Natural Rubber and Butadiene Rubber Blend Using Diblock Copolymer of Isoprene–Butadiene as Compatibilizer

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SYNOPSIS

Blends of natural rubber (NR) and butadiene rubber (BR) have been studied with or without diblock copolymers of isoprene–butadiene (BIR). It was found that NR/BR blends displayed the optimal properties at about 4 wt % of BIR from the tensile measurements of NR/BR blends. Increase of molecular weight of BIR resulted in the decrease of tensile properties, but had no significant effect on their hardness. Abrasion resistance of rubber blends containing BIR was about 30% higher than that without BIR. The molecular weight of BIR did not show a remarkable effect on the abrasion index. Differential scanning calorimetry and dynamic mechanical analyses of rubber blends suggested a two-phase structure even in the presence of BIR. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Blending of polymers has been an extensively used technique in many practical applications, especially in the rubber industry. However, the problem of incompatibility arises in many polymer blends and the desired properties are often lost on mixing.[1] There are several methods that can be used to characterize the compatibility of polymer blends.[2] Natural rubber (NR) and butadiene rubber (BR) blends were reported to be mutually compatible by observing a single glass transition temperature in dilatometric measurements,[3] whereas the microscopic investigations of the NR/BR blend showed it to be heterogeneous.[4] From dynamic loss measurement by Corish,[1] only one single intermediate loss peak was found in the vulcanized NR/BR blend. A similar study was done by Bauer and Dudley[5] by measuring the dynamic shear of a NR/BR gum blend and the blends at different stages of cure. They found that the original two loss peaks observed in the uncured blend joined into one intermediate loss peak on vul-

canization. This means that there was phase separation between NR and BR prior to vulcanization.

Despite the close values of the solubility parameters of 8.25 and 8.21 ($cal^{1/2}/cm^{1/2}$) for NR and BR, respectively, no single-phase blends are obtained.[4] Different carbon black distribution in *cis*-polyisoprene (NR) and *cis*-polybutadiene (BR) phases was observed by Hess et al.[6] Interphase distribution of curatives in NR/BR blends was studied by Leblanc[7] using various vulcanization systems. He demonstrated that premixing of curatives into each rubber at its optimal concentration before blending of the elastomers could improve the cross-linking behaviors.

One method to promote the interfacial connectivity in two-phase rubber blends is to introduce a block or graft copolymer that contains two segments identical or miscible with each phase.[8] The objective of this study is to investigate the effect of diblock copolymers of isoprene and butadiene (BIR) as a compatibilizer for blends of NR and BR. In this paper, effects of the quantity and molecular weight of BIR are reported. The blend ratio of NR/BR at 60/40 was chosen throughout this work, because this composition is often used in automobile tires. It was also reported by Folt and Smith[9] that this proportion

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showed minimum viscosity among NR/BR blends using the capillary extrusion method. A reduction of blend viscosity implied increasing free volume accompanying immiscible polymer blends.[10] Therefore, 60/40 is assumed to be the most incompatible proportion of the NR/BR blend that is suitable for compatibilization study.

EXPERIMENTAL

Synthesis of Diblock Copolymer of Isoprene–Butadiene

Diblock copolymer of isoprene–butadiene (BIR) was synthesized by anionic polymerization using n-butyl lithium (n-BuLi) as the initiator. A specified amount of purified 1,4-butadiene monomer was first injected into dried cyclohexane under N_2 atmosphere in a high-pressure-resistant reaction vessel. The initiator was added to start the polymerization. The amount of n-BuLi was changed depending on the prescribed molecular weight of the copolymer. Polymerization of butadiene was carried out at 55°C for about 1 h. The reaction reached almost 100% conversion. Purified isoprene monomer was then injected into the reaction vessel, which was kept at 55°C in a water bath for approximately 1 h. The polymerization was then stopped by addition of a few milliliters of methanol. BIR was purified by precipitation in a large quantity of methanol and dried in vacuo at 50°C to constant weight. The molecular weight of BIR was determined by gel permeation chromatography using tetrahydrofuran as the eluent and the flow rate was 1.5 mL/min. Standard polystyrene was used for calibration of molecular weight. From the analysis of their infrared spectra, 1,2-and 3,4-vinyl groups in the isoprene part were found to

