Effects of Different Interphases on the Mechanical Properties of Cured Silanized Silica-Filled Styrene–Butadiene/Polybutadiene Rubber Blends for Use in Passenger Car Tire Treads

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ABSTRACT: Polybutadiene (BR) and styrene–butadiene (SBR) rubbers containing the same loading of precipitated silica nanofiller were prepared. The silica surfaces were pretreated with bis(3-triethoxysilylpropyl) tetrasulfide to chemically bond the silica to the rubber. The rubber compounds were mixed together for different times and at different temperatures to produce SBR/BR blends. The mass fraction and composition values of the interphases in the blends were subsequently determined with modulated-temperature differential scanning calorimetry. These properties changed substantially as a function of mixing temperature and mixing time. The hardness, tensile strength, elongation at break, stored energy density at break, tear strength, modulus, abrasion resistance, heat buildup, and loss tangent of the cured blends were measured over a wide range of test conditions. Elongation at break, stored energy density at break, tearing energy, and abrasion resistance benefited from increases in the mass fraction of the interphase. The remaining properties were influenced mainly by the filler loading and mixing time of the two rubber compounds. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1868–1878, 2009

Key words: blends; interpenetrating networks (IPN); mechanical properties; rubber; silicas

INTRODUCTION

Natural rubber, styrene–butadiene (SBR) rubber, polybutadiene (BR) rubber, and many more rubbers are often mixed together to produce blends for use in tire tread compounds, hoses, and conveyor belts.[1,2] Dissimilar rubbers are immiscible or partially miscible and, when brought into contact in air, may not form strong interfacial adhesion between them.[3] To increase the durability, performance, and service life of rubber blended components, it is essential to optimize the interfacial adhesion strength between dissimilar rubbers such the ones mentioned previously. Moreover, this will help to minimize the risk of unexpected sudden joint failure in service, enhance materials selection, and joint design and improve environment and safety in service. The formation of any heterogeneous system, for example, a polymeric one, is accompanied by the formation of an interphase, which determines the important properties of that system.[4] Thermal diffusion between two miscible or partially miscible polymers results in an interfacial phase developing. With increasing diffusion

time, in most cases, the thickness of the interphase increases too and the concentration profile changes.[5] The interface is characterized by a two-dimensional array of atoms and molecules that are impossible to measure, whereas the interfacial layer or interphase has a large enough assembly of atoms or molecules to have its own properties, for example, modulus, strength, heat capacity, and density.[4] The interphase is an intermediate region for two phases in contact, the composition, structure, and properties of which may vary across the region and which may differ from the composition, structure, and properties of either of the two contacting phases.[6]

The interphase is, therefore, the result of molecular diffusion between pure phases. Rubber blends have a significant role in the tire industry, which continuously tries to attain a better compromise between wear resistance, rolling resistance, and ice-grip and wet-grip properties of tire tread compounds. Rubbers used in the manufacture of tire tread compounds, for instance, SBR, BR, and natural rubber, are partially miscible when blended and may have weak interfacial adhesion.[7] The development of a strong interphase between dissimilar rubbers is an important factor in the durability and performance of rubber blends in service.

Several techniques, for example, differential scanning calorimetry (DSC), have been used to

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determine the fraction of polymers contained in the mixed regions between microphases.[8–14] It is also possible to measure the volume fraction of interfacial material by means of thermal techniques.[15] One method applied to phase-separated block copolymers uses the change in heat capacity due to the glass transition of each block relative to the corresponding values for these homopolymers to estimate the quantity of polymer in the microphase.[16] The heat capacity cannot be measured accurately with DSC. Modulated-temperature differential scanning calorimetry (M-TDSC)[16,17] 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 (T_g) and signals from interphases developing from partially miscible rubbers during blending. Moreover, M-TDSC differs from conventional DSC in that a low-frequency sinusoidal (e.g., sawtooth) perturbation, ranging from approximately 0.001 to 0.1 Hz (1000–10 s), is overlaid on the baseline temperature profile. In this instrument, the calorimeter block is subjected to a temperature ramp that is linear when averaged over time but which 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.[16]

In recent years, synthetic precipitated white silica nanofiller has been replacing colloidal carbon blacks in industrial rubber articles, for example, passenger car tires, and offers significant benefits to the rubber properties.[18] However, silicas are acidic[19] and interact with the basic accelerators to cause long cure times, slow cure rates,[20] and a loss of crosslink density in sulfur-cured rubbers.[21] There is also a tendency for the filler to adsorb moisture because the surfaces of silicas are polar and hydrophilic.[22] This adversely influences cure and mechanical properties of rubber vulcanizates. In addition, strong interaction between the silica particles increases viscosity,[23,24] which causes excessive wear and tear of the processing equipment. Bifunctional organosilanes such as bis(3-triethoxysilylpropyl) tetrasulfide (TESPT; Scheme 1) are primers for the treatment of silica surfaces to remedy the problems mentioned previously and make silica more suitable for use in rubber compounds.

