

Particle Size Distribution, Mixing Behavior, and Mechanical Properties of Carbon Black (High-Abrasion Furnace)-Filled Powdered Styrene Butadiene Rubber

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Received 13 February 2004; accepted 17 July 2004

DOI 10.1002/app.21210

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: High-abrasion furnace black (HAF, grade N330)-filled powdered styrene butadiene rubber [P(SBR/HAF)] was prepared and the particle size distribution, mixing behavior in a laboratory mixer, and mechanical properties of P(SBR/HAF) were studied. A carbon black-rubber latex coagulation method was developed for preparing carbon black-filled free-flowing, noncontact staining SBR powders, with particle diameter less than 0.9 mm, under the following conditions: carbon black content > 40 phr, emulsifier/carbon black ratio > 0.02, and coating resin content > 2.5 phr. Over the experimental range, the mixing torque τ_α of P(SBR/HAF) was not as sensitive to carbon black content and mixing temperature as that of HAF-filled bale SBR (SBR/HAF), whereas the temperature build-up ΔT showed little dependency on carbon black content. Compared with SBR/HAF, P(SBR/HAF) showed a 20–30% mixing energy reduction with high carbon black content (>30 phr), which confers to powdered SBR good prospects for internal mix-

ing. Carbon black and the rubber matrix formed a macroscopic homogenization in P(SBR/HAF), and the incorporation step is not obvious in the internal mixing processing results in these special mixing behaviors of P(SBR/HAF). A novel mixing model of carbon black-filled powdered rubber, during the mixing process in an internal mixer, was proposed based on the special mixing behaviors. P(SBR/HAF) vulcanizate showed better mechanical properties than those of SBR/HAF, dependent primarily on the absence of free carbon black and a fine dispersion of filler on the rubber matrix attributed to the proper preparation conditions of noncontact staining carbon black-filled powdered SBR. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2494–2508, 2004

Key words: carbon black-filled powdered rubber; styrene butadiene rubber (SBR); particle size distribution; mixing; mechanical properties

INTRODUCTION

To incorporate a filler into an elastomer normally requires the use of rolling mills or internal mixers. The operation of these machines requires large expenditures of energy. It was found that incorporating a filler into an elastomer latex, to form a pourable powder (i.e., filler-filled powdered rubber), could effectively reduce the energy consumed during mixing.^{1–8}

Generally, powdered rubber should constitute pulverulent, tack-free, and free-flowing particles, with diameters less than 1.0 mm.⁸ In the late 1970s and 1980s, and in the last few years, a number of papers were published concerning the preparation and properties of filler-filled powdered rubber using various

methods,^{1–7} although no paper addressed the issue of the subsequent pollution of filler-filled powders, especially with respect to the contact staining of carbon black-filled powdered rubber. Usually, free carbon black will exist on the surface of carbon black-filled powdered rubber particles prepared using these traditional methods, thus inducing the pollution and the contact staining of free carbon black, which will continue to influence the application of carbon black-filled powdered rubber.

In recent years some publications have reported on the use of powdered rubbers, especially for filler-filled (with such materials as carbon black, silica, clay, etc.), powdered rubber.^{9–17} However, these publications mainly focused on the processing of powdered rubber, without much detail about the preparation process. At the same time, rheological properties, especially mixing rheological properties, were also ignored. As we know, mixing rheological properties, that is, the mixing behavior, of powdered rubber in an internal mixer are very important because they can help to optimize the commercial production of carbon black-filled powdered rubber. Several reports have been published on the processing of powdered rubber, but

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 59773010.

Contract grant sponsor: Guangdong Province Natural Science Foundation; contract grant numbers: 970554 and 031366.

discussions on the mixing behavior of filler-filled powdered rubber in an internal mixer, based on torque rheometer data, are rare.

This article reports on the preparation of carbon black [high-abrasion furnace black (HAF)] filled powdered styrene butadiene rubber [P(SBR/HAF)], with wide ranges of carbon black and aromatic oil content, that is noncontact staining. The particle size distribution, mixing behavior in an internal mixer, and mechanical properties of P(SBR/HAF) were studied and, as a comparison, HAF-filled bale SBR (SBR/HAF) were also prepared and discussed.

EXPERIMENTAL

Materials

A commercially available grade of emulsion SBR latex (SBR 1502 latex; solid content, 20.1 wt %), supplied by Lanzhou Chemical Industry Co. (China), was used for preparing carbon black-filled powdered SBR, whereas bale emulsion SBR (SBR 1502; Lanzhou Chemical Industry Co.) was used as a comparison. High-abrasion furnace black (HAF, grade N330) was supplied by Shanghai LIDE Chemical Co. (China). The coating resin used in the production of powdered SBR was prepared in the laboratory by emulsion polymerization.¹⁸ A 10 wt % CaCl₂ water solution was prepared in the laboratory and used as a coagulation agent. The other agents were used as purchased commercially.

Sample preparation and physical testing

P(SBR/HAF) was prepared as follows^{19,20}:

1. Distilled water and emulsifier were charged to a container, and the mixture was stirred for 10 min to make emulsifier solution.
2. Carbon black was added to the emulsifier solution prepared above, and stirred for 20 min to form a carbon black emulsion.
3. Emulsion SBR latex and coating resin were added to the carbon black emulsion, prepared above, with low-shear agitation to form a "powdering system," with continuous stirring. Heating was carried out in a water bath, and maintained for 30 min after the temperature of the powdering system reached 85°C.
4. If the recipe calls for aromatic oil, this would then be added to the mixture, with continuous stirring for 20 min.
5. A 10% CaCl₂ water solution was added to the mixture under high-speed agitation, with continuous stirring for 20 min.
6. The powdered rubber products were hot-filtered, washed with cold water, and dried on trays in a forced draft oven at 85°C for about 2 h.

TABLE I
Formulation of SBR Compound

Ingredient	Composition (phr) ^a
SBR	100
Zinc oxide	5
Stearic acid	2
Paraffin wax	1
Sulfur	1.75
Accelerator NS (<i>N</i> -oxydiethylene-2-benzothiazole sulfenamide)	1
Antiaiging agent 4010 NA	1
Carbon black (HAF, N330)	Variable
Aromatic oil	Variable

^a phr, parts per hundred parts rubber.

The particle size of the powdered rubber was determined by standard mesh screens.

The powdered rubber product, prepared using the technology described above, is P(SBR/HAF).

Physical testing

Composition of the compounds is given in Table I. The rubbers were preblended and the mixing procedure was carried out, in accordance with ASTM D 3185-99 and ASTM D 3186-97, using a 6-in. two-roll mill maintained at 50 ± 5°C.

The rubber compounds were compression molded into test specimens at 150°C according to the respective cure times (*t*₉₀) determined by the Monsanto moving die rheometer (MDR 2000; Monsanto, St. Louis, MO). Dumbbell-shape samples were cut from a 2-mm-thick molded sheet.

The tensile testing procedure was carried out according to test method A as described by ASTM D 412-98. An AG-1 testing machine (Shimadzu, Kyoto, Japan), operating at 500 mm/min, was used to determine the tensile properties of the vulcanizate. Readings of tensile strength, tensile modulus, M100 (modulus at 100% elongation) and M300 (modulus at 300% elongation), and percentage elongation at break were recorded directly from the digital displays at the end of each test. The test for hardness was carried out using a Shore A-type durometer according to ASTM D 2240-02. All tests were conducted at room temperature (23–25°C).

Mixing rheological studies

Both the powder and bale blends were prepared by mixing in a two-shaft internal roller mixer (model N50H; capacity, 78 mL) fitted to a Brabender Plastimeter (PLE 651, Brabender OHG, Duisburg, Germany).²¹ The blend compositions are listed in Table II. Because the mixing head is volume-sensitive, the

TABLE II
Mixing Recipes of P(SBR/HAF) and SBR/HAF^a

Rubber	Carbon black (phr)	Aromatic oil (phr)	Rubber	Carbon black (phr)	Aromatic oil (phr)
P(SBR/HAF)	0	0	SBR/HAF	0	0
P(SBR/HAF)	20	0	SBR/HAF	20	0
P(SBR/HAF)	30	0	SBR/HAF	30	0
P(SBR/HAF)	50	0	SBR/HAF	50	0
P(SBR/HAF)	70	0	SBR/HAF	70	0
P(SBR/HAF)	50	10	SBR/HAF	50	10
P(SBR/HAF)	50	20	SBR/HAF	50	20
P(SBR/HAF)	50	30	SBR/HAF	50	30
P(SBR/HAF)	50	50	SBR/HAF	50	50

^a Base composition: rubber, 100; ZnO, 5; stearic acid, 2; paraffin wax, 1; antiageing agent 4010 NA, 1; carbon black, variable; aromatic oil, variable

loaded amount (~ 65 g) was about 75% of the capacity with respect to the volume of the cavity and density of the material. The mixing chamber, heated by circulating oil, was fitted with a thermocouple at the bottom of the chamber to measure the material temperature. The ram pressure was supplied by a dead weight of 5.0 kg, which applies a ram pressure of about 285 kPa to the mixture by means of a lever arm.

