

# Using Modulated-Temperature Differential Scanning Calorimetry to Study Interphases in Blends of Styrene–Butadiene and Polybutadiene Rubbers Filled with a Silanized Silica Nanofiller

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**ABSTRACT:** Polybutadiene and styrene–butadiene rubber compounds containing a high loading of a precipitated silica nanofiller were prepared. The silica surfaces were pretreated with bis(3-triethoxysilylpropyl) tetrasulfide to prevent the silica from interfering with the reaction mechanism of sulfur cure in the rubber. The rubber compounds were mixed together for different times and at different temperatures to produce styrene–butadiene rubber/polybutadiene rubber blends. The mass fraction and composition of the interphase in the blends were subsequently determined with modulated-temperature differential scanning calorimetry. At 60–65°C, the mass fraction of the

interphase in the blend increased after the rubbers were mixed together for 10 min, and then it decreased significantly when the mixing time was increased to 20 min. When the two rubbers were mixed together for 7 min at 60–105°C, the mass fraction of the interphase in the blend increased slightly because of a higher mixing temperature. The composition of the interphase in the blend also changed with the mixing time and mixing temperature. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1644–1652, 2009

**Key words:** blending; differential scanning calorimetry (DSC); reinforcement; rubber; silicas

## INTRODUCTION

Adhesion or tack is an important property of unvulcanized rubber materials. It is the ability of two rubber surfaces to resist separation after they are brought into contact. The mutual adhesion, in which the two contacting bodies have different compositions and molecular structures, is of great practical importance for the manufacture of such products as tires and hoses. For example, styrene–butadiene rubber (SBR), polybutadiene rubber (BR), and natural rubber are blended to produce tire-tread rubber compounds.<sup>1</sup> Dissimilar rubbers are often immiscible or partially miscible and, when brought into contact in air, may not form strong interfacial adhesion.<sup>2</sup> There are numerous factors, such as the molecular weight of the rubber,<sup>2,3</sup> contact temperature,<sup>3</sup> contact time,<sup>2,3</sup> contact pressure,<sup>4</sup> and chemical additives,<sup>3,5</sup> that influence, some adversely, the strength of adhesion between rubbers, but little is known about their effects on the actual properties of interphases in rubber blends.

The interphase is an intermediate region for two phases in contact; its composition, structure, and properties may vary across the region, and they may differ from the composition, structure, and properties of either of the two contacting phases.<sup>6</sup> It is therefore assumed that the interphase is the result of molecular diffusion between pure phases. The development of a strong interphase between dissimilar rubbers is an important factor in the durability and performance of rubber blends in service.

The volume fraction of an interfacial material can be determined by means of thermal techniques.<sup>7</sup> One method applied to phase-separated block copolymers uses the change in the heat capacity due to the glass transition of each block with respect to the corresponding values for these homopolymers to estimate the quantity of the polymer in the microphase.<sup>8</sup> It is difficult to determine the heat capacity accurately and directly with conventional differential scanning calorimetry (DSC).

Modulated-temperature differential scanning calorimetry (M-TDSC) has several advantages in comparison with conventional DSC. For example, it is sufficiently sensitive and has good enough resolution to separate overlapping thermal events, which include the glass-transition temperature and signals from interphases developing from partially miscible rubbers during blending.<sup>9</sup> Moreover, M-TDSC

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differs from conventional DSC in that a low-frequency sinusoidal (e.g., sawtooth) perturbation, ranging from approximately 0.001 to 0.1 Hz (1000 to 10 s), is overlaid on the baseline temperature profile. With this technique, the calorimeter block is subjected to a temperature ramp that is linear when averaged over time and has a sinusoidal modulation. Heat capacity values can be determined readily and accurately with this technique. A full review of the technique was carried out by Reading.<sup>9</sup>

The aim of this study was to calculate the mass fraction of the interphase and determine its composition in some SBR/BR blends filled with a high loading of a silanized silica nanofiller with a newly developed M-TDSC method. The effect of increasing the mixing time and mixing temperature of silica-filled SBR and BR compounds on the properties of the interphase in the blends of these rubbers is of significant importance to the manufacturers of rubber-blended components and was investigated in this study.

## EXPERIMENTAL

### Materials: the rubbers, nanofiller, and curing chemicals

The raw rubbers were SBR (23.5 wt % styrene; Intol 1712, Polimeri Europa UK Ltd., Hythe, UK) and high-cis BR (96% 1,4-*cis*; Buna CB 24, Bayer, Newbury, UK; not oil-extended). The reinforcing nanofiller was Coupsil 8113, which was supplied by Evonik Degussa (Hanau, Germany). Coupsil 8113 is a precipitated, amorphous, white silica type of Ultrasil VN3; its surfaces were pretreated with bis(3-triethoxysilylpropyl) tetrasulfide (TESPT) to prevent the silica from interfering with the reaction mechanism of sulfur cure in the rubber. Coupsil 8113 is increasingly replacing colloidal carbon blacks in industrial rubber articles such as tires. It has 11.3 wt % silane, 2.5 wt % sulfur (included in TESPT), a 175 m<sup>2</sup>/g surface area (measured by N<sub>2</sub> adsorption), and a 20–54-nm particle size.