TESPT is used to enhance the reinforcing capability of fillers with silanol groups on their surfaces, such as precipitated silicas, and also forms an integral part of curing systems to improve the crosslinking network properties.[20] The tetrasulfane groups of the silane are rubber reactive[20] and react in the presence of accelerators at elevated temperatures with or without the presence of elemental sulfur to form crosslinks in rubbers containing carbon–carbon dou-

TESPT (Si69 coupling agent)
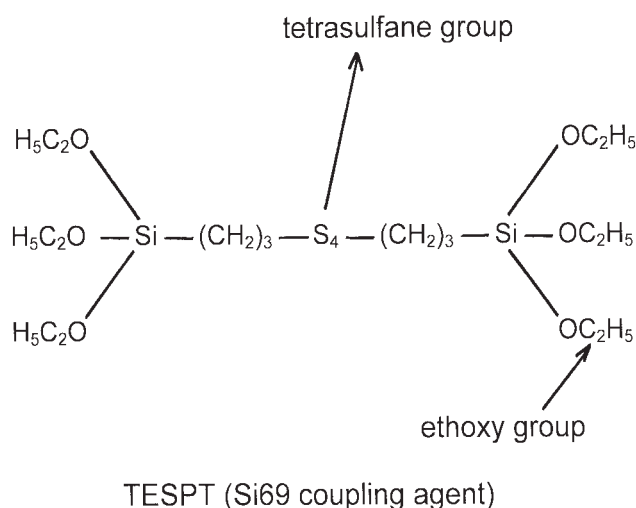
Scheme 1

ble bonds. The ethoxy groups react with the silanol groups on the surfaces of these fillers during compounding, and this leads to the formation of stable covalent rubber/TESPT bonds. Moreover, the TESPT reaction with silanol groups reduces their numbers, and the remaining groups become less accessible to the rubber chains because of steric hindrance.[20] These changes reduce the viscosity of rubber compounds and improve cure properties.[20]

The aim of this work was to evaluate effect of the mass fraction and composition of the interphase on the hardness, tensile strength, elongation at break, stored energy density at break, tear strength, modulus, abrasion resistance, heat buildup, and loss tangent (tan δ) of some cured SBR/BR blends over a wide range of test conditions. SBR and BR rubber compounds filled with a high loading of silanized silica nanofiller were prepared separately and then mixed together for different times and at different temperatures to produce the blends. The mass fraction and composition of the interphase in the blends were subsequently determined with the M-TDSC method. Scanning electron microscopy was also used to study the dispersion of silica particles in the rubbers.

EXPERIMENTAL

Materials: Rubber, filler, curing chemicals, antidegradants, and processing oil

The raw rubbers used were SBR rubber (23.5 wt % styrene, Intol 1712) (Polimeri Europa UK Ltd., Hythe, UK) and high-cis BR (Buna CB 24 Bayer, not oil extended) (Newbury, UK) with a minimum 96 wt % cis-1,4 content. The reinforcing filler was Coupsil 8113 (Evonik Industries AG of Hanau, Germany). Coupsil 8113 was a precipitated amorphous

white silica-type Ultrasil VN3 surfaces of which had been pretreated with TESPT. It had 11.3 wt % TESPT, 2.5 wt % sulfur (included in TESPT), a surface area of 175 m^2/g (as measured by N_2 adsorption), and a particle size of 20–54 nm.

In addition to the raw rubbers and filler, the other ingredients were *N-t*-butyl-2-benzothiazole sulfenamide (a safe-processing delayed-action accelerator, Santocure TBBS, Woluwe, Belgium), zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, United Kingdom), elemental sulfur (a curing agent, Solvay Barium Strontium, Hannover, Germany), *N*-(1,3-dimethylbutyl)-*N′*-phenyl-*p*-phenylenediamine (an antidegradant, Santoflex 13, Brussels, Germany), and heavy paraffinic distillate solvent extract aromatic processing oil (Enerflex 74, Milton Keynes, Milton Keynes, United Kingdom). The oil was added to reduce the rubber viscosity, and the antidegradant was added to protect the rubbers against environmental aging. The cure system consisted of TBBS, ZnO, and elemental sulfur, which were added to fully crosslink the rubbers. The procedures for measuring these curing chemicals for the BR and SBR rubber compounds were described previously.[24,25]

Mixing

The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small size laboratory mixer with counterrotating rotors. In these experiments, the Banbury rotors and the mixing chamber were maintained at 23°C (ambient temperature) during mixing. The rotor speed was 45 rpm. The volume of the mixing chamber was 78 cm^3, and it was 60% full during mixing. Haake Software version 1.9.1 was used to control the mixing conditions and to store data.

Two SBR and BR rubber compounds filled with 60 parts per hundred rubber by weight (phr) silanized silica nanofiller were prepared and then mixed together to produce SBR/BR (75:25 mass %) blends for this study (Table I). The mass fraction ratio of SBR to BR in typical SBR/BR tire tread blend compounds is 75:25.[18] To prepare the SBR compound, the filler was placed in the mixing chamber, and then, the raw rubber and processing oil were added. TBBS, ZnO, and antidegradant were added 4 min after the filler, rubber, and processing oil were mixed together, and mixing continued subsequently for an extra 6 min before the rubber compound was removed from the mixer. To mix the BR compound, the filler and rubber were mixed together for 10 min, and then, TBBS, elemental sulfur, and antidegradant were added together. Mixing continued subsequently for an extra 6 min before the rubber was removed from the mixer. Elemental sulfur was added to the BR compound to achieve the same optimum cure time as the SBR compound before the

TABLE I
Formulations, Cure Properties, and Viscosities of the SBR and BR Rubber Compounds

	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
Mooney viscosity (MU)	162	109
ODR results		
Minimum torque (dN m)	39	23
Maximum torque (dN m)	124	66
Δtorque (dN m)	85	43
t_{s1} (min)	5	12
t_{90} (min)	50	49
Cure rate index (min^{-1})	2.2	2.7

The total mixing times for compounds 1 and 2 were 16 and 10 min, respectively. t_{s1} is the time for the on set of cure and t_{90} is the time for the completion of cure.

two rubbers were mixed together to produce the blend. Before the curing chemicals were added, the rotors were stopped, and the rubber compounds were cooled to 40–50°C to avoid prescorching in the compounds during the subsequent mixing.

