Carbon Black Filled Powdered Natural Rubber: Preparation, Particle Size Distribution, Mechanical Properties, and Structures

Anqiang Zhang, Lianshi Wang, Yaling Lin, Xiongfei Mi

Department of Polymer Material Science and Engineering, College of Material Science and Engineering, South China University of Technology, Guangzhou 510640, China

ABSTRACT: Carbon black (HAF) filled powdered natural rubber (P(NR/HAF)) was prepared and the particle size distribution, mechanical properties, and micromorphology of P(NR/HAF) were studied. A carbon black–rubber latex coagulation method was developed for preparing carbon black filled free-flowing, noncontact staining NR powders with particle diameter less than 0.9 mm. A powdering mechanism model was put forward to describe the powdering process, which shows that the key technical points consist in the surfactant with good emulsification properties and the polymer coating resin with good film forming properties. SEM analysis shows that carbon black and rubber matrix have formed a macroscopic homogenization in the P(NR/HAF) particles without contact staining, and carbon black particles are well dispersed in rubber matrix with diameter of about 50–150 nm. P(NR/HAF) vulcanizate showed better mechanical properties than bale natural rubber/carbon black blends (NR/HAF) and simple NR latex/carbon black blends (NRL/HAF), which depends primarily upon the absence of free carbon black, the fine dispersion of filler on the rubber matrix, and the better interaction between carbon black and rubber matrix due to the proper preparation condition of noncontact staining carbon black filled powdered NR. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1763–1774, 2006

Key words: carbon black filled powdered rubber; natural rubber; particle size distribution; powdering mechanism; mechanical properties; SEM analysis

INTRODUCTION

The mixing of rubbers/fillers is the base stage in rubber processing, but the relatively high viscosity of these raw materials makes it necessary to utilize heavy machinery such as rolling mills or internal mixers, which consume large amounts of energy. The inherent costs of this energy and equipment are considerable, which greatly impair the economy of the production of elastomeric materials. 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 the mixing.[1–8]

According to Lin's "three-stage mixing" model[9,10] for filler filled powdered rubber during internal mixing, carbon black filled powdered rubber showed better mixing properties, including lower mixing energy consumption, shorter mixing time, and better filler dispersion. We also noticed that the non-contact staining of carbon black filled powdered rubber make the mixing plant cleaner and make it safer for the employee, for no free black would be floating anywhere.

In recent years some publications were concerned with the utilization of powdered rubbers, especially for filler (such as carbon black, silica and clay, etc.) filled powdered rubber or rubber/filler masterbatch.[11–18] But these publications mainly cared about the processing and application of powdered rubber, without much detail about the preparation process, especially ignored the dispersion of filler in rubber matrix and the microanalysis of the fracture of vulcanizate.

In this paper, carbon black (high abrasion furnace black, i.e., HAF) filled powdered natural rubber [P(NR/HAF)] with wide carbon black content and aromatic oil content were prepared, which is noncontact staining. The particle size distribution, mechanical properties, and microanalysis of the fracture sample of vulcanizate of P(NR/HAF) were studied; for comparison, HAF filled bale NR (NR/HAF) and natural rub-

ber latex/carbon black simple mixing blend (NRL/HAF) were also prepared and discussed.

EXPERIMENTAL

Materials

A commercially available grade of natural rubber latex (NR latex, solid content, 60 wt %), made in Malaysia, supplied by Guangdong Guangtaihe Rubber Co. (China), was used for preparing carbon black filled powdered NR. Bale natural rubber (SMR20, made in Malaysia, supplied by Guangdong Guangtaihe Rubber Co.) was used for comparison. High-abrasion furnace black (HAF, grade N330) was supplied by Shanghai LIDE Chemical Co. (China). The coating resins used in the production of powdered NR were prepared in the laboratory by emulsion polymerization with vinyl group of monomers.[19–21] By changing the ratio of vinyl group of monomers, the coating resins (M5–M10) with different glass transition temperatures (T_g) were prepared. The T_g of M5–M10 is 35.3, 45.5, 55.3, 84.2, 119.0, and 128.4°C, respectively, which was determined by DSC measurements.[19,20] A 10 wt % $CaCl_2$ water solution was prepared in the laboratory and used as a coagulation agent. The other agents were used as purchased.

Sample preparation and testing

The preparation of P(NR/HAF)

P(nr/haf) was prepared as follows[19–21]:

1. Distilled water and emulsifier of carbon black were charged to a container, and the mixture was stirred for 15 min to make emulsifier solution.
2. Carbon black was added to the emulsifier solution, and stirred at a high speed for 20 min to form carbon black emulsion.
3. NR latex was added to the carbon black emulsion, with low-shear agitation, to form a NR latex/carbon black blend; after stirring for 10 min, coating resin (If the recipe calls for coating resin) was added to form "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% $CaCl_2$ 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.
7. Weigh the dried products and compare the actual weight (W_a) with the calculated weight (W_c), if the difference between W_a and W_c are more than 1%, then steps (1)–(6) would be repeated. Here, the W_c includes the following: solid NR in NR latex, carbon black, oil (If the recipe calls for oil), and coating resin added to the mixture.

The resulting powdered rubber product is P(NR/HAF).