Table I   List of BIRs of Different Molecular Weights

Sample Code	Mol. Wt. × 10^{-3}
BIR-1	14
BIR-2	17
BIR-3	27
BIR-4	46
BIR-5	53
BIR-6	62
BIR-7	82
BIR-8	94
BIR-9	134
BIR-10	222

Table II   Formulation of NR/BR Blends

Ingredient	Parts by Weight
Natural rubber	60
Butadiene rubber	40
BIR	4
ZnO	5
Stearic acid	1
Carbon black (N330)	30 or 50
Sulfur	1.5
MSA[a]	1.5

[a] Accelerator: N-oxydiethylene-2-benzothiazole sulfenamide.

be approximately 10 mol %, whereas 1,2-vinyl group in the BIR part is about 15 mol %. The main configurations were cis-1,4-isomers. Block copolymers of different molecular weights were synthesized, which are shown in Table I.

Compounding of Rubber Blends

Natural rubber (RSS-1) and butadiene rubber (BR-01) from the Japan Synthetic Rubber Co. were used for this study. The formulation for the blends is given in Table II.

Mixing and Blending Procedures

Rubber blends were prepared by either of the two methods described as follows:

Method A: Masterbatch Operation

The following steps were performed:

(a) NR and BR were masticated separately to Mooney viscosity of 63 and 42, respectively. Masticated NR and BR were then mixed on the mill at 60/40 by weight, respectively, for 5 min. Zinc oxide, stearic acid, and sulfur were added and milled further for 15 min. This masterbatch was kept at room temperature for 24 h.

(b) The rubber masterbatch was compounded with BIR (varying concentration and molecular weight) and the accelerator N-oxydiethylene-2-benzothiazole sulfenamide (MSA) on the mill for 3 min and for 2 min, respectively. The resulted compound was kept at room temperature for 24 h.

(c) The compound was mixed with carbon black (N330, 30 phr) for 5 min, kept at room tem-

perature for 24 h, and then subjected to cur-
ing at 150°C.

Method B: Batchwise Operation

Each compound was prepared on a small two-roll
mill. NR and BR were first masticated separately
to Mooney viscosity of about 63 and 42, respectively.
The masticated NR and BR were mixed on the mill.
Other ingredients were added in the sequence as
shown in Table II. Total mixing time did not exceed
27 min and temperature was controlled below 55°C.

Method A was used first to investigate the effect
of concentration of BIR, which was varied in step
(b). After that experiment, a fixed amount of BIR
was used to investigate the effect of their molecular
weights on the properties of the rubber blends using
Method A or B.

Vulcanization

The cure time course of rubber compounds was de-
termined by a curemeter (JSR Curelasto Meter III).
The optimal cure time at 150°C was determined to
be T90 + 2 min for the slips of approximately 1 mm
thickness, which was used in tensile measurements.
For the test pieces of 9 mm thickness used for abra-
sion resistance measurements, the cure time was T90
+ 5 min, where T90 is the time required for the
torque to attain 90% of the maximum torque by the
curemeter.

Figure 2   Effect of BIR concentration on T_B of vulca-
nized NR/BR (60/40) blend containing 30 phr carbon
black: (●) no BIR; (○) with BIR-2; (△) with BIR-4; (□)
with BIR-8. The deviation is as described in Figure 1.

Physical Properties Measurements

Tensile properties were determined with a tensile
tester at room temperature with a strain rate of 100
mm/min. Hardness was measured according to
ASTM D2240 using the Zwick hardness tester to
determine the Shore A hardness. The abrasion index
was determined by an NBS abrader according to
ASTM D1630-83.

Differential scanning calorimetry (DSC) dia-
grams of the rubber blend gums were obtained with
a Perkin-Elmer DSC 7, using a scanning rate of
20°C/min from −150 to 50°C. The dynamic me-
chanical analysis (DMA) measurements of vulca-
nized specimens without carbon black were made
with a DMA instrument from Rheology Co. Sinu-
soidal tensile stress of 10 Hz was applied to the
specimen, and the tensile dynamic moduli (E' and
E'') and the loss tangent (tan δ) were measured with
the temperature increment of 2°C/min. The tem-
perature range was from −130 to 50°C.