Finally, when mixing ended, the rubber compounds were stored at ambient temperature ($\sim$ 23°C) for at least 24 h before their viscosity and cure properties were measured. The SBR and BR rubber compounds were then mixed together for 1, 7, and 20 min to produce the SBR/BR blends. The viscosity and cure properties of the blends were measured 12 h after mixing ended.

Mooney viscosity and cure properties of the rubber compounds and the blends

The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer (Wallace Instruments, Surrey, United Kingdom) according to a British standard.[26] The scorch time, which is the time for the onset of cure, and the optimum cure time, which is the time for the completion of cure, were determined from the cure traces generated at 140 $\pm$ 2°C by an oscillating disc rheometer curemeter (Monsanto, Swindon, United Kingdom) at an angular displacement of $\pm 3°$ and a test frequency of 1.7 Hz.[27] The cure rate index, which is a measure of the rate of cure in the rubber, was calculated with the method described in a British standard.[28] The rheometer tests ran for up to 2 h. The results of these experiments are also summarized in Tables I and II.

TABLE II
Mixing Conditions, Mooney Viscosities, Cure Properties, Mass Fractions, and
Compositions of the Interphases in the SBR/BR (75 : 25 Mass %) Blends

	Blend		
	3	4	5
Mixing conditions of the SBR and BR compounds			
Mixing time (min)	1	7	20
Mixing temperature (°C)	34–54	90–105	80–94
Mooney viscosity (MU)	108	96	78
ODR results			
Minimum torque (dN m)	27	24	21
Maximum torque (dN m)	96	97	93
Δtorque (dN m)	69	73	72
t_{s1} (min)	10	10	9.0
t_{90} (min)	35	43	45
Cure rate index (min^{-1})	4	3	2.8
Interphase properties in the uncured blends			
Mass fraction of the interphase (%)	59	85	90
Mass fraction of BR in the interphase (%)	21	25	18
Mass fraction of SBR in the interphase (%)	79	75	82
Mass fraction of BR to SBR in the interphase	0.27	0.33	0.22
Interphase properties 8 min before scorch at 140°C			
Mass fraction of the interphase	62	86	81
Mass fraction of BR in the interphase	38.5	27	27
Mass fraction of SBR in the interphase	61.5	73	73
Mass fraction of BR to SBR in the interphase	0.63	0.37	0.37

The mass fraction of BR to SBR in the interphase was calculated in the following fashion: for uncured blend 3 (provided as an example), the mass fraction of BR to SBR in the interphase was BR/SBR = 21/79 = 0.27.

Specific gravity and T_g of the SBR and BR rubbers and mass fraction of the interphase in the SBR/BR blends

The specific gravity was determined with 2 g of each pure rubber and by measurement of the liquid displacement in a calibrated cylindrical column of water. A modulated-temperature differential scanning calorimeter (model 2920, TA Instruments, New Castle, DE) was used to measure T_g of the rubbers and the mass fraction and composition of the interphase in the blends. An oscillation amplitude of 1°C and a period of 60 s were used throughout the investigations, which were conducted at a heating rate of 3°C/min. TA Instruments Graphware software was used to measure the heat flow, heat capacity, and differential of heat capacity. The calorimeter was calibrated with indium standards. Both temperature and baseline were calibrated as for conventional DSC. A standard aluminum pan and lid were used, and samples of rubber approximately 10–15 mg in weight were placed in the pan at ambient temperature, and 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 the flow of liquid nitrogen at a rate of 35 mL/min, which was used as the heat-transfer gas. The temperature was allowed to modulate back to ambient

as described previously. T_g of the pure rubbers and the mass fraction of the interphase and its composition for the SBR/BR blends were subsequently calculated for different mixing times and mixing temperatures with the procedure described previously.[16,17] The results are shown in Tables II and III. The measurements of the mass fraction of the interphase contained 5–8% error.

Test pieces and test procedure

After these measurements were completed, the rubber compounds were cured in a compression mold at 140°C with a pressure of 11 MPa. Pieces of rubber, each approximately 140 g in weight, were cut from a milled sheet 6 mm thick. Each piece was placed in the center of the mold to enable it to flow in all directions when pressure was applied. This prevented anisotropy from forming in the cured rubbers. To determine the mechanical properties of the

TABLE III
Specific Gravity, Mooney Viscosity, and T_g Values
of the Raw Rubbers

Compound	Specific gravity	Mooney viscosity (MU)	T_g (°C)
SBR	0.94	51	−50
BR	0.91	49	−107
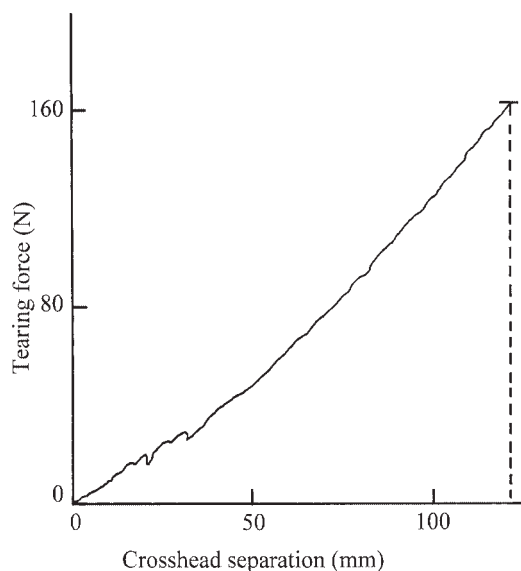
Figure 1 Typical record of the tearing force as a function of crosshead separation (data for blend 4; $T = 136$ kJ/m^2).

rubbers, sheets 23 × 23 cm^2 and approximately 2.4 mm thick were used, from which various samples for further tests were cut.