The preparation of NRL/HAF

NRL/HAF was the simple product obtained by mixing NR latex and carbon black, which was prepared as follows[19–21]:

1. Distilled water and carbon black were charged to a container, and the mixture was stirred for 5 min under high-speed agitation to make carbon black suspension.
2. NR latex was added to the carbon black suspension, with low-shear agitation, to form a NR latex/carbon black blend, which would agglomerate after a few minutes.
3. A 10% $CaCl_2$ water solution was then added to NR latex/carbon black mixture to coagulate all the blends.
4. The mixture products were filtered, washed with cold water, cut to small pieces, and dried on trays in a forced draft oven at 85°C for about 3 h.
5. Weigh the dried products and compare the actual weight (W_a) with the calculated weight (W_c), if the difference between W_a and W_c are more than 1%, then steps (1)–(4) would be repeated. Here, the W_c includes the following: solid rubber in NR latex and carbon black added to the mixture.

The resulting rubber/carbon black mixture product is NRL/HAF.

Particle size distribution and powdering index of P(NR/HAF) particles

The particle size distribution of the powdered rubber was determined by standard mesh screens. Powdering index (PI) was defined as the percentage of particles passing the 20-mesh (0.9 mm) screen, which was calculated as follows

$$PI = \frac{\text{Weight of particles passing the 20-mesh screen}}{\text{Weight of total product}} \times 100$$

TABLE I
Formulation of NR Compound[a]

Compound	Composition[a] (phr)
NR	100
Zinc oxide	5
Stearic acid	2
Paraffin wax	1
Sulfur	2.25
Accelerator NS (N-oxydiethylene-2-benzothiazole sulfenamide)	0.7
Anti-aging agent 4010 NA	1
Carbon black (HAF, N330)	Variable
Aromatic oil	Variable

[a] Parts per hundred parts rubber, phr.

Contact staining of P(NR/HAF) particles

Contact staining is the pollution that occurs when carbon black filled powdered rubber comes into contact with the environment.[9] For example, when the P(NR/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.

Contact staining level was divided into four grades, ranging from zero to three. Zero means noncontact staining, while three means the most serious contact staining. When we rubbed some P(NR/HAF) particles with white paper, if the paper was stained to very dark, then we consider the contact staining level is three, while if the paper keeps white as before, then we consider the contact staining level is zero. This regular is analogized to other levels.

Physical testing

The 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 3184–01 and ASTM D 3192–02 using a 6-in. two-roll mill.

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). Dumb-bell 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. A Shimadzu testing machine (AG-1) 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).

Scanning electron micrographs studies

Scanning electron micrographs were taken from PHILIPS XL30 FEG scanning electron microscope (SEM). 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

Particle size distribution of P(NR/HAF)

The particle size distribution of P(NR/HAF) prepared by application of coagulation method depends on a number of parameters: emulsifier/carbon black ratio, coating resin contents, carbon black contents, and oil contents. The following discussion will show these influences.

TABLE II
The Influence of Emulsifier/Carbon Black Ratio on the Particle Size Distribution of P(NR/HAF)[a]

Emulsifier/carbon black ratio (wt/wt)	Particle size distribution (wt %)				Powdering index (PI)	Contact staining index[b]
	>2.0 mm	0.9–2.0 mm	0.45–0.9 mm	<0.45 mm		
0	91.6	8.4	0	0	0	3
0.02	84.8	11.6	3.6	0	3.6	2
0.04	28.7	47.8	21.2	2.3	23.5	1
0.06	0	0	84.4	15.6	100	0
0.07	0	0	76.6	23.4	100	0
0.08	0	0	24.7	75.3	100	0

[a] Coating resin (M9), 10 phr; carbon black, 50 phr.
[b] The contact staining index defined as follows: very dark as 3, dark as 2, gray as 1, and noncontact staining as 0.

TABLE III
The Influence of Coating Resin Contents on the Particle Size Distribution of P(NR/HAF)[a]

Coating resin content (phr)	Particle size distribution (wt %)				Powdering index (PI)
	>2.0 mm	0.9–2.0 mm	0.45–0.9 mm	<0.45 mm	
0.0	21.3	68.1	9.9	0.7	10.6
2.5	3.2	1.2	93.3	2.3	95.6
5.0	1.1	1.8	88.5	8.6	97.1
7.5	0	1.7	86.9	11.4	98.3
10.0	0	0	84.4	15.6	100
12.5	0	0	75.0	25.0	100
15.0	0	0	74.6	25.4	100

[a] Emulsifier/carbon black = 0.06; carbon black, 50 phr; coating resin: M9.

Influence of emulsifier/carbon black ratio

As discussed in the previously published works,[9,19,20,22,23] carbon black emulsifier such as Triton[TM] X-100 can improve the dispersion of carbon black in water and form a stable carbon black emulsion. The existence of emulsifier can reduce not only the contact staining of products, but also the particle size of P(NR/HAF), as shown in Table II. Without emulsifier, NR latex will agglomerate with carbon black when the reaction system was heated, and therefore the powdering process cannot be continued and the product would not form as powder but as large block and has contact staining. With the increase in emulsifier/carbon black ratio, the ratios of particle size smaller than 0.9 mm (pass the 20-mesh screen) and 0.45 mm (pass the 40-mesh screen) increase remarkably. All of the particles can pass the 0.9 mm screen (i.e., PI is 100) when emulsifier/carbon black ratio is 0.06 or more. However, when the emulsifier/carbon black ratio is more than 0.08, the particle size of the product is so small that it may run off when filtering, so the suitable emulsifier/carbon black ratio is between 0.06 and 0.07. On the other hand, a small amount of emulsifier is effective to remove the contact staining of P(NR/HAF) particles; the P(NR/HAF) particles would show noncontact staining when the emulsifier/carbon black ratio is 0.06 or more, as shown in Table II.