The mixing was done as follows: when the mixer chamber reached the desired temperature, the rubber and other fillers were charged to the chamber and mixed at a given rotor speed for 8 min. For powdered rubber, powdered rubber and the other compounding agents were premixed together before being added to the internal mixer, and all the mixtures were added to the chamber within 1 min before the ram was down; for bale rubber, carbon black and other compounding agents were charged to the chamber first, followed by the bale rubber, and all processes were done within 1 min before the ram was down. To study the influence of carbon black content and aromatic oil content, the mixing conditions of 70°C and 50 rpm were used. The effect of temperature, in the range 50–100°C, and the effect of rotor speed, in the range 40–80 rpm, were studied with 50 phr carbon black content for P(SBR/HAF) and SBR/HAF. Identical instrumental settings were maintained throughout all the experiments and torque versus time data and power versus time data were recorded for each blend.

Scanning electron micrograph studies

Scanning electron micrographs (SEM) were taken in a Philips XL30 FEG scanning electron micrograph (Philips, Eindhoven, The Netherlands). The samples were covered with a layer of AuPd by sputtering treatment. The surface images were obtained with the SEM working at an acceleration voltage of 15 keV.

RESULTS AND DISCUSSION

Contact staining of P(SBR/HAF) particles

Contact staining is the pollution that occurs when carbon black-filled powdered rubber comes into contact with the environment. For example, when the P(SBR/HAF) particles come into contact with white paper, where friction is applied several times, if the paper remains white, we consider this to be an example of noncontact staining; if the paper became darkly stained, then we would consider that this kind of particles produces contact staining.

The contact staining level of P(SBR/HAF) is determined by the preparation technology of P(SBR/HAF), as shown in Table III. Sufficient carbon black surfactant, coating resin, heat treatment, and stirring are necessary to remove the contact staining of P(SBR/HAF) particles; the addition of oil can also reduce the pollution tendency. In the experimental range, the P(SBR/HAF) particles would be noncontact staining with the following preparation conditions: emulsifier/carbon black > 0.02, coating resin > 4 phr, and treatment time of 30 min at 85°C.

It was shown that carbon black would agglomerate into particles of about 1 μm in the water without surfactant, which caused poor dispersion in water. Some kinds of nonionic surfactants, such as Triton X-100, can improve the dispersion of carbon black in water. After carbon black was dispersed into very small particles in the water, heating accelerated the bonding among carbon black particles, rubber latex, and coating resin.

Particle size distribution of P(SBR/HAF)

The particle size distribution of materials, prepared by application of the coagulation method, depends on a number of parameters: emulsifier contents, coating resin contents, carbon black contents, and oil contents.

TABLE III
Influence of Preparation Condition on the Contact Staining Level of P(SBR/HAF) Particles

Sample	Emulsifier/carbon black	Coating resin (phr)	Aromatic oil (phr)	Heat treatment	Contact staining index ^a
A1	0	0	0	None	3
A2	0	4	0	None	3
A3	0	10	15	None	3
A4	0.01	2	15	None	3
A5	0.01	2	0	85°C, 30-min treatment	2
A6	0.02	0	0	85°C, 30-min treatment	2
A7	0.01	2	15	85°C, 30-min treatment	1
A8	0.02	2	0	85°C, 30-min treatment	1
A9	0.02	6	0	85°C, 30-min treatment	0
A10	0.04	4	15	85°C, 30-min treatment	0
A11	0.06	8	0	85°C, 30-min treatment	0

^a The contact staining index is defined as follows: very dark, 3; dark, 2; gray, 1; noncontact staining, 0.

The following discussion will elucidate these influences.

Influence of emulsifier/carbon black ratio

As discussed above, carbon black emulsifier can improve the dispersion of carbon black in water. The existence of emulsifier not only can reduce the contact staining of products, but can also reduce the particle size of P(SBR/HAF), as shown in Table IV. With increasing emulsifier/carbon black ratio, the ratios of particle size smaller than 0.9 mm (passing through the 20-mesh screen) and 0.45 mm (passing through the 40-mesh screen) substantially increase. More than 99.5% of the particles can pass through the 0.9-mm screen when the emulsifier/carbon black ratio is ≥ 0.04 .

Influence of coating resin contents

Coating resin is one of the key agents in the preparation of powdered rubber, which can coat the particles containing rubber and filler with a thin coating layer.¹⁹ The existence of the coating layer can reduce the adhesion and aggregation between rubber particles during coagulation, drying, storage, and transportation.

TABLE IV
Influence of Emulsifier/Carbon Black Ratio on the Particle Size Distribution of P(SBR/HAF)^a

Emulsifier/carbon black	Particle size distribution (wt %)			
	>2.0 mm	0.9 to 2.0 mm	0.45 to 0.9 mm	<0.45 mm
0	24.9	55.2	10.6	9.3
0.02	5.0	22.0	58.2	16.8
0.04	0	0.5	37.0	62.5
0.06	0	0.5	6.0	93.5
0.08	0	0.4	5.0	94.6

^a Coating resin, 5 phr; carbon black, 50 phr.

As shown in Table V, when the coating resin content is 5.0 phr, 99.5% of the P(SBR/HAF) particles with 50 phr HAF can pass through the 0.9-mm screen, and when the coating resin content reaches 7.5 phr, all the particles can pass through the 0.9-mm screen, and 95.9% of the P(SBR/HAF) particles can pass through the 0.45-mm screen, which showed that the coating resin can coat the P(SBR/HAF) particles and effectively reduce the particle size.

Influence of carbon black contents

In the preparation of carbon black-filled powdered rubber, carbon black was not only the reinforcing filler, but also the separating agent, which influences the particle size distribution of the powders. As shown in Table VI, when the carbon black content is less than 50 phr, the particle size distribution of P(SBR/HAF) was sensitive to the carbon black content, whereas when the carbon black content is more than 60 phr, 99.5% of the particle can pass through the 0.45-mm screen. The greater the carbon black content, the smaller the particle size. In other words, to achieve the same particle size distribution, the coating resin con-

TABLE V
Influence of Coating Resin Contents on the Particle Size Distribution of P(SBR/HAF)^a

Coating resin content (phr)	Particle size distribution (wt %)			
	>2.0 mm	0.9 to 2.0 mm	0.45 to 0.9 mm	<0.45 mm
0.0	26.6	53.2	17.5	2.7
2.5	5.2	23.3	44.8	16.7
5.0	0	0.5	37.0	62.5
7.5	0	0	4.1	95.9
10.0	0	0	2.6	97.4
12.5	0	0	2.5	97.5
15.0	0	0	2.0	98.0

^a Emulsifier/carbon black = 0.04; carbon black, 50 phr.

TABLE VI
Influence of Carbon Black Contents on the Particle Size Distribution of P(SBR/HAF)^a

Carbon black content (phr)	Particle size distribution (wt %)			
	>2.0 mm	0.9 to 2.0 mm	0.45 to 0.9 mm	<0.45 mm
0	84.7	13.5	1.2	0.6
20	10.6	8.6	55.6	25.2
40	0.5	0.8	45.3	53.4
50	0	0.5	37.0	62.5
60	0	0	0.5	99.5
80	0	0	0.4	99.6
100	0	0	0.4	99.6
120	0	0	0.3	99.7
150	0	0	0	100
200	0	0	0	100

^a Emulsifier/carbon black = 0.04; coating resin, 5 phr.

tent must be reduced as the carbon black content increases.

Influence of aromatic oil contents

Generally, aromatic oil is added to SBR as a softening agent to improve the processibility of SBR and the dispersion of carbon black in the rubber matrix. In the preparation of P(SBR/HAF), however, there are other functions for aromatic oil: wetting the surface of carbon black, improving the bonding between carbon black and rubber matrix, and at the same time, reducing the contact staining of product.

As shown in Table VII, the addition of aromatic oil can slowly reduce the particle size. The content of aromatic oil should not be too large, however, because it may cause the exudation of oil; the optimal aromatic oil content is <30 phr.

Mixing behavior of P(SBR/HAF) and SBR/HAF in a laboratory internal mixer

Because a quantitative evaluation is necessary for rubber processing, a detailed study on the mixing behav-

TABLE VII
Influence of Aromatic Oil Contents on the Particle Size Distribution of P(SBR/HAF)^a

Aromatic oil content (phr)	Particle size distribution (wt %)			
	>2.0 mm	0.9 to 2.0 mm	0.45 to 0.9 mm	<0.45 mm
0.0	0	0.5	37.0	62.5
5.0	1.6	2.6	24.7	71.2
10.0	1.5	1.0	16.0	81.5
15.0	0	0.5	12.0	87.5
20.0	0	0	11.0	89.0

^a Emulsifier/carbon black = 0.04; coating resin, 5 phr; carbon black, 50 phr.

ior of powdered SBR was developed. The Brabender Plasticorder, which is actually a torque-measuring rheometer, has been used effectively to study various mixing rheological properties of natural rubber and synthetic rubbers.^{15,16,20,21}

We studied the effect of carbon black content (0–70 phr), aromatic oil content (0–50 phr), mixing time, mixing temperature, and rotor speed on the mixing behavior of P(SBR/HAF) and SBR/HAF compounds, using an internal mixer attached to a Brabender Plasticorder.