Swelling tests and bound rubber measurements

The solvent used for the swelling tests and bound rubber determination was toluene. For the determination, 2 g of each rubber compound was cured in a compression mold to produce cylindrical samples 14 mm in diameter and 8 mm in height. The samples were then placed individually in 90 mL of the solvent in labeled bottles and allowed to swell for up to 8 days at ambient temperature (23°C). The weight of the samples was measured every day until it reached an equilibrium. It took up to 171 and 100 h for the filled BR and SBR rubber samples, respectively, to reach equilibrium. It took approximately 62 h for blend 3, 86 h for blend 4, and 51 h for blend 5 to reach equilibrium, respectively. The solvent was removed after this time elapsed, and the samples were dried in air for 9 h. The samples were subsequently dried in an oven at 85°C for 24 h and allowed to stand for an extra 24 h at ambient temperature before they were reweighed. The bound rubber was then calculated with an expression from ref. 21.

Hardness

To measure the hardness of the rubbers, cylindrical samples 12 mm thick and 28 mm in diameter were used. The samples were then placed in a Shore A durometer hardness tester (Shore Instrument & Manufacturing Co., New York), and the hardness of the rubber was measured at ambient temperature (25°C) over a 15-s interval, after which a reading

was taken. This was repeated at four different positions on the sample, and the median of the four readings was calculated.[29]

Cohesive tear strength

Rectangular strips, 114 mm long and 30 mm wide, were cut from the cured sheets of rubber and a sharp crack, approximately 40 mm in length, was introduced into the strips half way along the width and parallel to the length of the strip to form the trouser test pieces for the tear experiments. The tear tests were performed at an angle of 180°, ambient temperature (23°C), and a constant crosshead speed of 50 mm/min[30] in a Hounsfield mechanical testing machine (HTi Hounsfield Test Equipment Ltd., Redhill, UK). The tears produced in the rubber after the test pieces were fractured were 15–57 mm in length. In each experiment, the tearing force was recorded as a function of crosshead separation to produce traces from which an average force was measured. In some cases, the test produced only one peak on the trace from which a tearing force was calculated (Fig. 1). Sometimes tearing produced several peaks on the trace, which were used to calculate an average tearing force for the rubber (Fig. 2), or a continuous trace, where the peak force value was used for the rubber (Fig. 3). For each rubber, four test pieces were used. After we completed these measurements and followed the procedure described previously,[31] we determined the force values and placed them in eq 1 as follows:
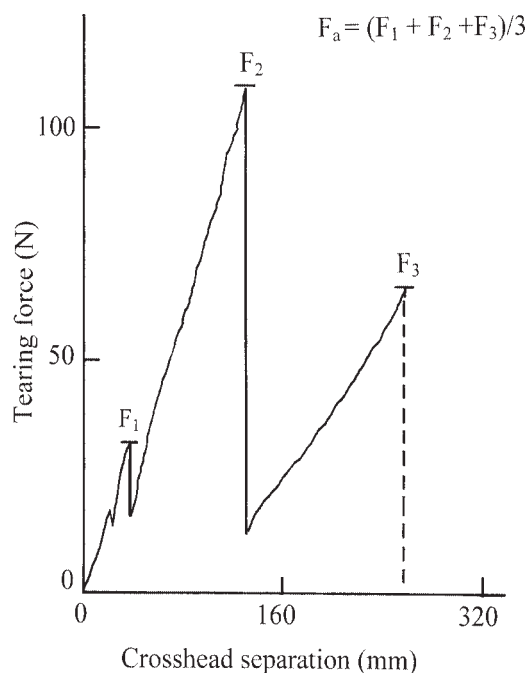
Figure 2 Typical record of the tearing force as a function of crosshead separation (data for blend 5; $T = 61$ kJ/m^2). F_1, F_2 and F_3 are peak force values.
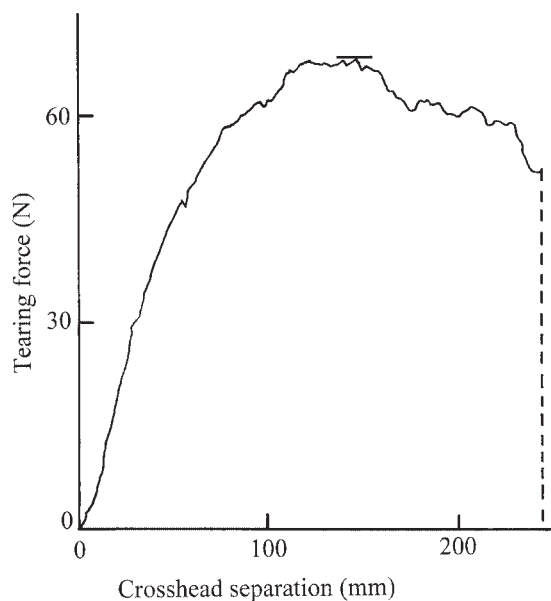
Figure 3 Typical record of the tearing force as a function of crosshead separation (data for the SBR vulcanizate; $T = 53$ kJ/m^2).

$$T = 2F/t \qquad (1)$$

where F is the force and t the thickness of the test piece, to calculate tearing energies (T's) for the rubbers. The median values of the T values were subsequently noted.