In addition to the raw rubbers and filler, the other ingredients were *N-t*-butyl-2-benzothiazole sulfenamide (Santocure TBBS, Flexsys, Dallas, TX; a safe-processing delayed-action accelerator with a melting point of 105°C), zinc oxide (ZnO; Harcros Durham Chemicals, Durham, UK; an activator), *N*-(1,3-dimethylbutyl)-*N*-phenyl-*p*-phenylenediamine (Santoflex 13, Flexsys; an antidegradant), a heavy, paraffinic-distillate, solvent-extract aromatic processing oil (Enerflex 74, Milton Keynes, United Kingdom), and elemental sulfur (Slovay Barium Strontium, Hannover, Germany; a curing agent). The oil was added to reduce the rubber viscosity, and the antidegradant was used to protect the rubbers against environmental aging. The cure system consisted of TBBS, ZnO,

TABLE I  
Formulations of the BR and SBR Rubbers

Formulation (phr)	Compound	
	1	2
BR	100	—
SBR	—	100
Silanized silica	60	60
TBBS	7.5	3
Santoflex 13	1	1
Enerflex 74	0	5
ZnO	0	0.5
Elemental sulfur	0.3	0

and elemental sulfur, which were added to fully crosslink the rubbers. Both SBR and BR rubber compounds filled with 60 phr silica were prepared and then mixed together to produce SBR/BR (75 : 25 by mass) blends for this study (Table I). The mass fraction of SBR with respect to BR in typical SBR/BR tire-tread blend compounds is 75 : 25.<sup>†</sup> The BR rubber needed 7.5 phr TBBS and 0.3 phr elemental sulfur and SBR needed 3 phr TBBS and 0.5 phr ZnO to fully cure. The procedures for measuring TBBS, ZnO, and elemental sulfur in these compounds have been described previously.<sup>10,11</sup>

### Mixing

The compounds were prepared in a Haake (Berlin, Germany) Rheocord 90, a small laboratory mixer with counter-rotating rotors. In these experiments, the Banbury rotors and the mixing chamber were maintained at 23, 34, 50, 67, and 86°C. The rotor speed was 45 rpm; the volume of the mixing chamber was 78 cm<sup>3</sup>, and it was 60% full. Haake software (version 1.9.1) was used for controlling the mixing conditions and storing data.

### Assessment of the silica dispersion in the rubbers

To select a suitable mixing time for incorporating the filler into the rubber, the rubber and filler were mixed together for different times. The filler was introduced first into the mixer, and then the raw rubber was added. The filler was added when the viscosity of the rubber was still relatively high, and this led to an improved dispersion.<sup>12</sup> The mixing time was increased to 16 min to disperse the silica particles fully in the rubber. The temperature of the rubber compounds during mixing increased from 23 (ambient temperature) to 105°C. Twenty-four hours after mixing ended, the rubbers were examined with scanning electron microscopy (SEM) to assess the filler dispersion.

The dispersion of the silica particles in the rubber was assessed with a Leo 1530 VP field-emission gun

**TABLE II**  
Specific Gravity, Mooney Viscosity, and Glass-Transition Temperature Values of the Rubbers

Rubber	Specific gravity	Mooney viscosity (MU)	Glass-transition temperature (°C)
SBR	0.94	52	-50
BR	0.91	49	-107

scanning electron microscope. Small pieces of the uncured rubber were placed in liquid nitrogen for 3 min and then fractured to create two fresh surfaces. The samples, 60 mm<sup>2</sup> in area and 5 mm thick, were coated with gold and then examined and photographed by SEM. The degree of dispersion of the silica particles in the rubber was subsequently studied from SEM photographs. After the SEM photographs were examined, suitable mixing times were used for adding the filler to the rubbers.

To prepare the SBR compounds, TBBS, ZnO, and antidegradant were added 4 min after the filler, rubber and processing oil were mixed together, and mixing was continued subsequently for an extra 6 min before the rubber compound was removed from the mixer. To mix the BR compounds, the filler was placed in the mixing chamber, and then the raw rubber was added. TBBS, elemental sulfur, and the antidegradant were added together 10 min after the filler and rubber were mixed together, and the mixing continued subsequently for an extra 6 min before the rubber was removed from the mixer.

Finally, when the mixing ended, the rubber compound was recovered from the mixer and milled to a thickness of about 6 mm for further work. The compounds were kept at the ambient temperature (~23°C) for at least 24 h before their viscosity and cure properties were measured.