RESULTS AND DISCUSSION

Tensile Properties of NR/BR Blends

Effect of BIR Concentration

Vulcanized rubber sheets with 30 phr carbon black
were prepared by Method A. They contained BIR-
2, BIR-4, or BIR-8 at various concentrations (2, 4,
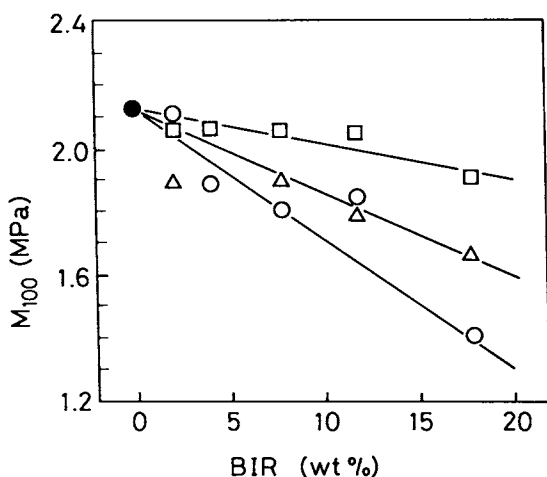8, 12, and 18 wt % of the NR/BR mixture). The

Figure 1   Effect of BIR concentration on 100% modulus
of vulcanized NR/BR (60/40) blend containing 30 phr
carbon black: (●) no BIR; (○) with BIR-2; (△) with BIR-
4; (□) with BIR-8. The tensile measurements were carried
out several times for each sample, and the values were the
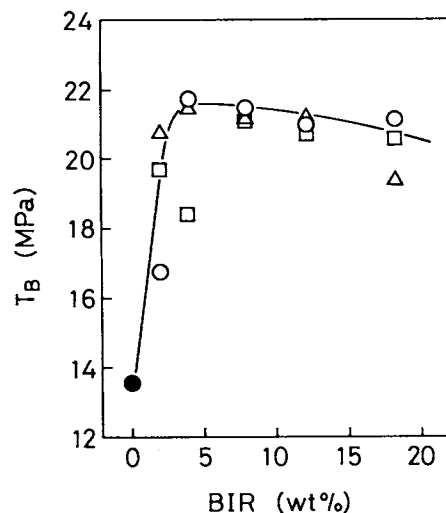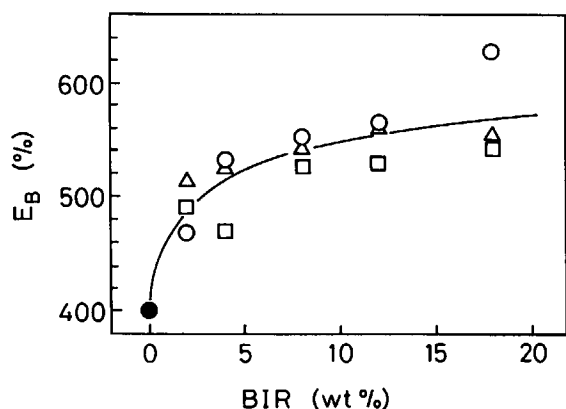averages with an error of 5%.

Figure 3 Effect of BIR concentration on E_B of vulcanized NR/BR (60/40) blend containing 30 phr carbon black: (●) no BIR; (○) with BIR-2; (△) with BIR-4; (□) with BIR-8. The deviation is as described in Figure 1.

results of tensile measurements, which were mean values of three to five measurements with an error ca. 5%, are shown in Figures 1–3. Modulus at 100% elongation (M_{100}), tensile strength (= tensile stress at break, T_B), and elongation at break (E_B) are plotted against BIR content in these figures. As the amount of BIR increases, the modulus tends to decrease (Fig. 1), whereas the tensile strength reaches a maximum value at about 4 wt % of BIR (Fig. 2). E_B increases rapidly at the beginning, then approaches an almost constant value when BIR content is higher than 4 wt % (Fig. 3). These results suggest that the quantity of BIR that is to be added to the blends should be in the order of 4–5 wt % by weight to obtain good tensile properties.
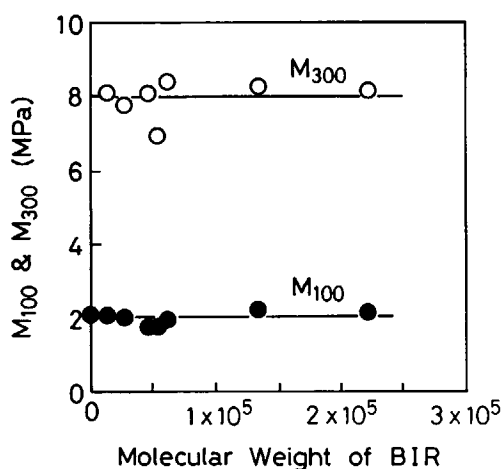