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. The existence of the coating layer can reduce the adhesion and aggregation between rubber particles during coagulation, drying, storage, and transportation. Coating resin is a kind of polymer resins, which is prepared by the copolymerization of two kind of vinyl monomer,[20] and so its glass transition temperature (T_g) changes with the mixture ratio of two monomers. In the previously published works, these coating resins have been used in the preparation of P(SBR/HAF),[9,10,20–23] P(NBR/HAF)[24] and P(CR/SRF),[25,26] etc. It was found that these coating resins can not only coat the particles containing rubber and filler effectively with a thin coating layer but also reinforce the vulcanizates of rubber blends.

As shown in Table III, when the coating resin content is 7.5 phr, PI of the P(NR/HAF) is 98.3, and when the coating resin content reaches 10 phr, PI reaches 100, which showed that the coating resin can coat the P(NR/HAF) particles, prevent the P(NR/HAF) particles from adhesion, and reduce the particle size effectively.

TABLE IV
The Influence of T_g of Coating Resin on the Particle Size Distribution of P(NR/HAF)[a]

T_g of coating resin (°C)	Particle size distribution (wt %)				Powdering Index (PI)
	>2.0 mm	0.9–2.0 mm	0.45–0.9 mm	<0.45 mm	
35.3 (M5)	0	2.1	84.7	14.2	98.1
45.5 (M6)	0	2.5	86.7	10.8	97.5
55.3 (M7)	0	2.3	89.5	8.2	97.7
84.2 (M8)	0	4.9	83.8	11.3	95.1
119.0 (M9)	0	0	84.4	15.6	100
128.4 (M10)	0	3.5	93.9	2.6	96.5

[a] Emulsifier/carbon black = 0.06; coating resin, 10 phr; carbon black, 50 phr.

TABLE V
The Influence of Carbon Black Contents on the Particle Size Distribution of P(NR/HAF)[a]

Carbon black content (phr)	Particle size distribution (wt %)				Powdering index (PI)
	>2.0 mm	0.9–2.0 mm	0.45–0.9 mm	<0.45 mm	
20	14.1	22.7	59.0	4.2	63.2
30	8.2	12.2	71.4	8.2	79.6
40	2.3	7.2	80.8	9.7	91.5
45	0	4.7	81.8	13.5	95.3
50	0	0	84.4	15.6	100
60	0	0	65.6	34.4	100
70	0	0	54.7	45.3	100

[a] Emulsifier/carbon black = 0.06; coating resin (M9), 10 phr.

Influence of glass transition temperature (T_g) of coating resin

As shown in Table IV, all the coating resins, with T_g varying from 35.3 to 128.4°C (M5–M10), can coat the P(NR/HAF) particles effectively. More than 95% of the particles can pass through the 0.9-mm screen no matter what kind of the coating resin is added. Although all the particles can pass through the 0.9-mm screen, coating resin M9 shows the best coating property, i.e., PI is 100.

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 will influence the particle size distribution of the powders. As shown in Table V, when carbon black content is less than 40 phr, the particle size distribution of P(NR/HAF) was sensitive to the carbon black content, and it changed obviously with the variation of carbon black content; while carbon black content is more than 50 phr, all the particles can pass the 0.9 mm screen. The greater the carbon black content, the smaller the particle size. In another words, to achieve narrow particle size distribution, the coating resin content must be reduced as carbon black content increase.

Influence of aromatic oil contents

Generally, aromatic oil is added to rubber as a softening agent to improve the processibility of rubber and the dispersion of filler in the rubber matrix. As shown in Table VI, the adding of aromatic oil slowly increases the particle size because aromatic oil induces the swelling of some particles. But the content of aromatic oil should not be too large, for it may cause the exudation of oil.

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

Morphology of P(NR/HAF)

Figure 1(a) shows the SEM morphology of P(NR/HAF) particles without contact staining, which shows that a P(NR/HAF) particle, having a diameter about 0.25 mm, is irregular in shape. The P(NR/HAF) particle was bonded by several small granules with diameters between 50 and 100 μm, which are called secondary particles, as shown by the arrow marked "A" in Figure 1(a). Figure 1(b) showed that secondary particles were aggregated from several smaller aggregations of rubber/carbon black particles, these aggregations, having mean particle diameter about 5–10 μm, were called primary particles, as shown by the arrow marked "B" in Figure 1(b). As shown in Figure 1(b), primary particles have a smooth surface for they were coated by a thin coating layer. Carbon black was uniformly dispersed into the rubber matrix and covered by NR, no free carbon black particles were observed in the surface of the particle, and so the particle show noncontact staining.