#### Viscosity, specific gravity, and cure properties of the rubber compounds

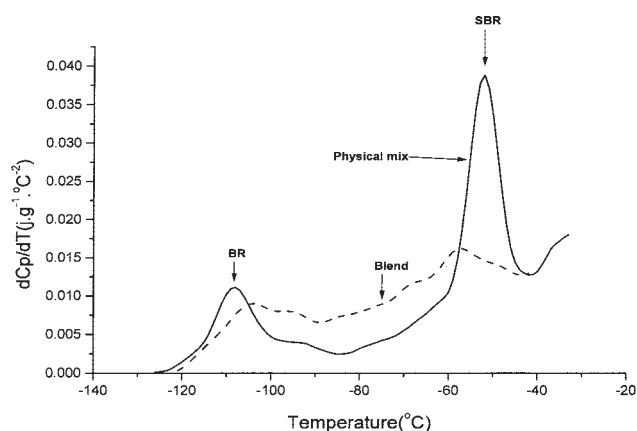
The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer according to the British standard,<sup>13</sup> and the results were expressed in Mooney units (MU). The specific gravity was determined with 2 g of each pure rubber and by the measurement of the liquid displacement in a calibrated cylindrical column of water (Table II). The scorch time, which is the time for the onset of cure ( $t_{s1}$ ), and the optimum cure time, which is the time for the completion of cure ( $t_{90}$ ), were determined from the cure traces generated at 140 ± 2°C by an oscillating disc rheometer cure meter (ODR) at an angular displacement of ±3° and a test frequency of 1.7 Hz.<sup>14</sup> The cure rate index, which is a measure of the rate of cure in the rubber, was calculated with the method described previously.<sup>15</sup> The rheometer tests ran for up to 2 h.

#### Glass-transition temperatures and mass fractions of the interphase in the blends

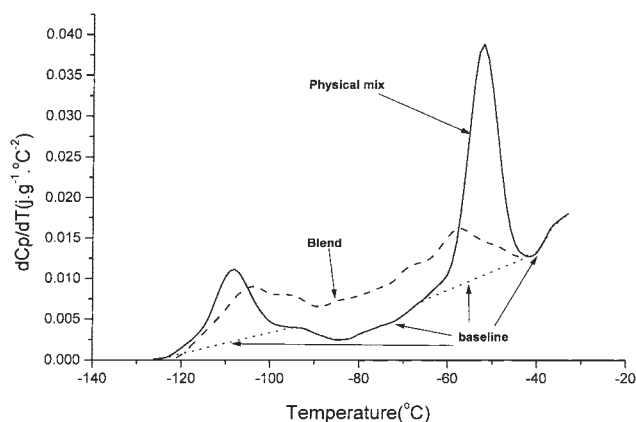
A modulated-temperature differential scanning calorimeter (TA Instruments, New Castle, DE) was used. An oscillation amplitude of 1°C and a period of 60 s were used throughout the investigation, which was conducted at a heating rate of 3°C/min. TA Instruments Graphware software was used to measure the heat flow, the heat capacity, and the differential of the heat capacity. The calorimeter was calibrated with indium standards. Both the temperature and baseline were calibrated as for conventional DSC. A standard aluminum pan and lid were used, and rubber samples of approximately 10–15 mg were placed in the pan at the ambient temperature; the lid was subsequently closed under some nominal pressure. The assembly was placed in the chamber of the calorimeter, and the temperature was lowered to -140°C with a flow of liquid nitrogen, which was used as the heat-transfer gas, at a rate of 35 ml/min. The temperature was allowed to modulate back to the ambient temperature as described previously. The glass-transition temperature of the pure rubbers was measured (Table II), and the mass fraction of the interphase and its composition for the SBR/BR blends were subsequently calculated at different mixing temperatures and for different mixing times.

#### RESULTS AND DISCUSSION

Data for the differential of the heat capacity with the temperature ( $dC_p/dT$ ) versus the temperature for the SBR/BR blend and for a physical mixture (samples of pure SBR and BR rubbers placed in physical contact) are shown in Figure 1. Both samples were prepared at 60–65°C for 5 min. The increase in the increment of the heat capacity ( $\Delta C_p$ ) at the glass-transition temperature of both rubbers for a



**Figure 1** Typical plot of  $dC_p/dT$  versus the temperature for (---) the SBR/BR blend and (—) SBR/BR physical mixture. The samples were mixed at 60–65°C for 5 min.