Figure 5 Effect of molecular weight of BIR on T_B of vulcanized NR/BR (60/40) blend containing 30 phr carbon black. BIR content was 4 wt %. The deviation is as described in Figure 1.

Effect of Molecular Weight of BIR

A constant (4 wt %) of each BIR (nos. 1, 3, 5, 6, 9, and 10) were added to the blend of NR/BR (60/40). Compounding Method A was used with 30 phr carbon black. Tensile properties of these specimens were measured five times per sample, and the average ones are shown in Figures 4, 5, and 6 as plots of 100 and 300% modulus (M_{100} and M_{300}), T_B, and E_B vs. molecular weight of BIR, respectively. In these cases, the deviation was also within 5%. From Figure 4, it can be seen that 100 and 300% moduli are relatively unaffected by the molecular weights of BIR. T_B of these specimens decreased as the molecular weight of BIR increased and finally approached the

Figure 4 Effect of molecular weight of BIR on M_{100} and M_{300} of vulcanized NR/BR (60/40) blend containing 30 phr carbon black. BIR content was 4 wt %. The deviation is as described in Figure 1.
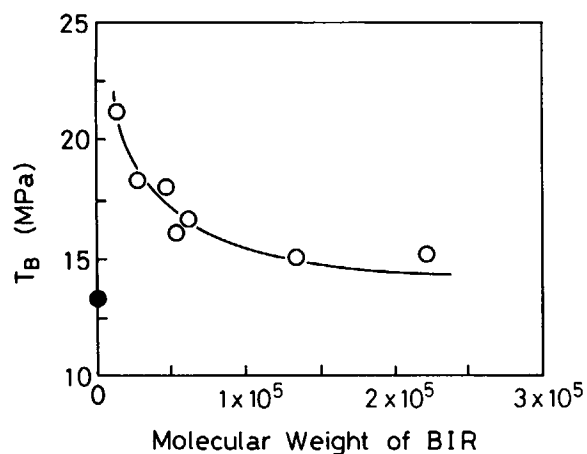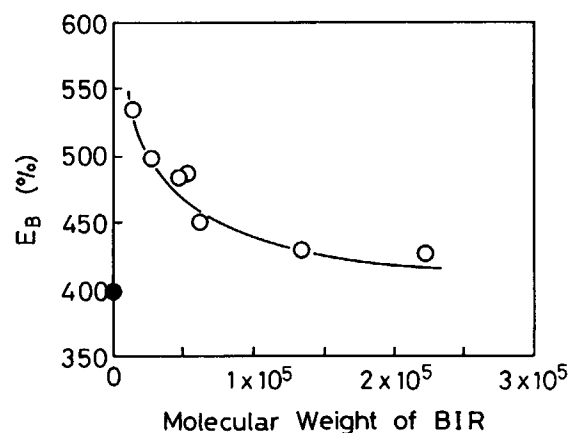

Figure 6 Effect of molecular weight of BIR on E_B of vulcanized NR/BR (60/40) blend containing 30 phr carbon black. BIR content was 4 wt %. The deviation is as described in Figure 1.