According to the report from Goodrich and Porter,²² the torque observed in a Brabender mixing head is

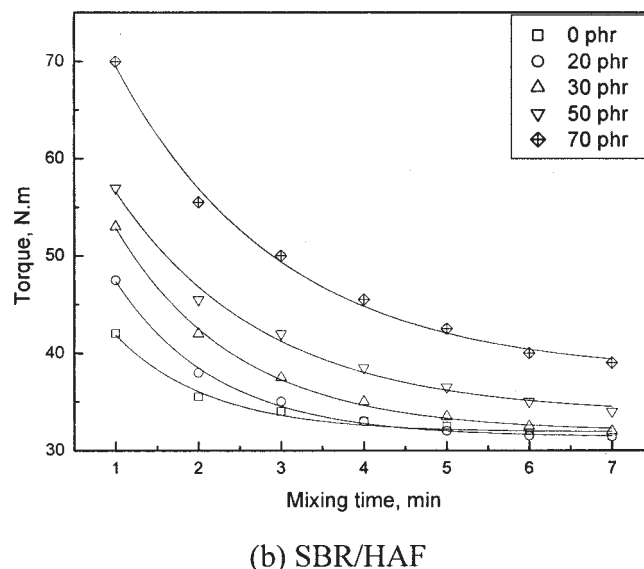
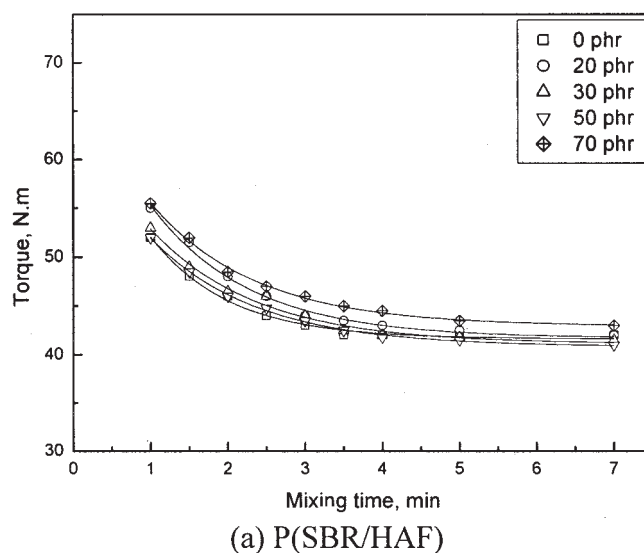


Figure 1 Mixing torque–time curves with different carbon black contents at 50 rpm and 70°C: (a) P(SBR/HAF); (b) SBR/HAF.

TABLE VIII
Relational Expression of τ_α versus t with Different Carbon Black Contents

Carbon black content (phr)	Relational expression of τ_α versus t	
	P(SBR/HAF)	SBR/HAF
0	$\tau_\alpha = 41.6 + 27.9e^{-0.98t}$	$\tau_\alpha = 31.9 + 24.0e^{-0.88t}$
20	$\tau_\alpha = 41.7 + 29.7e^{-0.78t}$	$\tau_\alpha = 31.4 + 36.1e^{-0.81t}$
30	$\tau_\alpha = 41.1 + 24.5e^{-0.73t}$	$\tau_\alpha = 31.9 + 41.4e^{-0.68t}$
50	$\tau_\alpha = 40.8 + 23.3e^{-0.74t}$	$\tau_\alpha = 33.7 + 38.9e^{-0.56t}$
70	$\tau_\alpha = 42.9 + 27.9e^{-0.74t}$	$\tau_\alpha = 37.9 + 52.5e^{-0.51t}$

governed by the standard rheological properties with the following relations:

$$\sigma_\alpha = K_1\tau_\alpha \quad (1)$$

$$\gamma_\alpha = K_2S \quad (2)$$

where

$$S = (2\pi/60)R \quad (3)$$

and where σ_α is the apparent shear stress; τ_α is the apparent torque; γ_α is the apparent shear rate; S is the angular rotor speed; R is the rotor speed used; and K_1 and K_2 are instrumental constants.

The apparent shear viscosity is expressed as

$$\eta_\alpha = \sigma_\alpha/\gamma_\alpha = K_1\tau_\alpha/K_2S = Q(\tau_\alpha/S) \quad (4)$$

where $Q = K_1/K_2$.

Equation (4) shows that τ_α/S is directly proportional to the apparent shear viscosity η_α , and if the rotor speed is constant, η_α can be directly expressed by apparent torque τ_α .

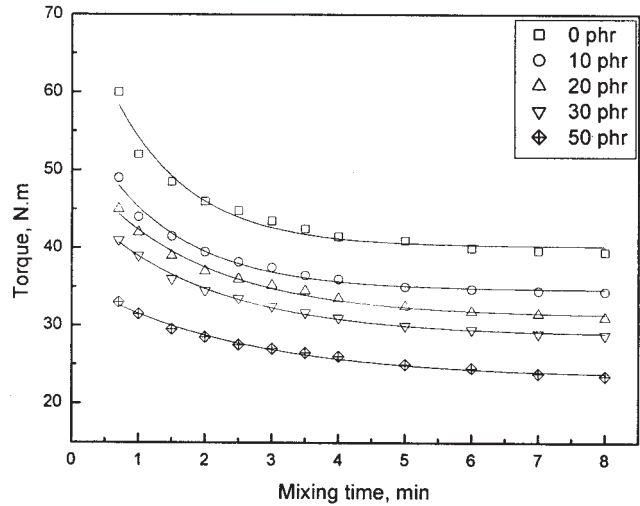
In this article, these relationships were preferred for expressing the mixing rheological properties (i.e., the mixing behavior in a laboratory internal mixer) of P(SBR/HAF) and SBR/HAF.

Influence of carbon black content

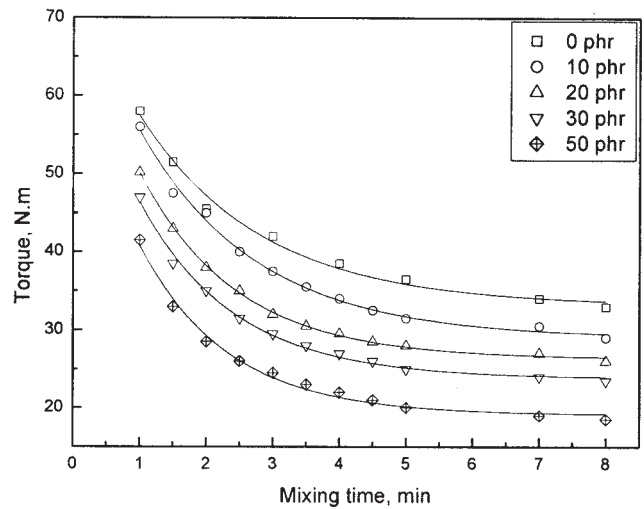
Figure 1 shows the effect of carbon black content on the apparent torque τ_α of P(SBR/HAF) and SBR/HAF. The equations listed in Table VIII are the relational expressions fitting to the τ_α versus t curves in Figure 1, using the following exponential expression:

$$\tau_\alpha = \tau_{\alpha 0} + ae^{bt} \quad (5)$$

where $\tau_{\alpha 0}$ expresses the equivalence torque, a is the coefficient, and b is the exponent index. The greater the absolute values of the coefficient and exponent index, the greater the dependency of τ_α on mixing time t .



(a) P(SBR/HAF)

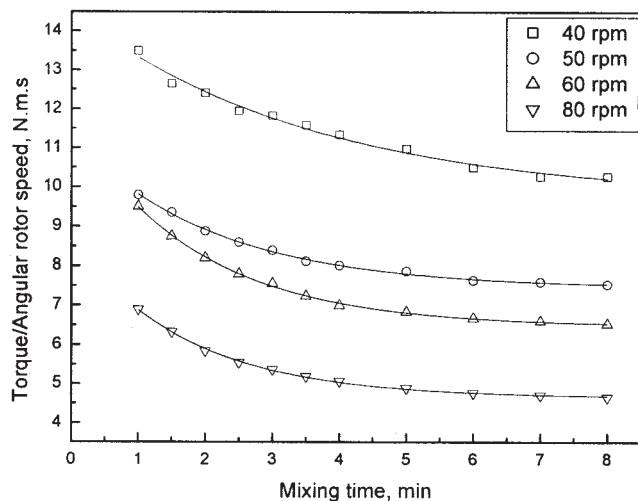


(b) SBR/HAF

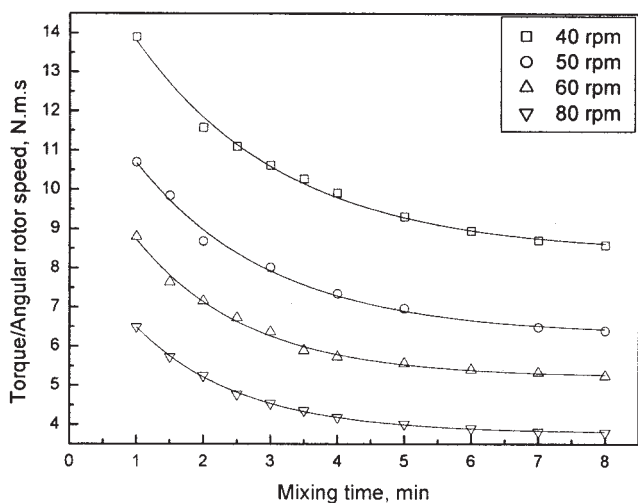
Figure 2 Mixing torque–time curves with different aromatic oil contents at 50 rpm and 70°C: (a) P(SBR/HAF); (b) SBR/HAF.