**Figure 2** Typical plot of  $dC_p/dT$  versus the temperature for (---) the SBR/BR blend and (—) SBR/BR physical mixture, showing the baseline. The samples were mixed at 60–65 $^\circ C$  for 5 min.

component is proportional to its mass fraction in the system under investigation. The heat capacity versus the temperature cannot provide information about the interphase, glass-transition temperature, or its composition distribution, but the  $dC_p/dT$ -versus-temperature data (Fig. 1) can provide that information.<sup>16</sup>

Figure 2 shows  $dC_p/dT$  versus the temperature for a diffuse interphase in the SBR/BR blend prepared at 60–65 $^\circ C$  for 5 min and for a physical mixture of the two pure SBR and BR samples (75 : 25) prepared in the same way. The data in this figure show that the value of  $dC_p/dT$  versus the temperature for the SBR/BR blend is larger than that for the pure SBR and BR samples (physical mixture) between the glass-transition temperatures of SBR and BR. The SBR/BR blend has a single interphase, and this interphase does not exhibit a separate glass-transition temperature, but it occurs continually between the glass-transition temperatures of the constituent rubbers.

### Background of the analysis

The  $dC_p/dT$ -versus-temperature signal can be described by a Gaussian function for polymers and miscible polymer blends. However, the  $dC_p/dT$ -versus-temperature signals for a rubber 1/rubber 2 physical mixture cannot be described well by the sum of two Gaussian functions because of the shift of the baseline between the glass-transition temperatures. Thus, the  $dC_p/dT$ -versus-temperature signal includes a nonbaseline for multiphase systems (Fig. 1). Because a Gaussian function was used for the quantitative analysis of the interphase in these multiphase systems, the nonconstant baseline had to be corrected.

The values of the  $dC_p/dT$ -versus-temperature signal for rubber 1/rubber 2 physical mixtures above

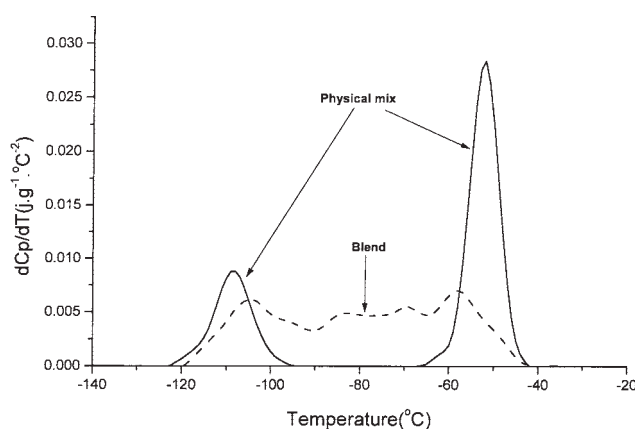
and below the two glass-transition temperatures are considered the baseline for the  $dC_p/dT$  signals of these multiphase systems. For the glass transitions, baselines that were linear with the temperature from the starting and end points of the glass-transition temperature were chosen. An example is given in Figure 2 for the blend. When the  $dC_p/dT$ -versus-temperature signal is analyzed with a multi-Gaussian function for multiphase systems, this baseline must be subtracted from the raw  $dC_p/dT$ -versus-temperature signal. Figure 3 shows the baseline-corrected  $dC_p/dT$ -versus-temperature signal for the blend and the physical mixture after 5 min at 60–65 $^\circ C$ .

For an interphase,  $dC_p/dT$  may be considered the sum of  $i$  subsystems with an individual glass-transition temperature for each subsystem as follows:

$$\begin{aligned}
 [dC_p/dT]_{\text{interphase}} &= \sum_{i=1}^N [dC_p/dT]_i \\
 &= \sum_{i=1}^N \frac{\Delta C_{p_i}}{[\omega_{di}(\pi/2)^{0.5}] \exp\left[\frac{-2(T-T_{gi})^2}{(\omega_{di})^2}\right]}
 \end{aligned} \quad (1)$$

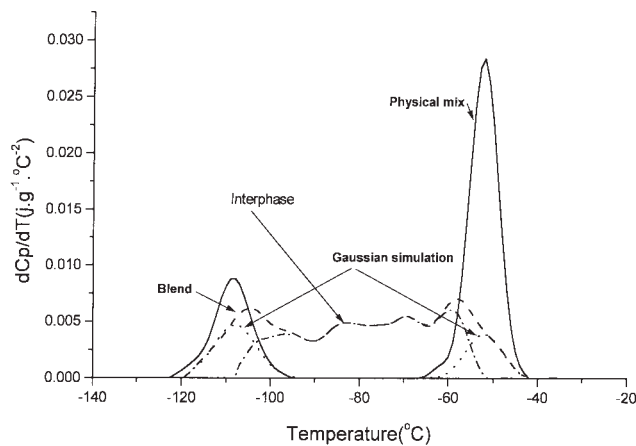
where  $N$  is less than 10,  $\Delta C_{p_i}$  is the increment of the heat capacity,  $T_{gi}$  is the glass-transition temperature, and  $\omega_{di}$  is the half-width of the  $i$ th subsystem in the interphase.<sup>16</sup> With eq. (1), the interphase can be analyzed quantitatively. Figure 4 shows a typical interphase region after baseline correction and peak resolution. Finally, an interphase curve was obtained by subtraction of the blend curve from a Gaussian simulation of the same curve (Fig. 5).