TABLE VI
The Influence of Aromatic Oil Contents on the Particle Size Distribution of P(NR/HAF)[a]

Aromatic oil content (phr)	Particle size distribution (wt %)				Powdering index (PI)
	>2.0 mm	0.9–2.0 mm	0.45–0.9 mm	<0.45 mm	
0.0	0	0	84.4	15.6	100
5.0	0	0.5	80.8	18.7	99.5
10.0	0	0.8	80.0	19.2	99.2
15.0	0	1.3	74.4	24.3	98.7
20.0	0	2.2	76.7	21.1	97.8

[a] Emulsifier/carbon black = 0.06; coating resin (M9), 10 phr; carbon black, 50 phr.
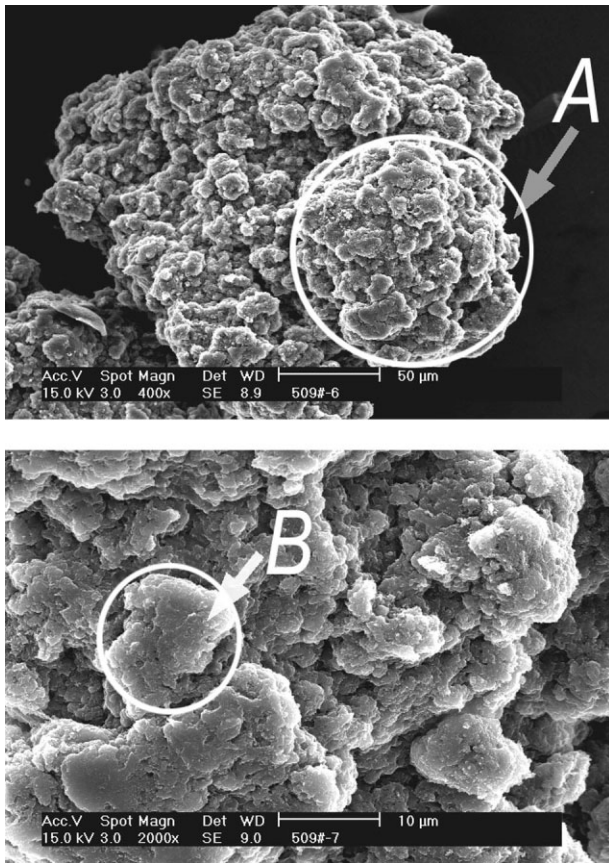
Figure 1 The SEM morphology of a typical P(NR/HAF) particle without contact staining (carbon black content: 50 phr): (a) ×400, (b) ×2000.

Figure 2(a) shows the SEM morphology of a P(NR/HAF) particle with contact staining, indicating that the particle was also made up of secondary particles and primary particles, with uncovered carbon black particles distributing on the surface of the P(NR/HAF) particle, as pointed by the arrows. Figure 2(b) shows that uncovered carbon black particles with diameters between 100 and 200 μm can be observed on the coarse surface of the particle (as pointed by the arrows). The poor interaction of carbon black and rubber matrix and the free carbon black constituted the main staining source for the contact staining of P(NR/HAF) particles.

The dispersion of carbon black in P(NR/HAF) particles

Figure 3 is the cross section of a typical P(NR/HAF) particle without contact staining. As shown in Figure 3(a), carbon black and rubber matrix have formed macrohomogenous blend. It was found that there are a number of small cavity at the surface and cross section of the P(NR/HAF) particle, as shown by the arrows marked "C" in Figure 3(a), which makes it

easy to be dried. Figure 3(b) shows that the carbon black particles are well dispersed with diameter about 50–150nm, which have almost approached the best dispersion level of carbon black in rubber matrix by traditional mixing technology. This means that carbon black can very well be dispersed in rubber matrix using the preparation technology of P(NR/HAF) with very low shear rate and low energy consumption.

**Powdering mechanism of P(NR/HAF)**

The powdering mechanism of P(NR/HAF) during the preparation is shown in Figure 4, based on the preparation technology and the SEM analysis of P(NR/HAF) particles. When NR latex mixed with carbon black emulsion under stirring, adsorption will happen between NR latex emulsion particles and carbon black particles, and the NR emulsion particles will micro-coacervate with carbon black particles to form the "primary aggregations" or "primary particles" with diameter of 5–10 μm. So the powdering system was

(a)

