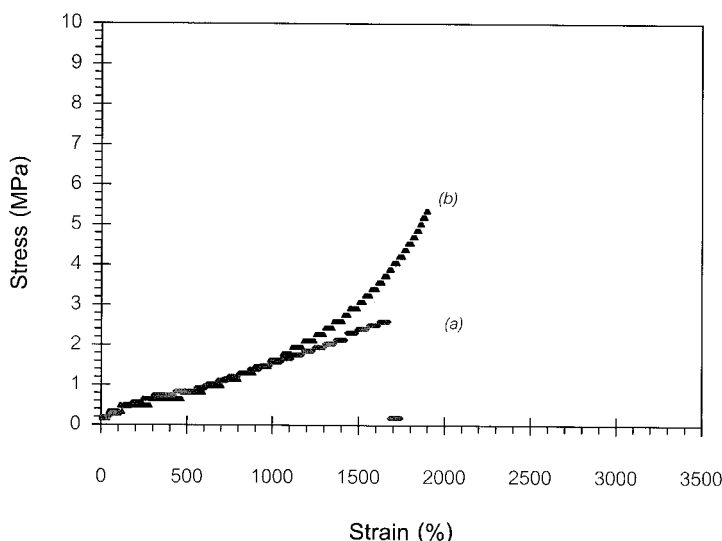


Figure 3 Stress-strain curves of the NR/AR blends (20/80 w/w NR/AR): (a) the normal blend and (b) the blend containing block copolymer 1.

TABLE III
Tensile Strengths (MPa) of Various Rubber Blends

Block copolymer	Tensile strength (MPa) of blends at various compositions		
	20% NR	50% NR	80% NR
Control	2.13 ± 0.47	4.33 ± 0.68	5.18 ± 0.26
1	4.62 ± 0.94	5.91 ± 0.48	7.91 ± 0.42
2	3.46 ± 0.92	6.45 ± 0.74	9.24 ± 1.34
3	2.96 ± 0.68	6.61 ± 0.27	7.10 ± 1.29
4	1.80 ± 0.43	6.29 ± 0.23	10.79 ± 1.43
5	1.26 ± 0.28	6.85 ± 0.41	9.98 ± 0.97
6	1.41 ± 0.17	7.65 ± 0.17	8.03 ± 0.39

should not be compared or correlated with the percentage PI deduced from the M_w of the copolymer and the M_w of the PI macroiniferter.

Figure 2 compares stress–strain behaviors of a normal blend (80 wt % NR) to that of the blend containing the block copolymer. The slope of the graph representing the tensile modulus of the normal blend was not remarkably increased when the block copolymer was incorporated. Previous work by Bualek et al.⁵ showed that the tensile strength and tensile elongation of a NR/BR blend significantly increased when a poly(isoprene–butadiene) block copolymer was used. However, the tensile modulus of the NR/BR blend decreased slightly (~0.2 MPa) on the addition of the block copolymer (5 wt %). In this regard, it seems more natural to consider the tensile strength and tensile elongation rather than the tensile modulus when evaluating the effectiveness of a compatibilizer in an immiscible rubber blend.

Care should be taken when comparing the strain values of those blends listed in Table II. Some specimens (especially the one with high NR content) extended up to the maximum limitation of the machine's crosshead travel distance, and thus, the test had to be terminated. However, the ultimate tensile strengths of the two samples were significantly different and could be used as an indicator of the block copolymer effectiveness. As shown in Figure 2, block copolymer 2 (50% PI) improved the tensile strength of the blend. Similarly, the rubber blend with a 20/80 NR/AR ratio also had a higher tensile strength when block copolymer 1 (87% PI) was used (Fig. 3). These results suggest that the block copolymers might have acted as compatibilizers, enhancing the tensile strength of the blends. To examine whether all of the block copolymers with different chain lengths and compositions were effective, Table III should be considered.