Table III   Abrasion Index and Hardness of Vulcanizates of Rubber Blends Containing 4 Wt % BIR and 30 or 50 phr Carbon Black

Sample Code	Compounding Method	Carbon Black (phr)	BIR	Abrasion[a] Index	Hardness[a] (Shore A)
A1	A	30	No	190	54.1
A2	A	30	BIR-2	245	—
A3	A	30	BIR-4	243	54.7
A4	A	30	BIR-6	249	54.8
A5	A	30	BIR-9	243	56.4
A6	A	30	BIR-10	243	56.5
B1	B	50	No	354	69.1
B2	B	50	BIR-1	393	67.6
B3	B	50	BIR-3	437	68.0
B4	B	50	BIR-5	444	67.9
B5	B	50	BIR-6	419	68.4
B6	B	50	BIR-7	462	68.9
B7	B	50	BIR-9	460	—
B8	B	50	BIR-10	440	—

[a] The measurements were carried out two or three times per sample. The values were averages with an estimated error of less than 10%.

values of the specimen without BIR, i.e., about 14 MPa (the first point in Fig. 5). This seems to be reasonable since the molecular weight of BIR is finally near to that of the matrix rubber. E_B increased by the addition of the lowest molecular weight BIR, due to the plasticizing or softening effect of BIR. However, E_B decreased as the molecular weights of BIR increased and finally approached the values of the specimen without BIR, i.e., about 400% (the first point in Fig. 6). It seems that the higher the molecular weight of BIR the less effective it is as a softener.

Abrasion Properties of NR/BR Blends

Because BR possesses much higher abrasion resistance than that of NR, blending of NR and BR is known to improve the abrasion property of NR. In many technological applications, especially for automobile tires, the optimal NR/BR ratio was 60/40 from this viewpoint. It was one of the main purposes of the present study to investigate whether the addition of BIR can improve the abrasion property of NR/BR blends.

The abrasion index and hardness of various specimens containing 4 wt % BIR and 30 or 50 phr carbon black are listed in Table III. These values were averages of measurements carried out several times per sample, and their errors were estimated to be at most ±10%. From the results shown in Table III, it can be seen that the addition of BIR did improve

the abrasion resistance of the blends by 30%. This was the case for the specimens prepared by Method A containing 30 phr carbon black as well as for those prepared by Method B containing 50 phr carbon black. Rubber blends containing 30 phr carbon black were also prepared by Method B, of which the values of the abrasion index were found to lie between 227 and 256, i.e., in the same range as those prepared by Method A.

The hardness values of the specimens listed in Table III show a very small tendency to increase
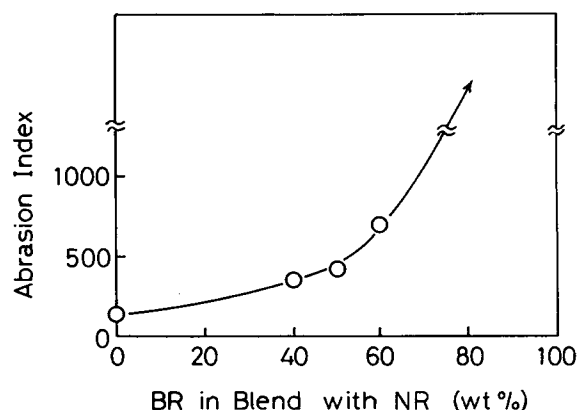
Figure 7   Effect of composition on abrasion index of vulcanized NR/BR blends with no BIR containing 50 phr carbon black. The measurements were carried out two or three times for each sample. The results were averages with an estimated error of less than 10%.
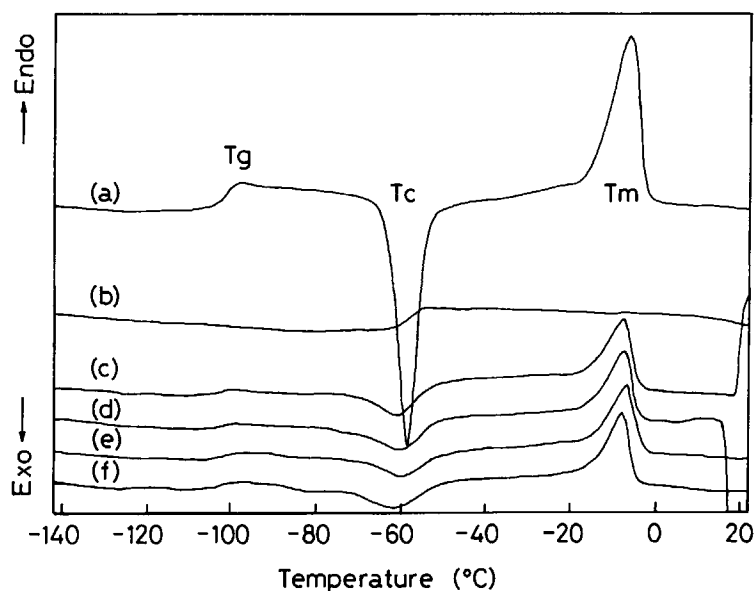
Figure 8 DSC diagrams of rubber gums: (a) masticated pure BR; (b) masticated pure NR; (c) NR/BR (60/40) with no BIR; (d) NR/BR (60/40) with 4 wt % BIR-7; (e) NR/BR (60/40) with 4 wt % BIR-3; (f) NR/BR (60/40) with 4 wt % BIR-1.