Tensile properties

The tensile stress, elongation at break, and stored energy density at break of the rubbers were determined in uniaxial tension in a Hounsfield mechanical testing machine with dumbbell test pieces 3.6 mm wide with a central neck 25 mm long. These samples were die-stamped from sheets of cured rubber. The tests were performed at 23°C and a crosshead speed of 50 mm/min.[32] For each rubber, three test pieces were fractured, and the median of the three values was subsequently noted. Hounsfield DAPMAT computer software was used to store and process the data.

Moduli at different strain amplitudes

The moduli of the vulcanizates at 50, 100, 200, and 300% strain amplitudes and Young's modulus were measured in uniaxial tension with dumbbell test pieces. The tests were carried out at ambient temperature (23°C) and a crosshead speed of 50 mm/min[32] in a HT Hounsfield mechanical testing machine. QMAT-DONGLE (HTi Hounsfield Test Equipment Ltd., Redhill, UK) version 2003 computer software was used to process the data.

Abrasion resistance

To determine the abrasion resistance of rubbers 1 and 2, molded cylindrical test pieces 8 mm thick and 16 mm in diameter were cured. The tests were performed at 23°C in accordance with BS 903: Part A9: 1995 with method A.1 (Zwick abrasion tester 6102, Croydon, United Kingdom, and abrasion standard rubber S1). For each rubber, three samples were tested to calculate the relative volume loss (Δv).[33] The abrasion resistance of the blends was measured by the application of a similar procedure and with standard rubber S2, a typical tire compound formulation.[34] The abrasion resistance was expressed as an abrasion resistance index (ARI). An index value of greater than 100% indicated that the test compound was more resistance to abrasion than the standard rubber under the conditions of the test. The ARI values recorded for the three rubbers were greater than 100%, and therefore, they had a higher resistance to abrasion than the standard rubber against which they had been indexed.

Heat buildup

The heat buildup of the blends was determined in accordance with BS903 Part A50. The stroke (0.25 feet) and static load (24 lb) equated to the middle values for the stroke and displacement listed in ASTM D 623. The load applied during testing was equivalent to 1 MPa. The samples were tested at ambient temperature (23°C). The test duration was 30 min in total: 5 min of static and 25 min of dynamic flexing. The height of the test pieces was measured, with the test pieces having been allowed to cool to ambient temperature and with testing in accordance with the standard, and the permanent set was calculated. The test pieces were cut open, and the internal structure of the test pieces was examined for evidence of porosity. A porous structure would have indicated that some breakdown of the rubber had occurred on testing. The test pieces would be reported as showing signs of onset of failure.[35]

Tan δ

Tan δ is the ratio between the loss modulus and elastic modulus. The loss modulus represents the viscous component of the modulus and includes all of the energy dissipation processes during dynamic strain. Tan δ was measured in a DMAQ800 model CFL-50 instrument (TA Instruments) with Universal Analysis 2000 Software version 4.3A. Test pieces 35 mm long, 13 mm wide, and approximately 2.40 mm thick were used. The tests were performed at frequencies of 1, 20, and 100 Hz. The samples were deflected by 256 μm (nominal peak-to-peak

displacement) during the test, and the sample temperature was raised from −140 to 100°C in 3°C/min steps.

RESULTS AND DISCUSSION

Effects of the mixing time and mixing temperature on the composition and mass fraction of the interphase in the SBR/BR blend

The mass fraction of the interphase in the blend (Table II) increased from 59 to 90% after the two compounds were mixed together for 20 min. The composition of the interphase also changed. As the mixing time was increased from 1 to 7 min, the mass fraction ratio of BR to SBR in the interphase increased from 0.27 to 0.33. When the mixing time was raised to 20 min, the mass fraction of BR to SBR in the interphase decreased to 0.22. Evidently, mixing times longer than 7 min replaced BR with SBR in the interphase.

The properties of the interphase changed during a prescorch time of 8 min at 140°C. The blends had scorch times of 9–10 min. The mass fraction of the interphase in the blend increased from 62 to 81%, and the mass fraction ratio of BR to SBR in the interphase decreased from 0.63 to 0.37 when the mixing time was increased to 20 min (Table II). A strong interphase was formed in the blend during the prescorch stage of the cure cycle at elevated temperature, and the BR component of the interphase decreased.