TABLE IX
Relational Expression of τ_α versus t with Different Aromatic Oil Contents

Aromatic oil content (phr)	Relational expression of τ_α versus t	
	P(SBR/HAF)	SBR/HAF
0	$\tau_\alpha = 40.8 + 23.3e^{-0.74t}$	$\tau_\alpha = 33.7 + 38.9e^{-0.56t}$
10	$\tau_\alpha = 34.6 + 22.9e^{-0.77t}$	$\tau_\alpha = 29.0 + 46.8e^{-0.57t}$
20	$\tau_\alpha = 31.2 + 19.6e^{-0.57t}$	$\tau_\alpha = 26.3 + 47.5e^{-0.69t}$
30	$\tau_\alpha = 28.7 + 17.4e^{-0.53t}$	$\tau_\alpha = 23.8 + 45.7e^{-0.71t}$
50	$\tau_\alpha = 23.3 + 12.4e^{-0.42t}$	$\tau_\alpha = 19.1 + 46.1e^{-0.76t}$



(a) P(SBR/HAF)



(b) SBR/HAF

Figure 3 Mixing torque–time curves at different rotor speeds at 70°C: (a) P(SBR/HAF); (b) SBR/HAF.

In Figure 1(b), the torque of SBR/HAF clearly increases with increasing carbon black content, whereas in Figure 1(a) the torque of P(SBR/HAF) changes only slightly with increasing carbon black content, and the τ_α versus t curves are nearly overlapping. Table VIII shows that with increasing carbon black content, the dependency of τ_α on mixing time of SBR/HAF has a tendency to increase, whereas for P(SBR/HAF) the dependency is almost constant. These results indicate that the mixing torque of P(SBR/HAF) has a low dependency on carbon black content and mixing time.

TABLE X

Relational Expression of τ_α/S versus t at Different Rotor Speeds

Rotor speed (rpm)	Relational expression of τ_α/S versus t	
	P(SBR/HAF)	SBR/HAF
40	$\tau_\alpha/S = 9.72 + 4.79e^{-0.28t}$	$\tau_\alpha/S = 8.40 + 8.47e^{-0.45t}$
50	$\tau_\alpha/S = 7.46 + 3.80e^{-0.48t}$	$\tau_\alpha/S = 6.30 + 7.18e^{-0.50t}$
60	$\tau_\alpha/S = 6.47 + 5.20e^{-0.54t}$	$\tau_\alpha/S = 5.22 + 6.43e^{-0.61t}$
80	$\tau_\alpha/S = 4.64 + 4.00e^{-0.58t}$	$\tau_\alpha/S = 3.78 + 5.12e^{-0.64t}$

Influence of aromatic oil content

Aromatic oil is added to SBR as a softening agent to improve the processibility of SBR and the dispersion of carbon black in the rubber matrix. The test samples were filled with 50 phr carbon black, whereas the aromatic oil content was varied. Figure 2(a) and (b) show the mixing torque of P(SBR/HAF) and SBR/HAF with different aromatic oil contents. The relational expressions listed in Table IX were fitted to the curves in Figure 2. Here, the tendencies of the τ_α versus t curves for the two kinds of blends are roughly identical, whereas the dependency of τ_α on mixing time of P(SBR/HAF) is just about half that of SBR/HAF.

Influence of rotor speeds

The τ_α/S versus t curves, obtained during mixing of P(SBR/HAF) and SBR/HAF, are shown in Figure 3. Each composite was mixed at 70°C for 8 min at a selected rotor speed, in the range of 40–80 rpm. The curves plotted in Figure 3, and the relational expressions listed in Table X, showed that the tendencies of the τ_α/S versus t curves are roughly similar, whereas

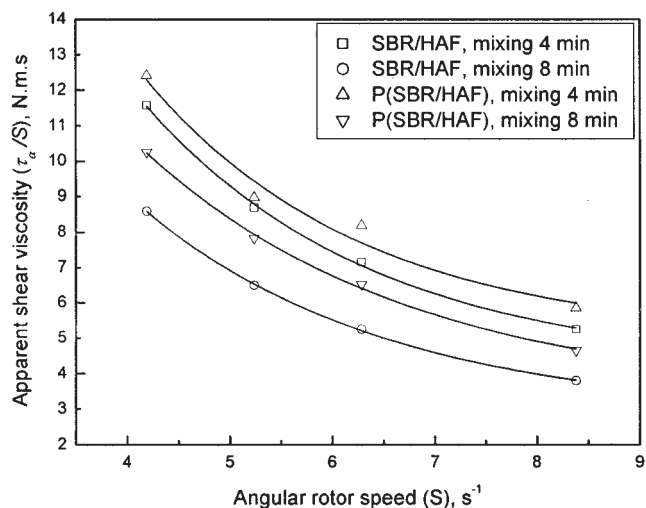


Figure 4 Apparent shear viscosity versus angular rotor speed for P(SBR/HAF) and SBR/HAF at 70°C.

TABLE XI
Relational Expression of τ_α/S versus S in Different Time of Mixing

Mixing time (min)	Relational expression of τ_α/S versus S	
	P(SBR/HAF)	SBR/HAF
In the 4th min	$\tau_\alpha/S = 4.98 + 52.7e^{-0.472S}$	$\tau_\alpha/S = 4.12 + 47.6e^{-0.444S}$
In the 8th min	$\tau_\alpha/S = 4.12 + 34.2e^{-0.380S}$	$\tau_\alpha/S = 2.81 + 33.3e^{-0.418S}$

the sensitivity of τ_α on mixing time of P(SBR/HAF) is about 70–90% that of SBR/HAF.

The plot of apparent shear viscosity (τ_α/S) versus angular rotor speed is shown in Figure 4. The shear viscosity values are plotted at 4 and 8 min, and for

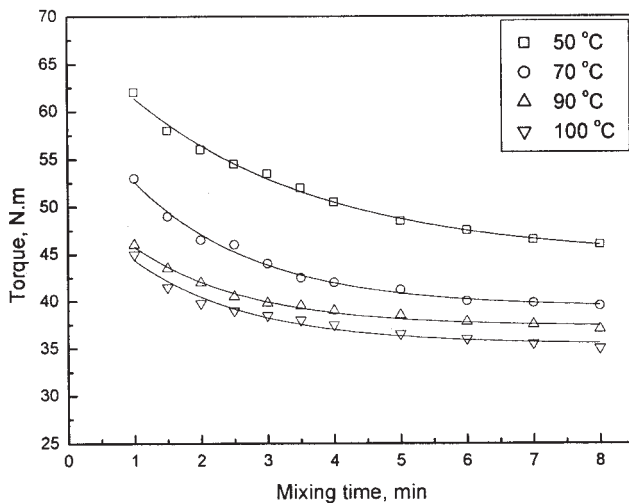
both P(SBR/HAF) and SBR/HAF the shear viscosity decreased with increasing shear rate. Again, the apparent shear viscosity values at these two times of mixing for P(SBR/HAF) are higher than those for SBR/HAF. The coefficient of the exponential term of the expressions, which indicates the dependency of apparent shear viscosity on angular rotor speed, is listed in Table XI and shows that this dependency for P(SBR/HAF) is 5–10% higher than that for SBR/HAF. For both blends, the dependency increased slightly in the later stage of mixing.