with the molecular weight of BIR in the series of specimens containing 30 phr carbon black, whereas for the specimens with 50 phr carbon black, no significant trend can be noticed.

Abrasion properties of NR/BR blends having different compositions were also studied. The results are shown in Figure 7. These samples were prepared by Method B and contain 50 phr of carbon black. For pure BR vulcanizate, the abrasion index was larger than 10,000 units. It is seen that the abrasion resistance of the blends increases with increasing BR content in the blends. In particular, a sharp increase was observed for the blends containing more than 60 parts of BR, suggesting a phase inversion, i.e., the matrix seemed to change from the NR to the BR phase at this composition of blends.

Morphology of NR/BR Blends

Differential Scanning Calorimetric (DSC) Measurement

DSC measurements of rubber gum with or without addition of BIR were performed. Typical results are shown in Figure 8 for (a) masticated pure BR, (b) masticated pure NR, and (c) a blend of NR/BR (60/40) and those with (d) 4 wt % of BIR-7, (e) BIR-3, and (f) BIR-1. The first curve showed the glass transition temperature (T_g) of BR at $-101°C$, crystallization peak (T_c) at $-59°C$, and the melting peak (T_m) at $-6°C$. The second curve showed a glass transition temperature of NR at $-58°C$. Incidentally, the T_g of NR lies in the same region as that of the crystallization peak of BR. Hence, the T_g of

Table IV Results from DSC Diagrams of NR, BR, and Their Blends without and with BIRs (Nos. 1, 3, 5, 6, and 7) as Rubber Gum (No Vulcanizing Ingredients)

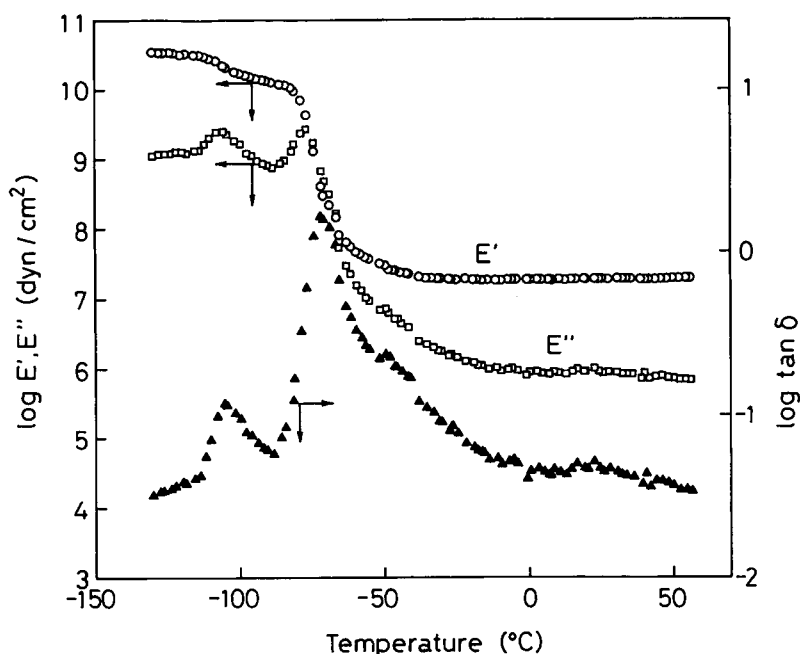| Rubber	T_g (°C)	ΔH_g (J/g)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
BR	−100.8	0.55	−58.5	−34.2	−6.3	29.8
NR	−58.3	0.51				
NR/BR (60/40)	−101.3	0.18	−60.9	−8.4	−7.9	12.3
NR/BR + BIR-1	−101.4	0.15	−60.8	−6.8	−8.1	10.9
NR/BR + BIR-3	−100.9	0.18	−59.5	−6.7	−7.2	11.0
NR/BR + BIR-5	−101.2	0.12	−59.1	−10.8	−7.8	10.8
NR/BR + BIR-6	−101.0	0.15	−58.6	−10.6	−7.8	10.2
NR/BR + BIR-7	−101.1	0.14	−60.3	−6.8	−8.0	10.6