After the determination of the area under the curve of a physical mixture for individual peaks as well as a simulated Gaussian one, the following



**Figure 3** Typical plot of  $dC_p/dT$  versus the temperature for (---) the SBR/BR blend and (—) SBR/BR physical mixture after the baseline correction in Figure 2. The samples were mixed at 60–65 $^\circ C$  for 5 min.





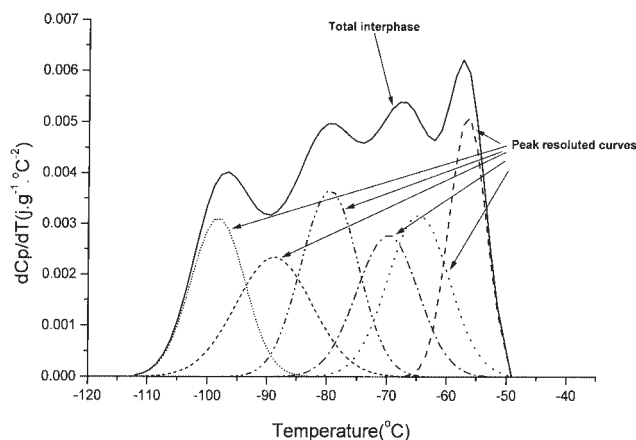
**Figure 4** Typical plot of  $dC_p/dT$  versus the temperature for the SBR/BR blend after the peak resolution in Figure 3, showing the interphase region.

equations may be used to determine the mass fraction of the interphase and its composition:<sup>17</sup>

$$\delta_1 = \omega_{10} \left( 1 - \frac{\Delta C_{p1}}{\Delta C_{p10}} \right) \quad (2)$$

$$\delta_2 = \omega_{20} \left( 1 - \frac{\Delta C_{p2}}{\Delta C_{p20}} \right) \quad (3)$$

where  $\delta_1$  and  $\delta_2$  are the mass fractions in the interphase of rubbers 1 and 2, respectively;  $\omega_{i0}$  is the mass fraction of the rubbers before mixing;  $\Delta C_{p1}$  and  $\Delta C_{p2}$  are increments of  $dC_p/dT$  at the glass-transition temperatures of the pure rubbers in the blend (the area under the Gaussian simulation curve); and  $\Delta C_{p10}$  and  $\Delta C_{p20}$  are increments of  $dC_p/dT$  at the



**Figure 5** Typical plot of  $dC_p/dT$  versus the temperature for the SBR/BR blend, showing a typical interphase obtained by subtraction of the blend curve from the Gaussian simulation of the same curve. The area under the curve is a measure of the mass fraction of the interphase. The sample was prepared at 60–65°C for 5 min.

glass-transition temperatures of the pure rubbers (the area under the curve of the physical mixture). The amount of interphase in a blend is determined as follows:

$$\begin{aligned} \text{Percent of interphase} &= \frac{(\text{Amount of interphase})}{(\text{Total amount of blend})} \times 100 \\ &= (\delta_1 + \delta_2) \times 100 \end{aligned} \quad (4)$$

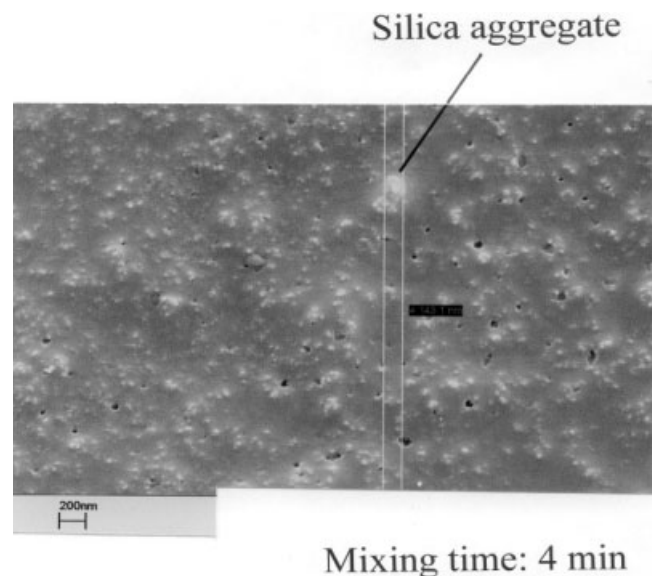
It is important to obtain an accurate value of  $\Delta C_p$ . The quantity  $\Delta C_p$  is defined as follows:

$$\Delta C_p = \int_{T_i}^{T_e} [dC_p/dT] dT \quad (5)$$

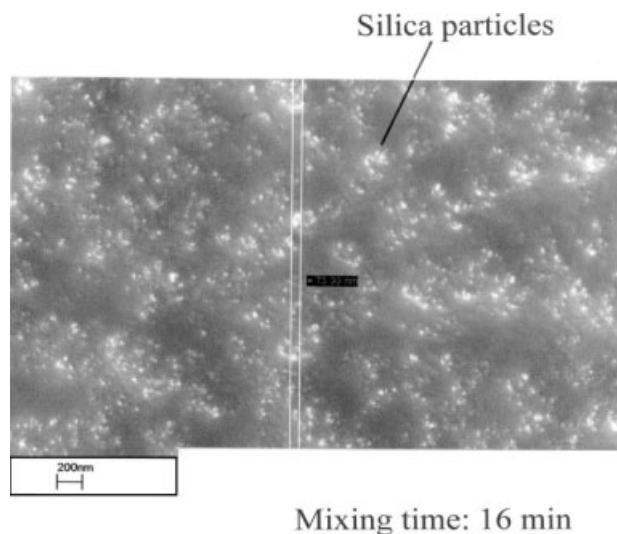
where  $T_i$  and  $T_e$  are the initial and final values of the temperature in the glass-transition region (Fig. 1). Thus, according to eq. (5), it is possible to obtain accurate  $\Delta C_p$  values experimentally.<sup>18</sup>

### Silica dispersion in the rubbers

To disperse the silica particles fully in the rubbers, the mixing time was increased to 16 min. Large silica aggregates (ca. 144 nm) were seen in the rubber matrix after short mixing times, such as 4 min (Fig. 6), and the aggregate size decreased to about 74 nm as the mixing time was increased to 16 min (Fig. 7). The size of the particles in Figure 7 was fairly similar to the actual particle size of the filler (20–54 nm). It was concluded that maximum mixing times of 10 and 16 min were sufficient to fully disperse the silica particles in the SBR and BR rubbers, respectively.



**Figure 6** SEM photograph showing a typical poor dispersion of the silica particles in the rubber (mixing time = 4 min). Data for the BR rubber are shown.



**Figure 7** SEM photograph showing a typical good dispersion of the silica particles in the rubber (mixing time = 16 min). Data for the BR rubber are shown.

**Effect of the mixing time of the SBR and BR compounds on the cure properties, mass fraction, and composition of the interphase in the SBR/BR blend**

The ODR test results for the two SBR and BR compounds and the SBR/BR blend and the composition and mass fraction of the interphase in the blend as a function of the mixing time are shown in Tables III and IV, respectively. The minimum and maximum torque values were 23–25 and 94–99 dN m, respectively (Table IV). It appears that when the SBR and BR compounds were mixed together for longer

**TABLE III**  
Mooney Viscosities and Cure Properties of the BR and SBR Rubbers

	Compound	
	1	2
Mooney viscosity (MU)	162	109
ODR results		
Minimum torque (dN m)	39	23
Maximum torque (dN m)	124	66
$\Delta_{\text{torque}}$ (dN m)	85	43
$t_{s1}$ (min)	5	12
$t_{90}$ (min)	49	49
Cure rate index ( $\text{min}^{-1}$ )	2.3	2.7

times, the torque values of the blend were not affected.  $\Delta_{\text{torque}}$ , which is an indication of crosslink density changes in the blend,<sup>19</sup> increased from 70 to 75 dN m after 10 min of mixing and then decreased slightly to 73 dN m. The scorch and optimum cure times of the blend were not affected by increases in the mixing time of the two compounds and remained at 10 and 28–30 min, respectively. The cure rate index rose from 5 to  $5.6 \text{ min}^{-1}$  as a function of the mixing time up to 10 min, although it subsequently decreased to  $5 \text{ min}^{-1}$  after the mixing time was increased to 20 min.

The mass fraction of the interphase in the blend increased from 72 to 88% after the two compounds were mixed together for 10 min. It then decreased to 63% when the mixing time was increased to 20 min. The composition of the interphase also changed. At prolonged mixing times, the mass fraction of BR with respect to SBR in the interphase increased from

**TABLE IV**  
Mixing Conditions, Cure Properties, Mass Fractions, and Compositions of the Interphase in the SBR/BR Blends

	Compound			
	3	4	5	6
Mixing conditions				
Mixing temperature ( $^{\circ}\text{C}$ )	60–65	60–65	60–66	60–65
Mixing time (min)	5	7	10	20
ODR results				
Minimum torque (dN m)	24	25	24	23
Maximum torque (dN m)	94	97	99	96
$\Delta_{\text{torque}}$ (dN m)	70	72	75	73
$t_{s1}$ (min)	10	10	10	10
$t_{90}$ (min)	30	29	28	30
Cure rate index ( $\text{min}^{-1}$ )	5	5.3	5.6	5
Interphase properties				
Mass fraction of the interphase (%)	72	82	88	63
Mass fraction of BR in the interphase (%)	13.5	21	22.4	32
Mass fraction of SBR in the interphase (%)	86.5	79	77.6	68
Mass fraction of BR to SBR in the interphase	0.16	0.27	0.29	0.47

The SBR and BR compounds were mixed together for different times. The mass fraction of BR with respect to SBR in the interphase was calculated as follows: for compound 3,  $\text{BR/SBR} = 13.5/86.5 = 0.16$ .