As shown in Table III, the tensile strength of the normal blend increased with increasing NR content, which was due to the fact that the NR was stronger than the AR. Our earlier study²³ also found that the strength was increased at the expense of oil and heat resistance in AR. In terms of block copolymer efficacy,

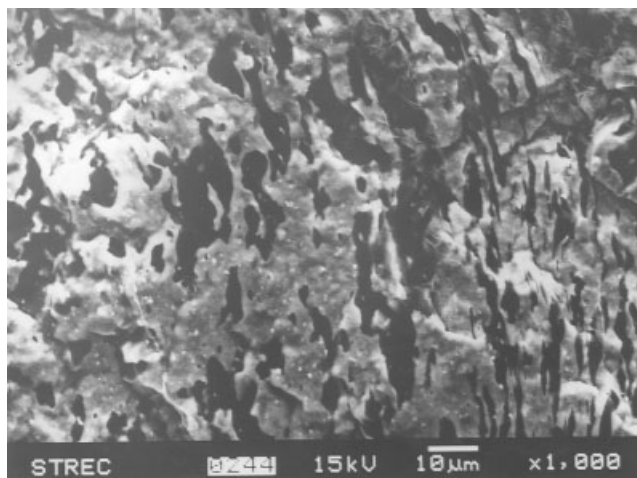


Figure 4 Scanning electron micrograph of the NR/AR blend (50/50 w/w NR/AR).

the tensile strength of the blends with 50 and 80 wt % NR increased after all of the block copolymers were used. It was rather difficult to identify the best block copolymer for each blend ratio when we considered that differences in the tensile strengths of the various blends (at a fixed blend ratio) were not too large. It seemed that all of the block copolymer were effective, regardless of their molecular parameters (chain length and composition).

For the rubber blends with high AR content (20 wt % NR), only block copolymer 1 remarkably increased the tensile strength. The tensile strengths of the blends that contained copolymers 2–4 were comparable to that of the control (a normal blend) after the standard deviations were considered. In addition, the tensile strengths of the blends containing block copolymers 5 and 6 were slightly lower than that of the normal blend.

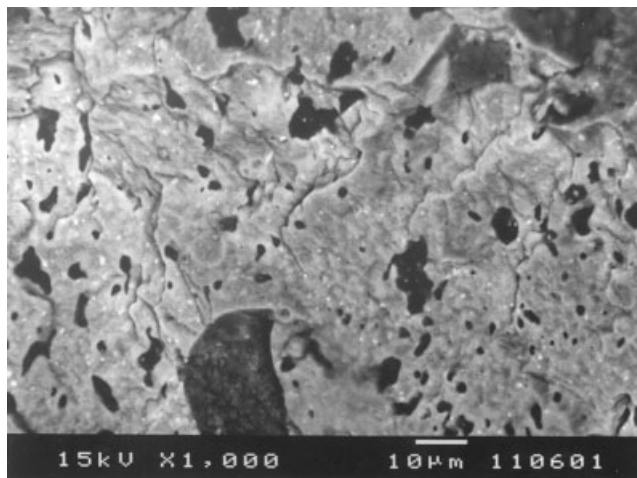


Figure 5 Scanning electron micrograph of the NR/AR blend (80/20 w/w NR/AR).

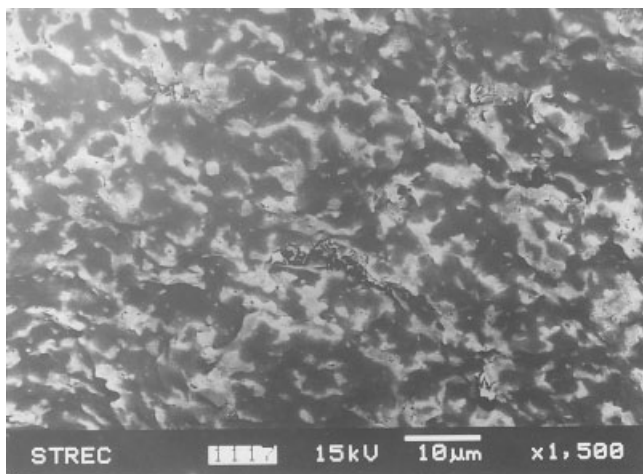


Figure 6 Scanning electron micrograph of the NR/AR blend (20/80 w/w NR/AR).