(b)
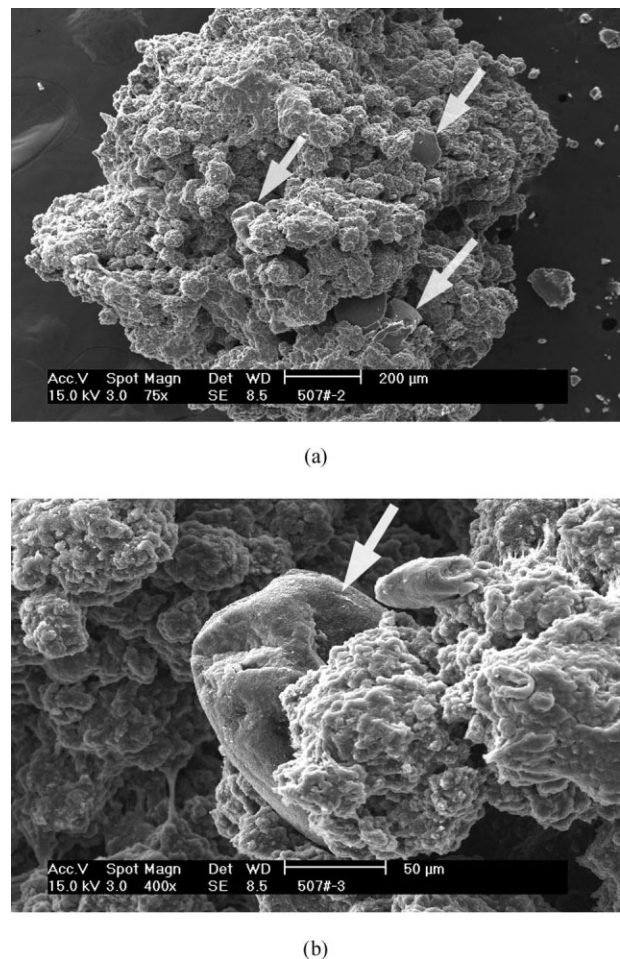
Figure 2 The SEM morphology of a typical P(NR/HAF) particle with contact staining (carbon black content: 50 phr): (a) ×75, (b) ×400.
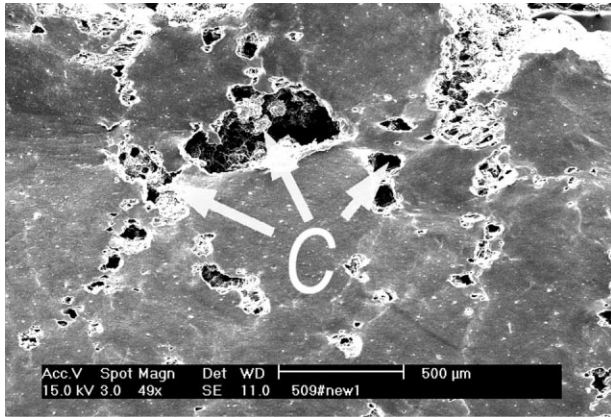
(a)
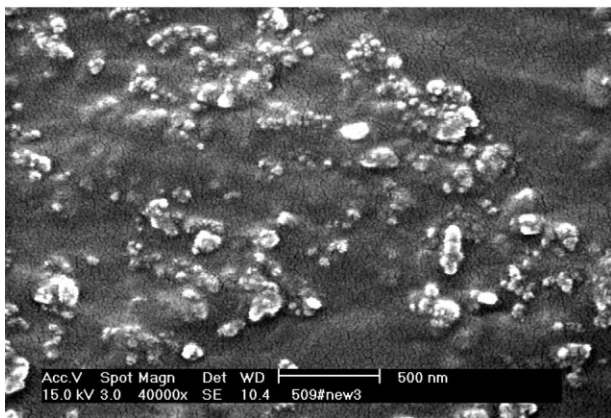
(b)

Figure 3 The SEM morphology of the cross section of a typical P(NR/HAF) particle without contact staining (carbon black content: 50 phr): (a) ×50, (b) ×40,000.

changed from mixed emulsion to suspending liquid. Excessive emulsifier can help to make the primary particles stable. Then a thin coating layer was formed on the surface of primary particles after the addition of coating resin. When the coagulation agent was added to the mixture under high-speed agitation, the agglomeration of primary particles occurred and the "secondary particles" with diameter of 50–100 μm were formed. After hot-filtrate and screening, several secondary particles were bonded together to form P(NR/HAF) particles.

In the powdering process, the formation step of "primary particles" has a decisive effect on the contact staining degree of P(NR/HAF). If carbon black particles were embedded by NR emulsion particles, the P(NR/HAF) particles would have noncontact staining. Without the addition of emulsion, carbon black would agglomerate to large aggregate in water and disperse badly in the NR matrix, and some carbon black aggregate will be exposed at the surface of P(NR/HAF) particles without the coating of rubber, and so the P(NR/HAF) particles with contact staining were prepared. PI was mainly decided by the formation step of coating layer. If coating resin formed a prefect coating layer on the surface of primary particle, then PI will be high. If coating layer can not coat primary particle fully or coating layer is too thin, then coating layer will be destroyed in the later process and the product particles will agglomerate. Thus PI will be low. So emulsifier of carbon black and coating resin are the most important key agents in the preparation of free-flowing P(NR/HAF) without contact staining.
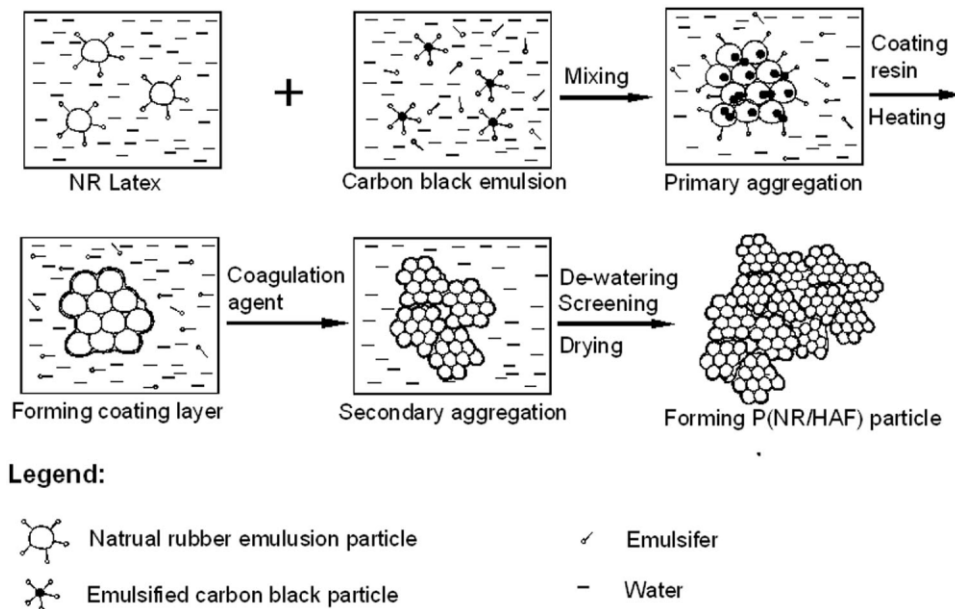
Figure 4 The sketch map of the powdering mechanism of carbon black filled powdered natural rubber.