Influence of mixing temperatures

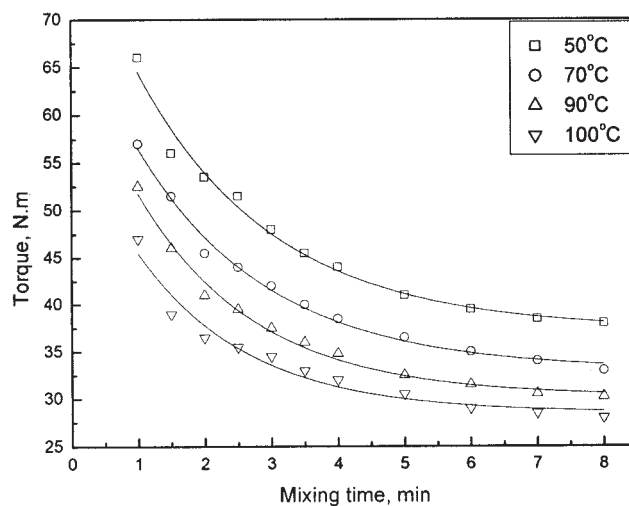
The torque–time ($\tau_\alpha-t$) curves of P(SBR/HAF) and SBR/HAF, obtained during mixing at 50 rpm at four different mixing temperatures, are plotted in Figure 5, and the corresponding (τ_α versus t) relationships are listed in Table XII. As expected, the torque decreases with increases in both temperature and time of mixing. The torque values are higher in the case of P(SBR/HAF) at any time of mixing with the same mixing temperature. The torque decreases more uniformly with increasing mixing temperature in the case of P(SBR/HAF). The coefficient of the exponential term of the expressions, listed in Table XII, indicates that P(SBR/HAF) has a lower sensitivity to mixing temperature, which is only about 30–60% that of SBR/HAF.

Unit mixing energy of P(SBR/HAF) and SBR/HAF

Unit mixing energy (W_{it}) indicates the total energy consumed to disperse the filler into unit rubber volume to a given dispersion level. It is an important



(a) P(SBR/HAF)



(b) SBR/HAF

Figure 5 Mixing torque–time curves at different blend temperatures and at 50 rpm: (a) P(SBR/HAF); (b) SBR/HAF.

TABLE XII
Relational Expression of τ_α versus t Under Different Mixing Temperatures

Mixing temperature (°C)	Relational expression of τ_α versus t	
	P(SBR/HAF)	SBR/HAF
50	$\tau_\alpha = 44.5 + 23.9e^{-0.34t}$	$\tau_\alpha = 37.2 + 44.2e^{-0.48t}$
70	$\tau_\alpha = 40.8 + 23.3e^{-0.54t}$	$\tau_\alpha = 33.7 + 38.9e^{-0.56t}$
90	$\tau_\alpha = 37.3 + 15.3e^{-0.58t}$	$\tau_\alpha = 30.2 + 38.1e^{-0.57t}$
100	$\tau_\alpha = 35.4 + 15.9e^{-0.57t}$	$\tau_\alpha = 28.4 + 31.0e^{-0.60t}$

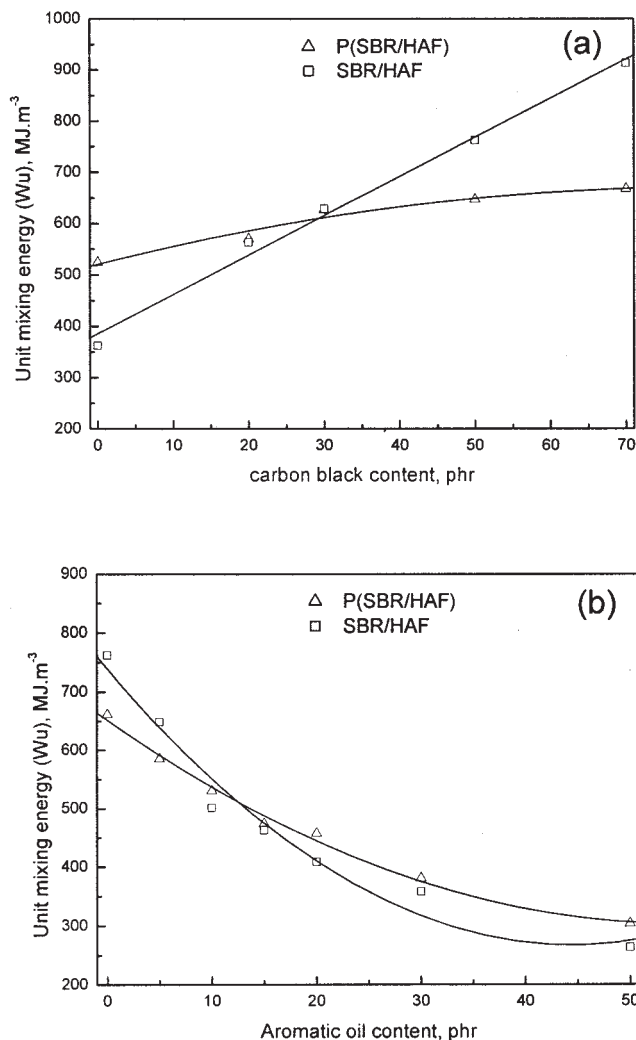


Figure 6 Relationship of unit mixing energy Wu of P(SBR/HAF) and SBR/HAF to (a) carbon black and (b) aromatic oil content, at 50 rpm and 70°C.

parameter to evaluate the processibility of filler-rubber systems. For the Brabender internal mixer, Wu can be determined by the following equation²³⁻²⁵:

$$Wu = Wt/V_b \quad (6)$$

where Wt is the total mixing energy (J) and V_b is the batch volume (m³). At any time of mixing, the total mixing energy (Wt) was given by the PC100 computer attached to the Brabender Plasticorder.

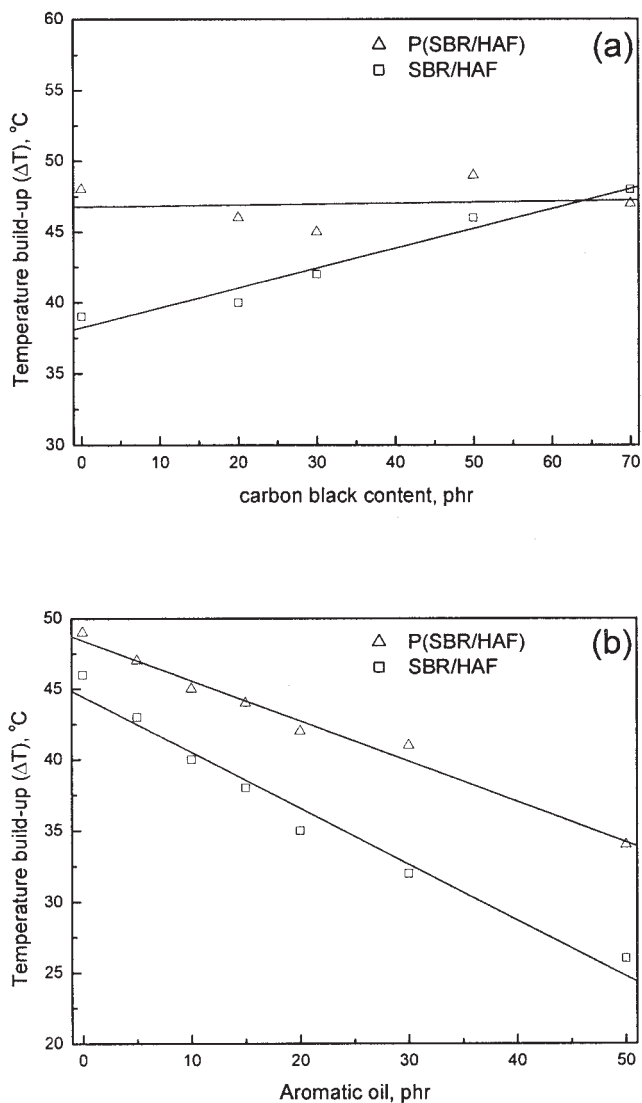


Figure 7 Relationship of temperature build-up of mixing ΔT of P(SBR/HAF) and SBR/HAF to (a) carbon black content and (b) aromatic oil content, at 50 rpm and 70°C.

Here, Wt is calculated from the area under the torque-time curve, at experimental conditions, using the following equation:

$$Wt = 2\pi R \int_{t_2}^{t_1} \tau_a dt \quad (7)$$

TABLE XIII
Relational Expression of Wu to Different Carbon Black and Aromatic Oil Contents

	Relational expression of Wu to carbon black content (x)	Relational expression of Wu to aromatic oil content (x)
P(SBR/HAF)	$Wu = -0.0226x^2 + 3.69x + 520.7$	$Wu = 0.116x^2 - 12.7x + 651.7$
SBR/HAF	$Wu = 7.66x + 385.4$	$Wu = 0.239x^2 - 21.2x + 738.9$

TABLE XIV
Relational Expression of ΔT to Different Carbon Black and Aromatic Oil Contents

	Relational expression of ΔT to carbon black content (x)	Relational expression of ΔT to aromatic oil content (x)
P(SBR/HAF)	Independent	$\Delta T = -0.284x + 48.4$
SBR/HAF	$\Delta T = 0.140x + 38.2$	$\Delta T = -0.394x + 44.4$

where R is the rotor speed used (rpm), t_1 is the initial time, t_2 is the final time, and τ_α is the mixing torque (dimensionless).