SEM micrographs revealed that morphologies of the blends with 50 and 80 wt % NR (Figs. 4 and 5) were totally different from those that contained 20 wt % NR (Fig. 6). In the former case, a typical dispersed-particle morphology was observed. The particle size of the acrylic particle (dark phase) decreased remarkably after the block copolymers were used (Figs. 7 and 8). A similar pattern was observed for the blends containing different block copolymers. This indicated that the block copolymers could act as emulsifiers, reducing the surface tension and minimizing the coalescence of the dispersed particles.²⁴ The result was also in a good agreement with the previous tensile strength results. In the case of blends that contained 20 wt % NR, a typical cocontinuous morphology was observed (Figs. 6 and 9). The morphologies of the blends containing different block copolymers were very similar to that of the normal blend, except for that of the blend that

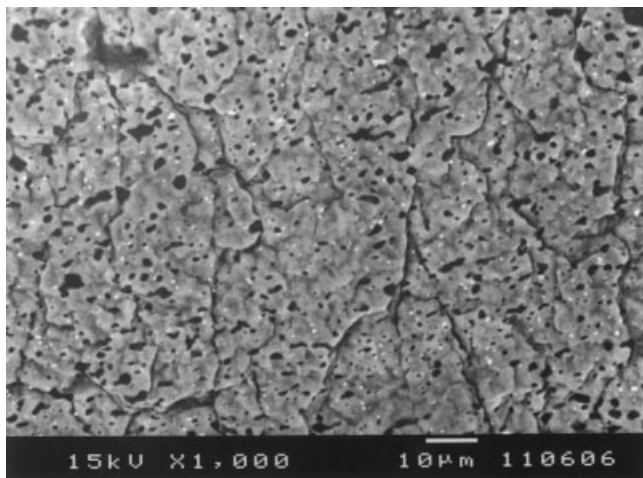


Figure 7 Scanning electron micrograph of the NR/AR blend (80/20 w/w NR/AR) containing block copolymer 2.

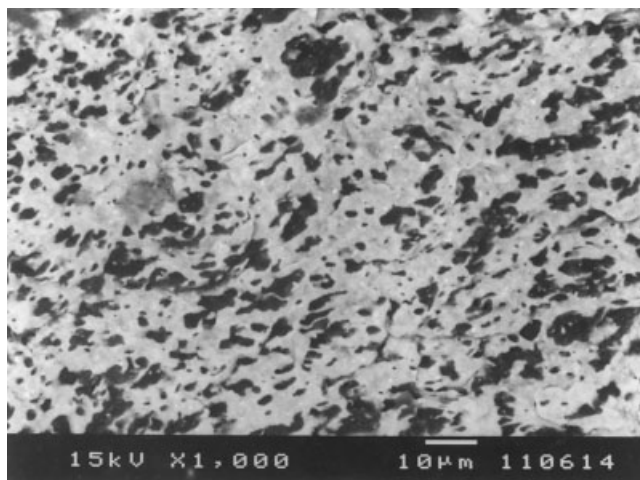


Figure 8 Scanning electron micrograph of the NR/AR blend (50/50 w/w NR/AR) containing block copolymer 2.

contained block copolymer 1, in which the area of the NR phase increased (Fig. 10).