Polymer interdiffusion has been the subject of numerous studies. Skewis[36] measured the rate of the 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 the 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:[37,38] the adherents must be mutually soluble or compatible, and the macromolecules must be very mobile. The latter requirement is temperature dependent. For pure SBR and BR rubbers, solubility parameters of 8.30 and 8.41 $(cal/cc)^{1/2}$ have been reported, respectively.[3,7] The small difference in the solubility parameters of the rubbers suggested that they were, at least, partially miscible, and therefore, adhesion by interdiffusion could have occurred. The presence of a large amount of reinforcing filler did not change the solubility parameters of the rubbers.[7] The T_g values of the SBR and BR rubbers were −50 and −107°C, respectively (Table III), which indicated a high degree of mobility for the macromolecules at ambient temperature. However, temperature during the mixing of the SBR and BR compounds rose to 105°C, and this increased the mobility of the chain
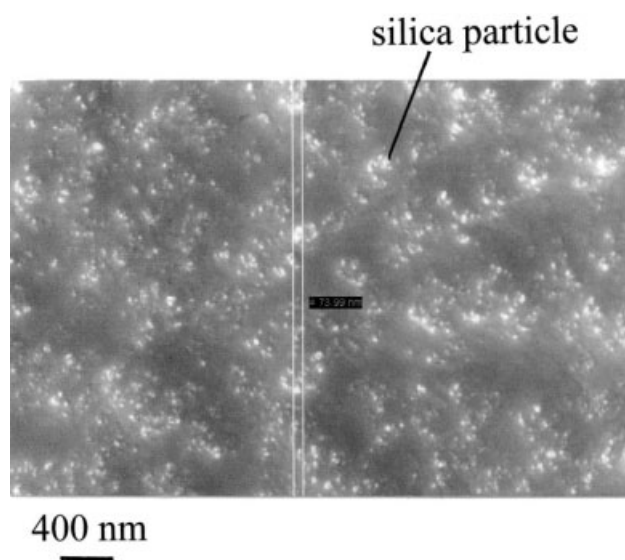
Figure 4 SEM photograph showing the dispersion of silica particles in the rubber (data for the BR rubber; mixing time = 16 min with good dispersion).

segments further, which facilitated a more extensive interdiffusion between the rubbers. In addition, the mixing time of the two compounds was increased to 20 min, which allowed sufficient time for the mutual diffusion of the SBR and BR macromolecules to take place.[36] This led to the formation of a strong interphase in the blends.

The large mass fraction of the interphase in the blends, up to 90% (Table II), indicated that significant molecular diffusion had taken place between the BR and SBR rubbers, which improved the adhesion between the two. Properties related to fracture were more likely to have benefited from the formation of strong interphases in the blend.

Filler dispersion and filler effects on the viscosity of the SBR and BR rubbers and SBR/BR blends

To optimize the reinforcing effect of the filler on the mechanical properties of the vulcanizates, it was essential to disperse the filler particles well in the rubber.[39] The BR and SBR compounds were mixed for 16 and 10 min, respectively, to achieve good dispersion of the silica particles in the rubbers (Fig. 4). However, a long mixing time, for example, 10 min, broke down the rubber and caused reductions in its molecular weight[40] and viscosity.[41] The reductions were due to chain scission or the mechanical rupture of the primary carbon–carbon bonds that were present along the backbone of the rubber chains.[42,43] The reinforcing effect of filler often compensates for the adverse effects produced by the scission of the chains and mechanical degradation of the rubber during processing.

The addition of the filler increased the viscosity of the raw rubbers, which rose from 51 MU (raw SBR)

TABLE IV
Bound Rubber and Mechanical Properties of the SBR and BR Rubber Vulcanizates and the Cured SBR/BR Blends

	Compound		Blend		
	1	2	3	4	5
Swelling test data					
Bound rubber (%)	93	66	69.5	73	73
Properties related to fracture					
Tensile strength (MPa)	12	23	26	23	26
Elongation at break (%)	516	1053	856	768	900
Stored energy density at break (mJ/m^3)	30	111	99	86	103
T (kJ/m^2)	71	59	40	92	92
Range of values	62–90	53–67	37–140	73–136	61–121
Δv (mm^3/mg)	15.5	126	—	—	—
ARI (%)	—	—	129	135	139
Heat buildup test results					
Initial static deflection (%)	—	—	15.5	14.5	14.1
Initial dynamic deflection (%)	—	—	18.6	18.7	19.0
Final dynamic deflection (%)	—	—	20.5	20.7	21.9
Temperature rise (°C)	—	—	62.5	64	67
Permanent set (%)	—	—	6.1	5.8	6.2
Test outcome[a]	—	—	No fail	No fail	No fail
Hardness (Shore A)	77	70	74	73	71
Young's modulus (MPa)	8.2	4.5	6.3	6.0	5.4
Modulus at different strain amplitudes (MPa)					
50%	2.5	1.6	2.5	2.1	2.0
100%	1.9	1.8	2.5	2.2	2.0
200%	2.2	2.2	3.1	2.9	2.8
300%	2.5	2.4	3.5	3.5	3.4

[a] There was no evidence of porosity in the rubber on an examination of the internal structure of the test pieces, and this was reported as "no fail."

to 109 and 49 MU (raw BR) to 162 MU, respectively (Table I). The viscosity of the SBR/BR blends was also affected by the mixing time. As expected,[40,41] a longer mixing time of 20 min reduced the viscosity of the blend from 108 to 78 MU (Table II). This was attributed to chain scission.[42,43]

Fillers increase rubber viscosity because of the formation of bound rubber.[21] The bound rubber contents of the BR and SBR rubber vulcanizates were 93 and 66%, respectively (Table IV), which indicated a high level of rubber–filler interaction. Similarly, the bound rubber contents of the blends 3–5 were 69.5–73%, which showed a strong interaction between the filler and rubber. It is known that bound rubber forms during mixing when filler dispersion occurs[44] and increases as a function of mixing temperature,[45] mixing time,[46] and storage time.[47] Because the mixing time increased to 20 min, the compound temperature rose to 105°C during mixing, and the blends were stored at ambient temperature ($\sim$ 23°C) for a total of 36 h before they were tested, bound rubber formation occurred.