TABLE VII
The Influence of Emulsifier/Carbon Black Ratio on the Mechanical Properties and Vulcanization Characteristics of P(NR/HAF)[a]

Properties	Emulsifier/carbon black ratio (wt/wt)					
	0	0.02	0.04	0.06	0.07	0.08
Scorch time (t_{10}), min	3.0	3.0	2.8	2.7	2.7	2.6
Optimized curing time (t_{90}), min	9.0	6.5	6.0	5.5	5.0	5.0
Tensile strength, MPa	21.0	21.6	22.3	25.5	24.8	21.3
100% Modulus, MPa	2.4	2.4	2.3	2.3	2.2	2.1
300% Modulus, MPa	7.2	7.1	7.1	7.2	7.2	6.7
Elongation at break, %	500	532	593	696	701	660
Permanent set, %	30	32	34	32	34	36
Tear strength, kN/m	70.0	69.5	75.2	85.3	87.7	67.6
Hardness (Shore A)	58	57	58	60	61	60

[a] Coating resin (M9), 10 phr; carbon black, 50 phr.

Mechanical properties of P(NR/HAF)

Influence of emulsifier/carbon black ratio

Most of emulsifier was removed away when the powdered rubber product was washed with water, i.e., the residual emulsifier content in product was low, and so the aim of adding emulsifier is to improve the dispersion of carbon black in the powdering system. The mechanical properties and vulcanization characteristics of P(NR/HAF), with different emulsifier/carbon black ratio, are presented in Table VII. Scorch time (t_{10}) and optimized curing time (t_{90}) decrease with the increasing of emulsifier content, whereas tensile strength and tear strength achieve maximum values with the emulsifier/carbon black ratio of 0.06–0.07. Proper emulsifier content can improve the dispersion of carbon black in the rubber matrix, thus contributing to the improvement of mechanical properties of P(NR/HAF). The more the emulsifier content, the better the dispersion of carbon black. But when the powdering system was coagulated, the excessive emulsifier was absorbed on surface of carbon black particles, which makes it difficult for carbon black particles to coagulate with NR latex. In the stage of washing prod-

uct, this part of carbon black may run off, and so the carbon black content of P(NR/HAF) is less. What is more, excessive emulsifier will also cause an increase in residual emulsifier content in rubber vulcanizate, thus harming the physical properties of P(NR/HAF). Thus the proper emulsifier/carbon black ratio is between 0.06 and 0.07.

Influence of Tg of coating resins

The mechanical properties and vulcanization characteristics of P(NR/HAF) with different coating resins, are presented in Table VIII. The 100% modulus, 300% modulus, tensile strength, and tear strength achieve maximum values when the coating resin with T_g of 119.0°C (M9) is added, for this coating resin has a suitable compatibility with NR. Thus the coating resin M9 can reinforce P(NR/HAF) effectively. Hardness increases slowly with increase in T_g of coating resins.

Influence of coating resin content

As shown in Table IX, optimized curing time (t_{90}) increases slowly with the increase in coating resin

TABLE VIII
The Influence of T_g of Coating Resin on the Mechanical Properties and Vulcanization Characteristics of P(NR/HAF)[a]

Properties	T_g of coating resin (°C)					
	35.3 (M5)	45.5 (M6)	55.3 (M7)	84.2 (M8)	119.0 (M9)	128.4 (M10)
Scorch time (t_{10}), min	3.0	3.0	2.8	2.7	2.7	2.6
Optimized curing time (t_{90}), min	6.0	5.5	5.5	5.5	5.5	5.0
Tensile strength, MPa	20.3	21.1	22.1	23.6	25.5	22.6
100% Modulus, MPa	2.0	2.1	2.1	2.2	2.3	2.1
300% Modulus, MPa	6.3	6.1	6.6	6.9	7.2	5.8
Elongation at break, %	500	532	593	690	696	660
Permanent set, %	30	32	36	32	32	36
Tear strength, kN/m	70.0	69.5	75.2	80.1	85.3	67.6
Hardness (Shore A)	57	58	59	60	60	62

[a] Emulsifier/carbon black = 0.06; Coating resin, 10 phr; carbon black, 50 phr.

TABLE IX
The Influence of Coating Resin Content on the Mechanical Properties and Vulcanization
Characteristics of P(NR/HAF)[a]

Properties	Coating resin content (phr)				
	2.5	5.0	10.0	15.0	20.0
Scorch time (t_{10}), min	3.0	2.8	2.7	3.0	3.5
Optimized curing time (t_{90}), min	4.5	5.0	5.5	6.0	7.5
Tensile strength, MPa	21.3	22.0	25.5	23.2	20.0
100% Modulus, MPa	1.8	1.9	2.3	2.7	2.9
300% Modulus, MPa	4.9	6.2	7.2	8.3	9.5
Elongation at break, %	658	669	696	685	683
Permanent set, %	24	28	32	34	36
Tear strength, kN/m	51.5	67.6	85.3	62.2	54.1
Hardness (Shore A)	58	59	60	62	65

[a] Emulsifier/carbon black ratio = 0.06; carbon black, 50 phr; coating resin: M9.

content, tensile strength, and elongation, and tear strength achieve maximum value when the coating resin content is 10 phr. The higher the coating resin content, the thicker the coating layer on the surface of P(NR/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(NR/HAF). Thus the proper coating resin content is 10 phr.