TABLE V  
Mooney Viscosities, Cure Properties, Mass Fractions, and Compositions of the Interphase in the SBR/BR Blends

	Compound		
	7	8	9
Mooney viscosity (MU)	108	104	96
Mixing temperature (°C)	60–65	80–90	90–105
ODR results			
Minimum torque (dN m)	25	23	24
Maximum torque (dN m)	97	94	96
$\Delta_{\text{torque}}$ (dN m)	72	71	72
$t_{s1}$ (min)	10	11	10
$t_{90}$ (min)	29	40	43
Cure rate index ( $\text{min}^{-1}$ )	5.3	3.5	3.0
Interphase properties			
Mass fraction of the interphase (%)	82	81	85
Mass fraction of BR in the interphase (%)	21	23.5	24.6
Mass fraction of the SBR in the interphase (%)	79	76.5	75.4
Mass fraction of BR to SBR in the interphase	0.27	0.31	0.33

The SBR and BR compounds were mixed together for 7 min at different temperatures to produce the blends.

approximately 0.16 to 0.47. The mass fraction of BR with respect to SBR in the interphase was calculated by the division of the mass percentage of BR by SBR (Table IV). Longer mixing times also replaced SBR with BR in the interphase.

#### Effect of the mixing temperature of the BR and SBR compounds on the Mooney viscosity, cure properties, mass fraction, and composition of the interphase in the SBR/BR blend

As expected, a longer mixing time reduced the viscosity of the blend from 108 to 96 MU (Table V). The rubber breaks down during mixing, and this causes a reduction in its molecular weight and viscosity.<sup>12,20,21</sup> The reduction is due to chain scission<sup>22</sup> or the mechanical rupture of the primary carbon-carbon bonds that are present along the backbone of the rubber chains. This is often compensated by the reinforcing effect of the filler.

The scorch time of the blend was unaffected and remained at 10–11 min, but its optimum cure time increased from 29 to 43 min as the mixing temperature of the two compounds was increased from 60 to 105°C. As a result, the cure rate index decreased from 5.3 to 3  $\text{min}^{-1}$ , and this indicated a slowdown of the curing rate in the rubber.  $\Delta_{\text{torque}}$  of the blend did not change and stayed at approximately 72 dN m. Similarly, the minimum and maximum torque values stayed at about 23–25 and 94–97 dN m, respectively. This suggested that increases in the mixing temperature of the two compounds had no obvious effect on the minimum torque or the extent of crosslinking in the blend, as indicated by the maximum torque value. The optimum cure time was the

only property that was affected by increases in the mixing temperature of the two compounds.

The mass fraction of the interphase in the blend increased from 82 to 85% because of the higher mixing temperature of the two compounds. The mass fraction of BR with respect to SBR in the interphase also increased from 0.27 to 0.33 when the mixing temperature was increased from 60 to 105°C. Clearly, higher temperatures during the mixing of the two compounds were beneficial to the formation of the interphase in the blend and increased the BR component of the interphase.

#### Effect of the prescorch time on the mass fraction and composition of the interphase in the SBR/BR blend

As shown in Table III, the scorch times of the BR and SBR compounds were 5 and 12 min, respectively. When the two compounds were mixed together for 1 min at 34–54°C and then tested in the ODR at 140°C, the scorch time of the blend was 10 min (Table VI). The blend (170 g) was subsequently placed in a hydraulic press at 140°C for 8 min (the prescorch time) under a pressure of 110 atm to produce sheets 2.5 mm thick. The rubber was then removed from the press and left at the ambient temperature to cool. The mass fraction and composition of the interphase in the blend were determined to evaluate the effect of the heat treatment on the interphase properties. For the blend prepared by the mixing of the two compounds for 1 min at 34–54°C, the mass fraction of the interphase was 59%, and the mass fraction of BR with respect to SBR in the interphase was approximately 0.27. However, when the

**TABLE VI**  
**Mooney Viscosities, Cure Properties, Mass Fractions, and Compositions of the Interphase in the SBR/BR Blends**

	Compound 10
Mooney viscosity (MU)	108
ODR results	
$t_{s1}$ (min)	10
$t_{90}$ (min)	35
Cure rate index ( $\text{min}^{-1}$ )	4
Minimum torque (dN m)	26
Maximum torque (dN m)	96
$\Delta_{\text{torque}}$ (dN m)	70
Interphase properties	
Mass fraction of the interphase (%)	59
Mass fraction of BR in the interphase (%)	21
Mass fraction of SBR in the interphase (%)	79
Mass fraction of BR to SBR in the interphase	0.27

The SBR and BR compounds were mixed together for 1 min at 34–54°C to produce the blend.

same blend was kept at 140°C for 8 min, the mass fraction of the interphase increased to 62%, and the mass fraction of BR with respect to SBR in the interphase rose to 0.63. A strong interphase was formed in the blend during the prescorch stage of the cure cycle at an elevated temperature, and the BR component of the interphase also increased (Table VII).