Cure properties of the SBR and BR rubber compounds and SBR/BR rubber blends

The oscillating disc rheometry (ODR) test results of the two SBR and BR compounds and the SBR/BR

blends are shown in Tables I and II, respectively. The scorch times of the BR and SBR compounds were 5 and 12 min, respectively, and the SBR compound had a faster rate of cure, with a cure rate index of 2.7 min^{-1}. The optimum cure times of the two compounds were almost the same, that is, 49–50 min (Table I). The cure properties of the SBR/BR blends were different from the two compounds [cf. compounds 1 and 2 [Table I] with blends 3–5 [Table II]). The scorch times of the blends were similar at 9–10 min. However, the optimum cure time rose from 35 to 45 min as mixing time was increased to 20 min. Blend 3 had the highest rate of cure, with a cure rate index of 4 min^{-1}. Δtorque (the difference between the maximum and minimum torque values on the cure traces of the rubbers and is an indication of crosslink density changes in the rubber) increased from 69 to 72 dN m, which indicated a small rise in the crosslink density of the blend.

Mechanical properties of the BR and SBR rubber vulcanizates and cured SBR/BR blends

The mechanical properties of the BR and SBR rubber vulcanizates and the three blends tested are summarized in Table IV. With the exception of T, abrasion resistance, hardness, and modulus, the remaining properties of the SBR vulcanizate were

TABLE V
Peak Tan δ and Test Temperature Data for the Five Compounds Tested at
Different Frequencies

	Compound				
	1	2	3	4	5
1 Hz					
Peak tan δ	0.45	0.66	0.48	0.51	0.47
Temperature (°C)	−87	−28	−35	−37	−39
20 Hz					
Peak tan δ	0.50	0.64	0.51	0.54	0.52
Temperature (°C)	−82	−25	−32	−33	−31
100 Hz					
Peak tan δ	—	—	0.55	0.60	—
Temperature (°C)	—	—	−22	−21	—

noticeably better than those of the BR. It was also interesting that the Δv of the BR rubber was approximately 88% lower than that of the SBR rubber.

The properties of the blends were influenced differently by changes in the mass fraction and composition of the interphase. For blends 3 and 5, the properties related to fracture improved as the mass fraction of the interphase was increased from 59 to 90%. For example, elongation at break, stored energy density at break, and T rose from 856 to 900%, 99 to 103 mJ/m^3, and 40 to 92 kJ/m^2, respectively. There was also improvement in the abrasion resistance, with the ARI rising from 129 to 139%, but the tensile strength remained unchanged at 26 MPa. Prolonged mixing reduces viscosity and mechanically damages rubber.[40,41] On this basis, the properties related to fracture were expected to deteriorate as a function of mixing time. However, as the results show, these properties improved. Weak interfacial adhesion between the two rubbers or the absence of an interphase in the blend could have caused the poor mechanical properties.[3,7] We concluded that increases in the aforementioned properties were due to the development of a strong interphase in the blends. The rubber properties, for example, tensile strength and stored energy density at break, increased as a function of crosslink density.[48] For the blends, Δtorque rose from 69 to 72 dN m (Table II), which indicated a small increase in the crosslink density of the rubber. However, this increase was too small to account for the large improvement recorded in the properties of the blends discussed previously. Therefore, the improvement was due to the increase in the mass fraction of the interphase in the blends.

The Shore A hardness and Young's modulus decreased from 74 to 71 and 6.3 to 5.4 MPa, respectively. Moreover, the modulus of the blend decreased by as much as 25% at 50% strain amplitude and by about 3% at 300% strain amplitude. These properties are often affected by the loading of filler and mixing time.[49] Because the blends had the same loading of silica, the reduction in the hardness and modulus was due to prolonged mixing, which mechanically damaged the rubber.[40–43] Notably, these properties did not benefit from a strong interphase in the blend. The tensile strength, elongation at break, and stored energy density at break of blend 4 were slightly inferior to those of blends 3 and 5 (Table IV).

The heat buildup tests showed no evidence of porosity in the blends on examination of the internal structure of the test pieces. The permanent set was 6.1–6.2%, and the blend temperature rose from 62.5 to 67°C. The fact that the blend became softer; that is, the Shore A hardness decreased from 74 to 71, and its temperature rose to 67°C in the heat buildup tests, which suggested that prolong mixing was detrimental to the blend, at least, as far as these properties were concerned.