Influence of carbon black content

Table X details the vulcanization characteristics and mechanical properties of P(NR/HAF) with different carbon black content. As a comparison, the mechanical properties of HAF-filled bale NR (NR/HAF) and the NR latex/HAF simple mixing and coagulation product (NRL/HAF) are shown in Table XI and Table XII, respectively.

As shown in Table X, when the carbon black content varies from 20 to 70 phr, optimized curing time (t_{90}) of P(NR/HAF) decreases with the increase in carbon black content. But carbon black contents have little effect on the optimized curing time (t_{90}) of (NR/HAF)

and (NRL/HAF). In the experimental range, carbon black content shows little influence on the tensile strength of P(NR/HAF), NR/HAF, and NRL/HAF, for natural rubber is a kind of self-reinforcing rubber. The 100% modulus, 300% modulus, and hardness of these three kinds of vulcanizates increase lineally with the increase in carbon black content. Tear strength achieved maximum values when carbon black contents for three kinds of vulcanizates are 45, 50, and 50 phr, respectively. With the increase in carbon black content, the permanent set of P(NR/HAF) changed little, while permanent set of NR/HAF and NRL/HAF gradually decreased.

In the same experimental condition, the tensile strength of three kinds of vulcanizates have following relation, P(NR/HAF) > NR/HAF > NRL/HAF; this relation is fit to the tear strength of the three kinds of vulcanizates too. The coating resins can reinforce the P(NR/HAF) vulcanizates, and so the P(NR/HAF) vulcanizates have the best tensile strength and tear strength. Permanent set of P(NR/HAF) vulcanizates is obviously greater than that of the other two kinds of vulcanizates, for coating resins are not elastic polymer and cannot completely recover after tensiled. In the

TABLE X
The Influence of Carbon Black Content on the Mechanical Properties and Vulcanization
Characteristics of P(NR/HAF)[a]

Properties	Carbon black (HAF) content, phr						
	20	30	40	45	50	60	70
Scorch time (t_{10}), min	4.0	3.5	3.0	2.8	2.7	2.6	2.5
Optimized curing time (t_{90}), min	9.0	7.0	6.5	5.5	5.5	5.0	5.0
Tensile strength, MPa	22.0	24.6	24.7	25.2	25.5	24.6	24.6
100% Modulus, MPa	1.2	1.4	2.2	2.2	2.3	2.6	2.8
300% Modulus, MPa	2.9	4.4	6.0	6.5	7.2	7.9	8.9
Elongation at break, %	801	743	710	703	696	651	583
Permanent set, %	30	30	32	32	32	32	30
Tear strength, kN/m	62.9	66.0	79.1	88.5	85.3	83.2	80.1
Hardness (Shore A)	50	52	57	58	60	65	71

[a] Emulsifier/carbon black ratio = 0.06; coating resin (M9), 10 phr.

TABLE XI
The Influence of Carbon Black Content on the Mechanical Properties and Vulcanization Characteristics of NR/HAF

Properties	Carbon black (HAF) content (phr)						
	20	40	50	60	70	80	100
Scorch time (t_{10}), min	5.5	5.0	5.0	4.5	4.0	4.0	3.5
Optimized curing time (t_{90}), min	10.0	9.5	9.0	9.0	8.5	8.3	8.0
Tensile strength, MPa	22.6	22.1	22.2	22.8	20.6	19.8	16.5
100% Modulus, MPa	1.5	2.0	2.8	3.2	4.2	5.4	5.8
300% Modulus, MPa	5.5	7.7	10.6	13.6	–	–	–
Elongation at break, %	589	512	410	352	275	253	225
Permanent set, %	32	32	28	28	26	24	20
Tear strength, kN/m	42.3	54.9	74.4	72.5	55.6	58.1	34.7
Hardness (Shore A)	50	52	59	64	72	76	78

powdering system, the impurity of NR latex and water decrease the surface activity of carbon black, and so it is difficult for P(NR/HAF) to form higher content of bound rubber. In the previous experiment, we found that the bound rubber content of P(NR/HAF) is lower than that of NR/HAF. Bound rubber contributed greatly to 300% modulus of vulcanizate. Thus 300% modulus of vulcanizate of P(NR/HAF) is lower than that of NR/HAF.

Influence of aromatic oil content

In the experimental range, aromatic oil showed little influence on the mechanical properties of P(NR/HAF). Tensile strength, 300% modulus and hardness decrease slowly with the increase in aromatic oil content, while optimized curing time (t_{90}), elongation, and permanent set shift in a narrow range, as shown in Table XIII. The content of aromatic oil should not be too large because it may cause the exudation of oil.