The diffusion theory of adhesion, also known as autohesion in the case of rubbers, states that the adhesion of two macromolecules in intimate contact results from the interdiffusion of the molecules of the superficial layers.<sup>23,24</sup> This interdiffusion allows the formation of an interphase between the two rubbers. In the case of polymer autohesion corresponding to the mutual diffusion of identical molecules, adhesion under a constant assembly pressure is a function of temperature and contact time, following Fick's classical law.<sup>25</sup> Therefore, the average interpenetration depth ( $\chi$ ) of one phase into another is determined as follows:

$$\chi = \exp(-E/2RT)t^{1/2} \quad (6)$$

where  $E$  is the diffusion activation energy,  $t$  is the contact time,  $R$  is the molar gas constant, and  $T$  is the sample temperature.

Polymer interdiffusion has been the subject of numerous studies. For example, Skewis<sup>26</sup> measured the rate of interdiffusion of butyl and SBR rubber chains when samples of the two rubbers were pressed against each other. He also showed that the

diffusion of polymer chains across the interface occurred when two samples of uncured rubbers were brought into intimate contact and that this interdiffusion enhanced the adhesion between the two rubbers.

There are two fundamental requirements that must be met to obtain adhesion by interdiffusion:<sup>25,27</sup> the adherates must be mutually soluble or compatible, and the macromolecules must be very mobile. The latter depends on increases in the temperature. For pure SBR and BR rubbers, solubility parameters of 8.30 and 8.41 ( $\text{cal/cc}^{1/2}$ ), respectively, have been reported.<sup>2,3</sup> The small difference in the solubility parameters of the rubbers suggests that they were at least partially miscible, and therefore adhesion by interdiffusion could have occurred. Note that the presence of a large amount of a reinforcing filler did not change the solubility parameters of the rubbers.<sup>3</sup> The glass-transition temperatures of the SBR and BR rubbers were –50 and –107°C, respectively (Table II), which indicated a high degree of mobility for the macromolecules at the ambient temperature. However, the temperature during the mixing of the SBR and BR compounds rose to 105°C, and this increased the mobility of the chain segments further, facilitating more extensive interdiffusion between the rubbers. In addition, the mixing time of the two compounds was increased to 20 min, and this was sufficient for the mutual diffusion of the SBR and BR macromolecules to take place<sup>26</sup> and for the formation of interphases in the blends.

The large mass fraction of the interphase in the blends (Tables IV–VII) indicated that significant molecular diffusion took place between the BR and SBR rubbers, which improved the adhesion between the two.

## CONCLUSIONS

From this study, the following can be concluded:

1. When the mixing time of the SBR and BR compounds was increased progressively from 5 to 10 min, the mass fraction of the interphase in the SBR/BR blend increased from 72 to 88%. However, as the mixing time of the two compounds was increased to 20 min, this had a detrimental effect on the mass fraction of the interphase in the blend. The mass fraction of BR with respect to SBR in the interphase also

**TABLE VII**  
**Mass Fractions and Compositions of the Interphase in the SBR/BR Blend After 8 min of Scorching at 140°C**

Blend	Mass fraction of the interphase (%)	Composition of the interphase (%)	Mass fraction of BR to SBR
SBR/BR	62	BR = 38.5, SBR = 61.5	0.63

The SBR and BR compounds were mixed together for 1 min at 34–54°C to produce the blend.



rose from 0.16 to 0.47 as the mixing time of the two compounds was increased to 20 min.

2. When the mixing temperature of the two compounds was increased from 60 to 105°C, the mass fraction of the interphase in the blend rose from approximately 82 to 85%. Similarly, the mass fraction of BR with respect to SBR in the interphase increased from 0.27 to 0.33.
3. The mass fraction of the interphase in the blend was 59% when the two compounds were mixed together for 1 min at 34–54°C, and the mass fraction of BR with respect to SBR in the interphase was 0.27. When the same blend was kept at 140°C for 8 min (the prescorch time), the mass fraction of the interphase was 62%, and the mass fraction of BR with respect to SBR in the interphase was about 0.63.

In summary, increasing the mixing time and mixing temperature of the two compounds helped to increase the mass fraction of the interphase in the SBR/BR blend and alter the composition of the interphase. A similar trend was also observed when the blend was kept at 140°C for 8 min (the prescorch time) during its cure cycle. The results suggested that strong interphases could be formed in the blend during the prescorch time of the rubber without a need for the two compounds to be mixed together for long times and at high temperatures before curing starts.

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