Figure 9   DMA diagram of vulcanized NR/BR (60/40) containing 4 wt % BIR-3 with no carbon black: (○) real part of elastic modulus (E'); (□) imaginary part of elastic modulus (E''); (▲) tan δ.

NR in the rubber blends could not be evaluated. Table IV lists the values of T_g, T_c, and T_m and the corresponding change of enthalpies ΔH_g, ΔH_c, and ΔH_m, respectively. The existence of T_g, T_c, and T_m of BR in NR/BR blends suggests that phase separation occurred in these blends, in spite of the fact that their solubility parameters are very close. The value of ΔH_m for 40 parts of BR in the blend is 12.3 J/g. The calculated value of ΔH_m for 100 parts of BR is approximately 30 J/g, which is equal to pure BR. This means that even in the presence of NR (60 parts) the crystallization behavior of BR in the blends (and, hence, the melting) was similar to that of the pure BR. However, as BIRs were added to the blends, the values of the ΔH_m of BR slightly decreased. The reduction of the ΔH_m of BR by BIR suggests a certain degree of mixing between BIR and BR.

Dynamic Mechanical Analysis (DMA)

A typical DMA diagram is shown in Figure 9 for the vulcanized NR/BR (60/40) blend containing BIR-3. The temperature at the maximum values of log tan δ and the value at 25°C of the real part of the elastic modulus of various samples are listed in Table V.

In accord with the DSC results, DMA measurements revealed that NR/BR blends showed two distinct glass transition temperatures corresponding to those of BR and NR at approximately −104 and −70°C, respectively. When BIRs were added to the blends, the T_g's of both BR and NR shifted to lower temperatures. The extent of temperature shifts depended on the molecular weights of BIR. For the molecular weight of BIR between 60,000 to 80,000, no temperature shifts were observed. Thus, it might be concluded that low molecular weight BIR (< 50,000) acts as a plasticizer for NR/BR blends.

The real part of the complex modulus (E'), which relates to the time-independent elastic behavior, increases with increasing molecular weight of BIR, as

Table V   DMA Measurements of NR/BR Blends (60/40) without Carbon Black

Compatibilizer		Temperatures at Maximum tan δ		E' at 25°C (MPa)
BIR	Mol. Wt.	(°C)	(°C)	
No	—	−104.0	−69.4	1.86
BIR-1	14,000	−108.6	−76.9	1.74
BIR-3	27,000	−105.3	−71.6	1.92
BIR-5	53,000	−106.0	−73.8	2.05
BIR-6	62,000	−103.8	−73.2	2.28
BIR-7	82,000	−103.9	−70.1	2.27

shown in Table V. This is nominally interpreted as an increase in cross-linking density of the vulcanizates. This might be due to the improvement of the binding between the interphases.

CONCLUSION

The optimal amount of BIR for NR/BR (60/40) blends was found to be 4 wt % of rubber, as indicated by their tensile properties. Addition of 4 wt % of BIR to NR/BR blends improved their abrasion resistance by 30% compared to the specimen without BIR, but no effect of the molecular weight of BIR was found. The tensile strength and elongation-at-break of rubber blends increased as low molecular weight BIR was added, but these values declined and approached to those of the specimen without BIR as the molecular weight of BIR increased. The modulus at 100 and 300% elongation and hardness of rubber blends showed no remarkable change as the molecular weight of BIR was varied. The morphology studies of rubber blends by DSC and DMA revealed that two-phase structures still existed though BIR was added. However, the improvement of their homogeneity could be deduced from the decrease of the enthalpy change of the melting peak of BR in DSC diagrams and increase of the dynamic modulus of the blends in DMA measurements.

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