Tan δ of the BR and SBR rubber vulcanizates and SBR/BR rubber blends

The energy loss in car tires during dynamic strain affects their service performance properties, such as rolling resistance.[44] Rolling resistance is related to the movement of the whole tire corresponding to deformation at a frequency 10–100 Hz and a temperature ranging from 50 to 80°C. To meet the requirements of high-performance tires, a low tan δ value at a temperature of 50–80°C to reduce rolling resistance and save energy and fuel is often required.[44] A high tan δ value (high hysteresis) at low temperatures, for example, −50 to −30°C, to obtain high-skid resistance and ice and wet grip is also essential.[44]

Figures 5–7 show tan δ as a function of test temperature at 1–100 Hz test frequencies. The peak tan δ values are also summarized in Table V. At 1 Hz, the peak tan δ values for the BR and SBR vulcanizates were 0.45 and 0.66 at −87 and −28°C, respectively. However, at 20 Hz, the peak tan δ of the BR
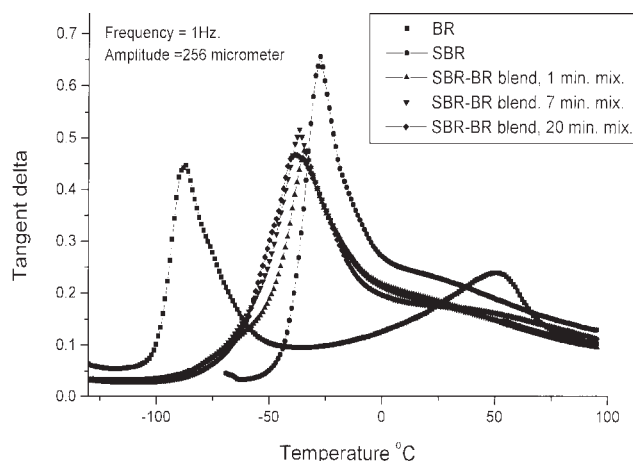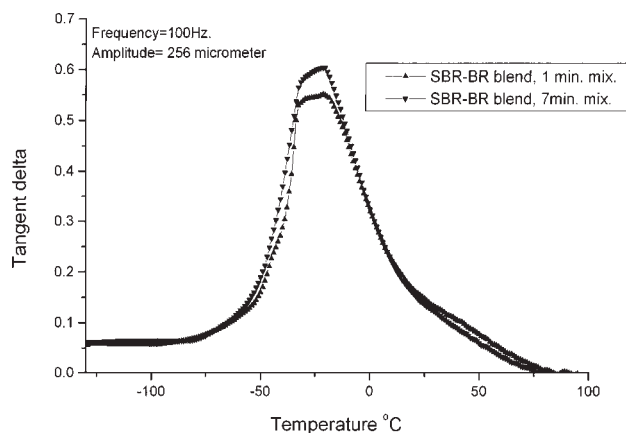
Figure 5 Tan δ versus the temperature at 1 Hz for compounds 1 and 2 and blends 3–5.

vulcanizate increased to 0.50, and that of the SBR rubber decreased to 0.64. Also, the peak values at 20 Hz were recorded at higher temperatures of −82 and −25°C, respectively (Table V).

For the SBR/BR blends, a similar trend was also observed, and the peak tan δ increased as a function of test frequency. The highest peak tan δ values of 0.51, 0.54, and 0.60 were recorded for blend 4 at −37, −33, and −21°C, respectively, as the test frequency was increased to 100 Hz (Table V). The same blend had the lowest tan δ values at temperatures higher than 50°C (Figs. 5–7). Also, increases in the test frequency shifted the peak tan δ of the blends to higher temperatures (Table V). As stated earlier, tan δ is the ratio between loss modulus and elastic modulus. The loss modulus represents the viscous component of the modulus and includes all of the energy dissipation processes during dynamic strain. Energy dissipation is related to the viscoelastic
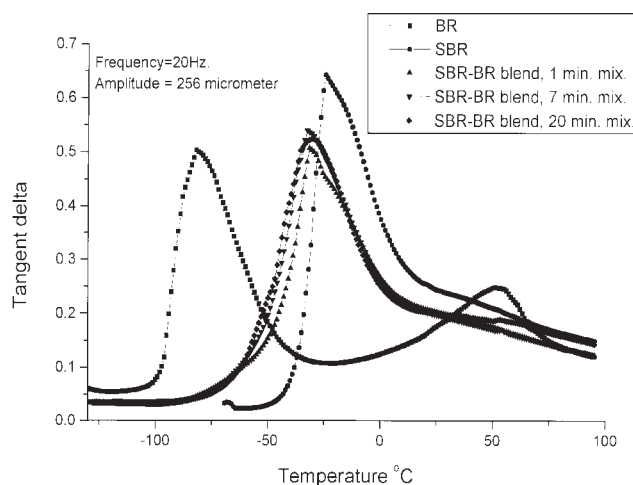
Figure 6 Tan δ versus the temperature at 20 Hz for compounds 1 and 2 and blends 3–5.

Figure 7 Tan δ versus the temperature at 100 Hz for blends 3 and 4.

behavior of rubber, which is temperature, deformation rate, filler loading, and viscosity dependent.[44,50] The increase in tan δ as a function of temperature and test frequency (Table V) was a viscoelastic-dependent behavior, and hence, increases in the mass fraction of the interphase and changes in its composition did not contribute to the tan δ values measured for the SBR/BR blends. Blend 4—with the highest peak tan δ at low temperatures, that is, −21 to −37°C (to obtain high-skid resistance and ice and wet grip); the lowest tan δ at high temperatures, that is, 50–100°C (to reduce rolling resistance and save energy and fuel); and an excellent abrasion resistance—could potentially be a suitable compound for use in tire tread.

CONCLUSIONS

From this study, we concluded that

1. Properties related to fracture, such as elongation at break, stored energy density at break, *T*, and resistance to abrasion, benefited from increases in the mass fraction and changes in the composition of the interphase in the SBR/BR blend.
2. Other properties, such as heat buildup, tan δ, hardness, and modulus, were influenced mainly by the filler loading, mixing time, and rubber viscosity and did not benefit from increases in the mass fraction and changes in the composition of the interphase in the blend.

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