Dolezal and Johnson²⁴ studied the relationship between mixing power–time curve and the properties of the batches. It was found that when the batches were dumped at the time when the “inflection point” appeared in the mixing power–time curve, the mechanical properties of the batches were in equilibrium. Thus, the time of the “inflection point” was determined as the dump time and the energy consumed to this point was taken as the total mixing energy Wt .

It was found that powdered rubber had a higher power peak than that of bale rubber.^{13,15} The mixing can be completed in one stage for the powdered rubber, whereas bale rubbers required 25–60% more energy in a second stage to reach the same degree of carbon black dispersion. Consequently, the mixing time and mixing energy of powdered rubber are largely reduced.^{8,24–26} Evans⁸ showed that, with the same time of internal mixing, powdered rubber, including nitrile rubber, polychloroprene rubber, natural rubber, and SBR, achieved better carbon black dispersion than that of bale rubber. However, studies on the mixing energy of carbon black and oil-filled powdered SBR are scarce. Figure 6 shows the unit mixing energy Wu of P(SBR/HAF) and SBR/HAF with different carbon black and aromatic oil contents. As expected, P(SBR/HAF) yielded 20 and 27% reduction in Wu with 50 and 70 phr carbon black content, respectively. However, with a low carbon black content the mixing energy needed for P(SBR/HAF) and SBR/HAF is almost identical, and P(SBR/HAF) yielded slightly higher Wu without any carbon black content. Figure 6 indicates that Wu decreases almost linearly with increasing oil content when the oil content is less than 30 phr; at contents > 30 phr, the rate of decrease slows down. The relational expressions of Wu to carbon black content and Wu to oil content are listed in Table XIII. These expressions show that the sensitivity of Wu of P(SBR/HAF) to oil content and carbon black content is about half that of SBR/HAF.

Temperature build-up during mixing (ΔT) of P(SBR/HAF) and SBR/HAF

Temperature build-up during mixing (ΔT), that is, the difference between discharge temperature and feed

temperature, is the result of internal friction between carbon black particles and molecular chains of the rubber and internal friction between rubber molecular chains. Previous studies indicated that the temperature build-up (ΔT) increases with increasing carbon black content, and decreases with the addition of a softening oil (such as aromatic oil).

Figure 7 shows the curves of ΔT versus carbon black content and ΔT versus aromatic oil content. As expected, ΔT of SBR/HAF increases with increasing carbon black content, whereas the fluctuation range of ΔT for P(SBR/HAF) is less than 5°C, which indicates that ΔT of P(SBR/HAF) is independent of carbon black content. For aromatic oil, the curves plotted in Figure 7(b), and the expressions listed in Table XIV, show that the sensitivity of ΔT of P(SBR/HAF) to oil content is about 70% that of SBR/HAF. It was found that, in general, P(SBR/HAF) has a higher ΔT than that of SBR/HAF, which is mainly attributable to the higher Mooney viscosity of P(SBR/HAF) compound at the early stage of internal mixing.

According to Palmgren’s internal mixing model, in mixing a batch of bale rubber, four elementary steps are involved: subdivision, incorporation, dispersion, and simple mixing.^{25–27} In fact, subdivision is necessary not only for incorporation but also for dispersion. For P(SBR/HAF), carbon black and the rubber matrix have formed a macroscopic homogenization before the powders are put into the chamber, as shown in Figure 9(b).¹⁹ The incorporation step is not obvious for P(SBR/HAF), whereas the

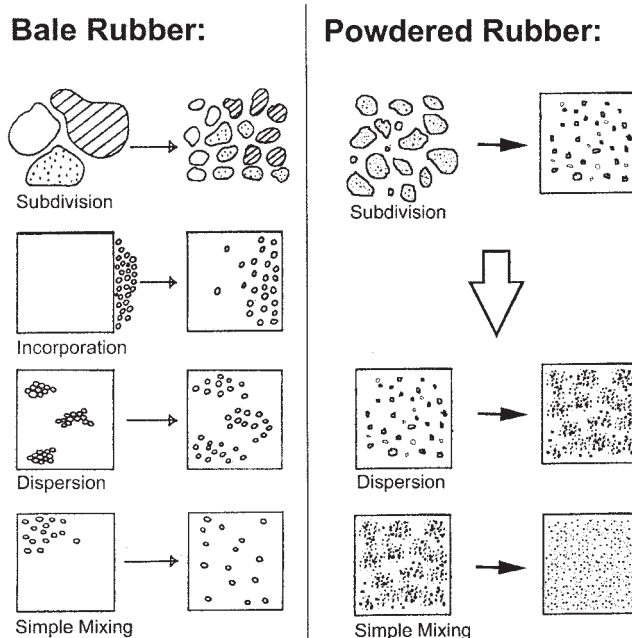


Figure 8 Primary difference between P(SBR/HAF) and SBR/HAF in internal mixing.

TABLE XV
Influence of Emulsifier/Carbon Black Ratio on the Mechanical Properties and
Vulcanization Characteristics of P(SBR/HAF)^a

Property	Emulsifier/carbon black ratio				
	0	0.02	0.04	0.06	0.08
Scorch time (t_{10}), min	10.5	9.5	8.5	7.0	6.5
Optimized curing time (t_{90}), min	19	14	12.5	11.5	11.0
Tensile strength, MPa	17.9	20.2	24.9	23.7	21.7
100% modulus, MPa	2.26	2.26	1.98	1.96	1.87
300% modulus, MPa	6.91	7.19	6.1	6.55	6.4
Elongation at break, %	609	644	740	666	620
Permanent set, %	14	16	16	16	16
Tear strength, kN/m	44.8	46.7	40.9	46.0	45.7
Hardness, Shore A	72	72	70	70	70

^a Coating resin, 5 phr; carbon black, 50 phr.

energy consumed in the subdivision and incorporation steps constitutes about 30–50% of the total energy of mixing. The energy reduction in these two stages results in low energy consumption for the internal mixing of P(SBR/HAF). The primary difference, with respect to internal mixing, between bale rubber and carbon-filled powdered rubber is shown in Figure 8. The difference of Wu values among P(SBR/HAF) compounds, with various contents of carbon black, mainly lies in the last two mixing steps mentioned above. This difference successfully explains the phenomena that, within the range of carbon black and aromatic oil content, the apparent shear viscosity, unit mixing energy, and temperature build-up during mixing of P(SBR/HAF) showed lower sensitivity to carbon black and aromatic oil content than did those of SBR/HAF.

Mechanical properties of P(SBR/HAF)

Influence of emulsifier/carbon black ratio

The mechanical properties and vulcanization characteristics of P(SBR/HAF), with different emulsifier/carbon black ratios, are presented in Table XV. Scorch

time (t_{10}) and optimized curing time (t_{90}) decrease with increasing emulsifier content, whereas tensile strength achieves a maximum value with the emulsifier/carbon black ratio of 0.04 to 0.06. Proper emulsifier content can improve the dispersion of carbon black in the rubber matrix, thus contributing to the improvement of tensile properties of P(SBR/HAF), although excessive emulsifier will also cause an increase in residual emulsifier content in rubber vulcanizate, thus harming the physical properties of P(SBR/HAF). Thus the proper emulsifier/carbon black ratio is between 0.04 and 0.06.

Influence of coating resin content

The vulcanization characteristics and mechanical properties of P(SBR/HAF), with different coating resin contents, are presented in Table XVI. Scorch time (t_{10}) and optimized curing time (t_{90}) decrease with increasing coating resin content, and tensile strength achieves a maximum value with the coating resin content of 2.5 to 7.5 phr; 100% modulus, 300% modulus, tear strength, and hardness increase with increasing coating resin content. The higher the coating resin

TABLE XVI
Influence of Coating Resin Content on the Mechanical Properties and Vulcanization Characteristics of P(SBR/HAF)^a

Property	Coating resin content (phr)						
	0	2.5	5.0	7.5	10.0	12.5	15.0
Scorch time (t_{10}), min	8.0	8.5	8.5	9.0	9.0	10.0	10.5
Optimized curing time (t_{90}), min	12.5	12.5	12.5	14	14	16.5	16.5
Tensile strength, MPa	22.3	23.8	24.9	23.0	22.8	20.1	19.4
100% modulus, MPa	1.64	1.73	1.98	2.03	1.98	2.24	2.35
300% modulus, MPa	5.72	6.11	6.1	6.13	6.38	6.30	6.38
Elongation at break, %	720	704	740	740	700	717	655
Permanent set, %	12	14	16	20	22	26	32
Tear strength, kN/m	34.7	40.2	40.9	41.6	44.8	45.1	46.9
Hardness, Shore A	66	68	70	70	71	75	75

^a Emulsifier/carbon black ratio = 0.04; carbon black, 50 phr.