Our explanation for the previous results follow. At the initial stage of blending NR (20 wt %) with AR (80 wt %), we believe that most of the block copolymers were in an AR phase due to the fact that weight fraction of the AR was four times greater than that of the NR. After that, these block copolymers tended to migrate into the interface because of the thermodynamic driving force. In this regard, the diffusion of polymer molecules is generally dependent on two factors, that is, the molecular weight of the diffusing chains and the free volume, or "hole," of the matrix polymer. According to the reptation theory,^{25,26} the self-diffusion coefficient of polymer molecule is inversely proportional to the square of the chain length, which means that the smaller the molecule is, the faster the diffusion will be. In addition, the free volume should also be sufficiently large to accept an

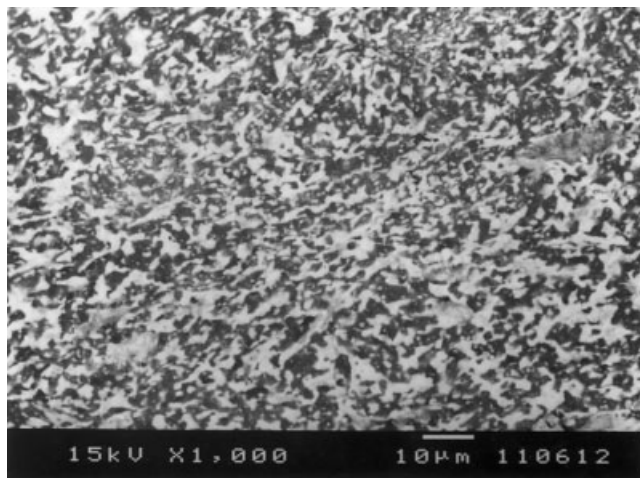


Figure 9 Scanning electron micrograph of the NR/AR blend (20/80 w/w NR/AR) containing block copolymer 2.

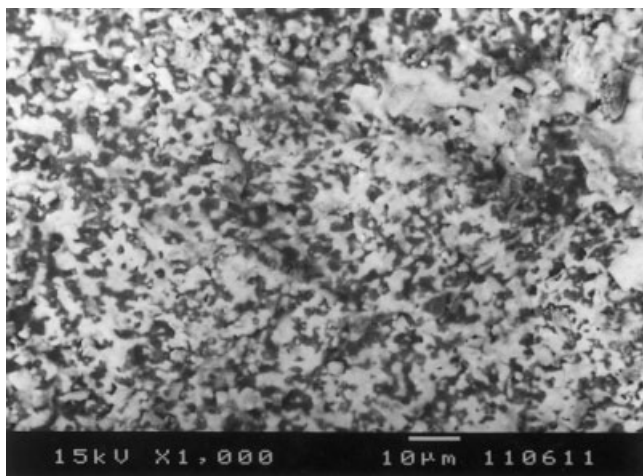


Figure 10 Scanning electron micrograph of the NR/AR blend (20/80 w/w NR/AR) containing block copolymer 1.

incoming molecular segment of the diffusing chains.^{27,28} The formation of the free volume, or hole, is attributed to the cooperative movement of the neighboring polymer chains. Relative to this work, it might be possible that the AR, which was less rubbery than the NR, provided less free volume than the NR, and thus, diffusion of the block copolymers through the AR phase was more difficult than that through the NR phase. Therefore, only block copolymer 1, having the lowest molecular weight, was able to diffuse to the interface and act as a compatibilizer for the NR/AR blend (20/80%w/w).

CONCLUSIONS

Poly(isoprene-butyl acrylate) block copolymers prepared with BDC as an iniferter may be used as compatibilizers in NR/AR blends. Compatibilization efficacy of these block copolymers depends on their molecular weight, composition, and blending ratio. For rubber blends that contained 50 and 80 wt % NR, a typical dispersed-particle morphology was observed, and all of the synthesized block copolymers could serve as a compatibilizer in the system, regardless of their molecular weight and composition. For the rubber blend that contained 20 wt % NR, a cocontinuous morphology developed. The best compatibilizer for this system was a block copolymer with an average molecular weight of 22,000 g/mol containing 87% PI.

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