TABLE XVII
Influence of Carbon Black Content on the Mechanical Properties and Vulcanization Characteristics of P(SBR/HAF)^a

Property	Carbon black (HAF) content (phr)							
	0	20	40	50	60	80	100	120
Scorch time (t_{10}), min	24.5	10.5	9.0	8.5	8.5	6.0	4.5	3.5
Optimized curing time (t_{90}), min	32	14	13	12.5	12	10.5	10	8
Tensile strength, MPa	3.56	22.9	23.7	24.9	22.6	19.2	14.8	12.2
100% modulus, MPa	1.19	1.35	1.78	1.98	2.31	3.20	4.91	6.43
300% modulus, MPa	1.76	2.92	4.90	6.1	8.34	12.1	—	—
Elongation at break, %	631	810	706	740	595	505	294	242
Permanent set, %	10	12	14	16	14	14	14	12
Tear strength, kN/m	13.7	29	41.0	40.9	44.2	40.5	31.6	22.5
Hardness, Shore A	50	60	67	70	73	77	84	88

^a Emulsifier/carbon black ratio = 0.04; coating resin, 5 phr.

content, the thicker the coating layer on the surface of P(SBR/HAF) particles, and if the layer is too thick to be broken, it will form internal defects in the rubber vulcanizate, thus depreciating the mechanical properties of P(SBR/HAF). Thus the proper coating resin content is 2.5 to 5 phr.

Influence of carbon black content and aromatic oil content

Tables XVII and XVIII detail the vulcanization characteristics and mechanical properties of P(SBR/HAF) with different carbon black content and aromatic oil content, respectively. As a comparison, the mechanical properties of HAF-filled bale SBR (SBR/HAF) are also shown in Table XIX.

In the experimental range, aromatic oil showed little influence on the mechanical properties of P(SBR/HAF), especially when the aromatic oil content was <10 phr.

For both P(SBR/HAF) and SBR/HAF, with increasing carbon black content, the 100% modulus, 300% modulus, and hardness all increase, whereas elongation and permanent sets decrease when the carbon black content is >50 phr, whereas the tensile

strength and tear strength achieve their maximum values in the range of 40–50 and 40–60 phr for P(SBR/HAF) and SBR/HAF, respectively. As shown in Tables XVII and XIX, when the carbon black content ranges from 0 to 50 phr, P(SBR/HAF) show greater tensile strength than that of SBR/HAF, which indicates that the coating resin can reinforce the SBR vulcanizate when the carbon black content is <50 phr.

SEM analysis of the morphology of P(SBR/HAF) particles

Figure 9(a) shows the SEM morphology of a P(SBR/HAF) particle without contact staining, which shows that a P(SBR/HAF) particle, having a diameter of about 0.9 μ m, has a smooth surface; carbon black was uniformly dispersed into the rubber matrix and covered by SBR; and no free carbon black particles were observed in the surface of the particle, as shown in Figure 9(b). The background of Figure 9(a) is the conducting tape. A number of small cavities were found at the surface of the P(SBR/HAF) particles, making it easy to dry.

TABLE XVIII
Influence of Aromatic Oil Content on the Mechanical Properties and Vulcanization Characteristics of P(SBR/HAF)^a

Property	Aromatic oil content (phr)				
	0	5	10	15	20
Scorch time (t_{10}), min	8.5	10.0	9.0	10.0	9.5
Optimized curing time (t_{90}), min	12.5	16.5	14	15	14
Tensile strength, MPa	24.9	23.5	23.8	20.1	19.9
100% modulus, MPa	1.98	2.07	1.98	1.83	1.93
300% modulus, MPa	6.1	6.67	6.38	5.77	5.02
Elongation at break, %	740	688	700	720	709
Permanent set, %	16	18	18	20	24
Tear strength, kN/m	40.9	46.3	44.8	47.5	44.8
Hardness, Shore A	70	74	71	70	69

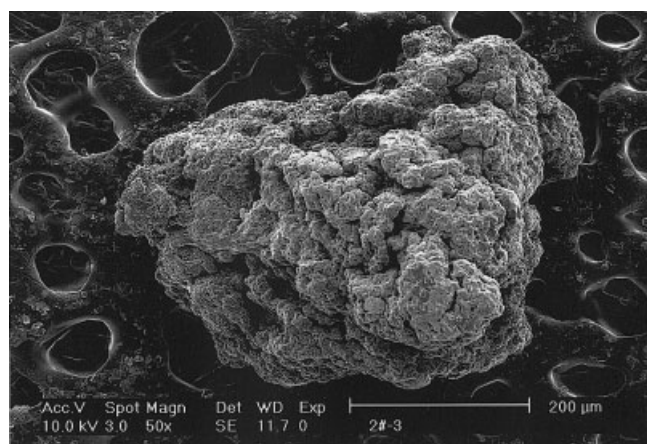
^a Emulsifier/carbon black ratio = 0.04; coating resin, 5 phr, carbon black, 50 phr.

TABLE XIX
Influence of Carbon Black Content on the Mechanical Properties and Vulcanization Characteristics of SBR/HAF

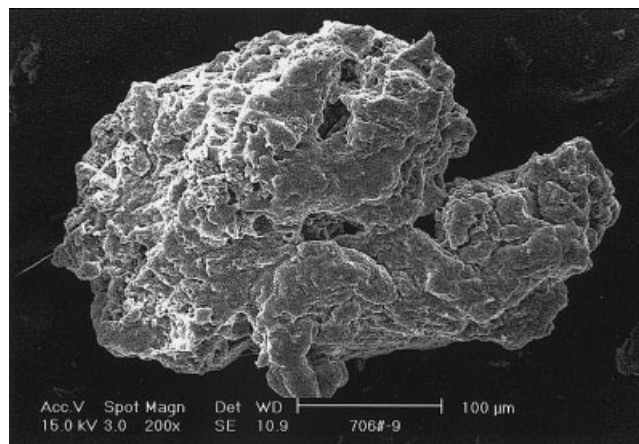
Property	Carbon black (HAF) content (phr)							
	0	20	40	50	60	80	100	120
Scorch time (t_{10}), min	24	12.5	9.5	7.5	7.5	6.5	5.5	4.5
Optimized curing time (t_{90}), min	32	22.5	22	19.5	21.5	20.5	20.5	21
Tensile strength, MPa	1.61	13.2	23.3	24.7	24.0	21.8	19.4	14.5
100% modulus, MPa	0.83	1.22	1.94	2.51	3.26	5.14	10.7	14.0
300% modulus, MPa	1.21	2.99	8.98	14.6	18.9	—	—	—
Elongation at break, %	460	592	580	530	393	274	164	112
Permanent set, %	6	6	10	16	14	12	12	10
Tear strength, kN/m	9.26	23.6	34.6	37.5	35.4	33.3	22.7	16.5
Hardness, Shore A	46	54	62	64	73	82	88	92

Figure 10(a) shows the SEM morphology of a P(SBR/HAF) particle with contact staining, indicating that the P(SBR/HAF) particle was bonded by several small granules. Figure 10(b) shows that these small granules were aggregated from several smaller aggregations of carbon black and rubber particles. Con-

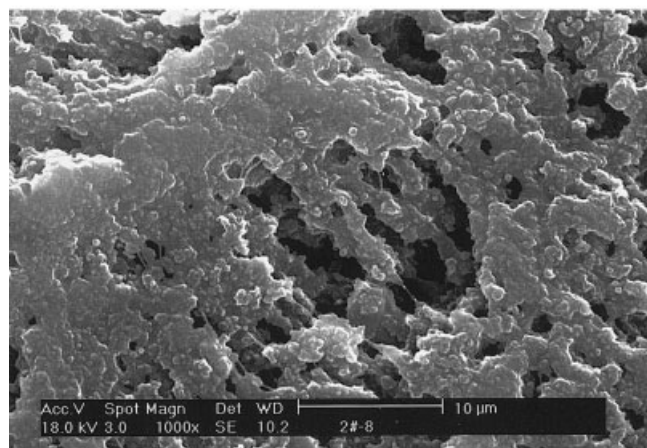
versely, with the noncontact staining P(SBR/HAF) particles, uncovered carbon black particles can be observed on the surface of the particle. This poor interaction of carbon black and rubber matrix and the free carbon black constituted the main staining source for the contact staining P(SBR/HAF) particles.



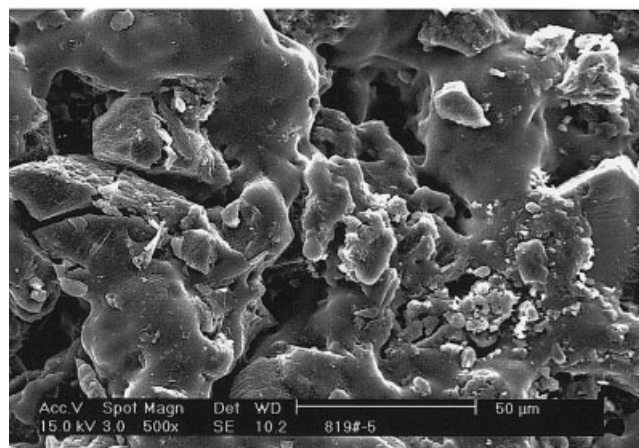
(a)



(a)



(b)



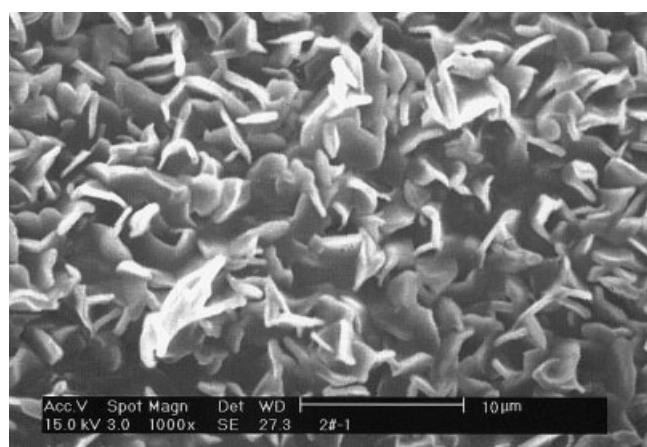
(b)

Figure 9 SEM morphology of a P(SBR/HAF) particle without contact staining: (a) $\times 50$, (b) $\times 1000$.

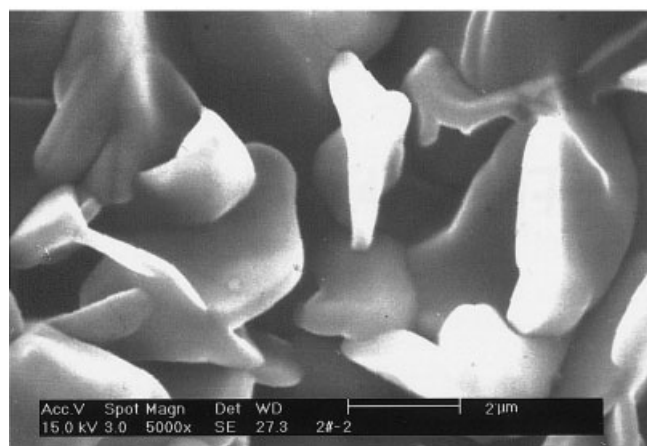
Figure 10 SEM morphology of a P(SBR/HAF) particle with contact staining: (a) $\times 200$, (b) $\times 500$.

SEM analysis of the tensile fracture surface of P(SBR/HAF) and SBR/HAF

Figure 11 shows the SEM microphotographs of the tensile fracture surface morphology of SBR/HAF. As shown in Figure 11, there are a number of special "valve structures" in the fracture surface of SBR/HAF vulcanizate. These "valve structures" also appeared in the fracture surface of P(SBR/HAF) vulcanizate, as shown in Figures 12 and 13, although the amount is smaller, and with increasing coating resin, the amount of the "valve structures" decreases. As reported, "valve structures" are the special structure for the tensile fracture surface of HAF-filled SBR.²⁸ As discussed above, coating resin is partly incompatible with the SBR matrix, and with increasing coating resin content, there are more defects in the P(SBR/HAF) vulcanizate, which results in a reduction of mechanical properties and the amount of "valve structures."

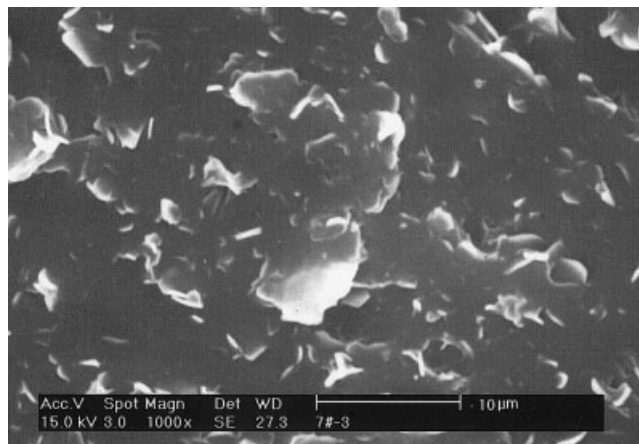


(a)

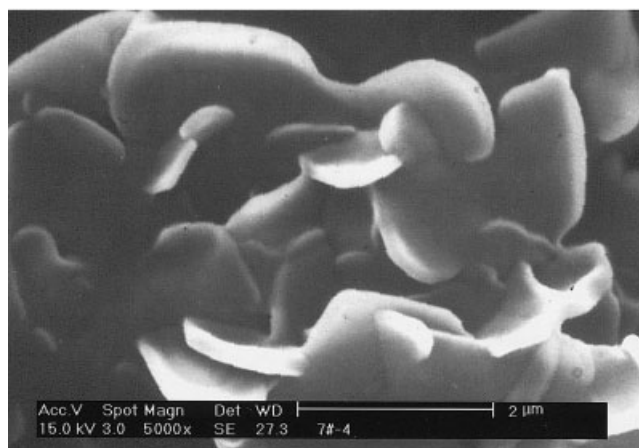


(b)

Figure 11 SEM microphotographs of tensile fracture surface of SBR/HAF: (a) $\times 1000$, (b) $\times 5000$.



(a)



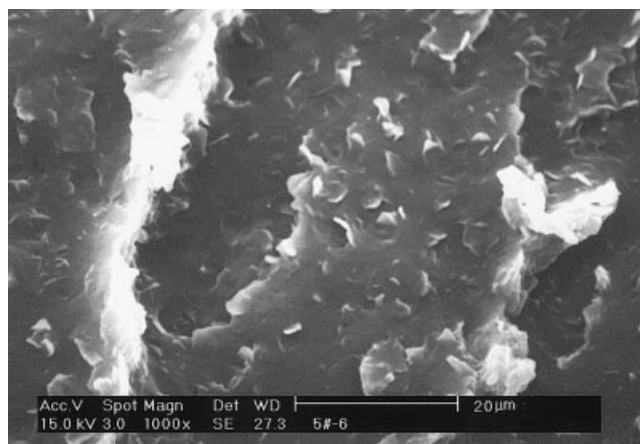
(b)

Figure 12 SEM microphotographs of tensile fracture surface of P(SBR/HAF) with 5 phr coating resin: (a) $\times 1000$, (b) $\times 5000$.

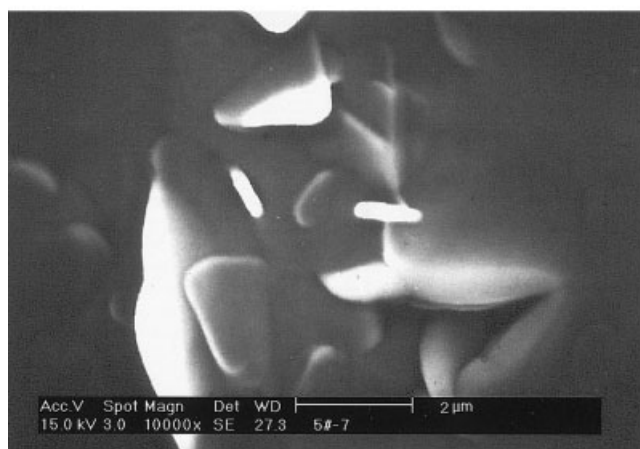
CONCLUSION

This article reported the investigation of the preparation, particle size distribution, mixing rheological properties in a laboratory internal mixer, and mechanical properties of carbon black (HAF)-filled powdered SBR. A carbon black-rubber latex coagulation method was developed for preparing the carbon black-filled free-flowing, noncontact staining SBR powders under the following conditions: carbon black content > 40 phr, emulsifier/carbon black ratio > 0.02 , and coating resin content > 2.5 phr.

Because of the differences between P(SBR/HAF) and SBR/HAF in morphology and macroscopic structure, the mixing behavior of these two blends in a laboratory internal mixer shows some differences. In the experimental ranges studied, the sensitivity of mixing torque of P(SBR/HAF) to mixing time, carbon black content, and aromatic oil content was about 30–90% of those of SBR/HAF, whereas the tempera-



(a)



(b)

Figure 13 SEM microphotographs of tensile fracture surface of P(SBR/HAF) with 15 phr coating resin: (a) $\times 1000$, (b) $\times 10,000$.

ture build-up ΔT of P(SBR/HAF) showed no dependency on carbon black content. Compared to SBR/HAF, P(SBR/HAF) showed a reduction of mixing energy with high carbon black content (>30 phr), which confers to filler-filled powdered SBR good prospects for internal mixing. Carbon black and the rubber matrix formed a macroscopic homogenization in P(SBR/HAF), and the incorporation step is not obvious in internal mixing processing results in the characteristics of the mixing behavior of P(SBR/HAF) discussed above.

Compared with SBR/HAF, P(SBR/HAF) vulcanizate showed superior mechanical properties that depend primarily on the absence of free carbon black and the fine dispersion of carbon black in the rubber matrix, attributed to the proper preparation technology of noncontact staining carbon black-filled powdered SBR.

The authors acknowledge the financial support through the National Natural Science Foundation of China (Grant 59773010) and Guangdong Province Natural Science Foundation (Grants 970554 and 031366).

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