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

Figure 5 and Figure 6 are the SEM photos of tensile fracture surface morphology of NR/HAF and P(NR/HAF) with 70 phr carbon black, respectively. As shown in Figure 5(a) and Figure 6(a), there are many crack in the tensile fracture surface of NR/HAF and P(NR/HAF). Figure 5(b) shows that the interaction of carbon black and rubber matrix of NR/HAF is poor, for there are many carbon black particles distributing in the surface, and the edge of carbon black particle and rubber matrix is clear. But the fracture surface of P(NR/HAF) is smoother, few filler particles can be seen in the surface, and edge between carbon black particle and rubber matrix is ambiguous. These phenomena show that the interaction of carbon black and rubber matrix is better, which results in the higher tensile strength of P(NR/HAF).

CONCLUSIONS

This paper studied the preparation, particle size distribution, mechanical properties, and the micromorphology of high abrasion furnace black (HAF) filled powdered natural rubber. A carbon black–rubber latex coagulation method was developed for preparing carbon black filled free-flowing, noncontact staining NR powders with particle diameter less than 0.9 mm under the following condition: carbon black content ≥40 phr, emulsifier/carbon black ratio ≥0.06, coating resin content ≥10 phr.

TABLE XII
The Influence of Carbon Black Content on the Mechanical Properties and Vulcanization Characteristics of NRL/HAF

| Properties	Carbon black (HAF) content (phr)						
	20	40	50	60	70	80	100
Scorch time (t_{10}), min	6.5	6.0	5.5	5.5	5.0	4.5	4.5
Optimized curing time (t_{90}), min	11.0	12.0	12.0	11.0	11.5	11.5	11.5
Tensile strength, MPa	19.5	19.6	20.2	19.3	18.6	18.4	18.3
100% Modulus, MPa	1.5	1.7	2.0	2.3	3.0	4.6	5.7
300% Modulus, MPa	2.7	3.4	4.6	5.9	8.8	–	–
Elongation at break, %	669	682	656	542	412	293	240
Permanent set, %	36	34	28	24	18	16	16
Tear strength, kN/m	20.6	37.3	72.1	70.6	55.2	52.6	29.8
Hardness (Shore A)	49	52	58	62	71	74	78

TABLE XIII
The Influence of Aromatic Oil Content on the Mechanical Properties and Vulcanization Characteristics of P(NR/HAF)[a]

| Properties	Aromatic oil content (phr)						
	0	2.5	5.0	7.5	10.0	12.5	15
Scorch time (t_{10}), min	2.7	2.7	2.8	3.0	3.0	3.0	3.3
Optimized curing time (t_{90}), min	5.5	5.7	5.9	6.0	6.0	6.2	6.5
Tensile strength, MPa	25.5	23.2	22.3	21.5	21.2	20.0	18.5
100% Modulus, MPa	2.3	2.3	2.3	2.2	1.9	1.7	1.6
300% Modulus, MPa	7.2	7.0	6.8	6.5	6.2	5.9	5.7
Elongation at break, %	696	690	702	710	720	705	711
Permanent set, %	32	32	32	34	34	36	36
Tear strength, kN/m	85.3	72.5	78.4	80.4	70.1	67.8	69.5
Hardness (Shore A)	60	60	59	58	57	57	55

[a] Emulsifier/carbon black ratio = 0.06; coating resin (M9), 10 phr, carbon black, 50 phr.

A powdering mechanism was put forward to describe the powdering process, which showed that the key technical point consists in the surfactant with good emulsification and the polymer coating resin with good film forming properties. SEM a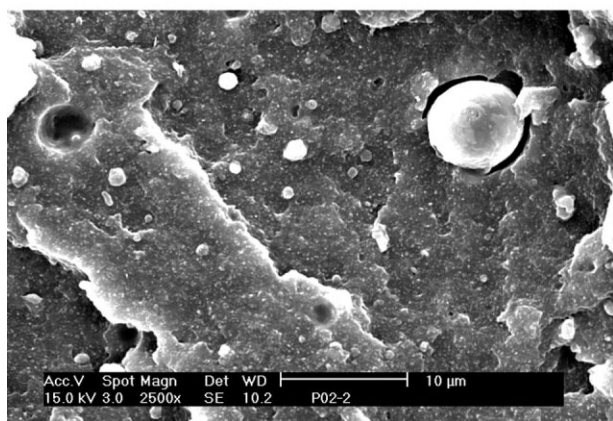nalysis showed that carbon black and rubber matrix have formed a macroscopic homogenization in P(NR/HAF), and carbon black particles are well dispersed with diameter of about 50–150 nm, which have almost approached the best dispersion level of carbon black in rubber matrix by traditional mixing technology.
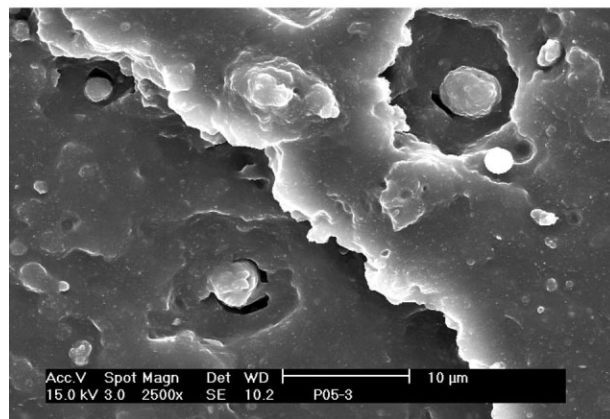

(a)
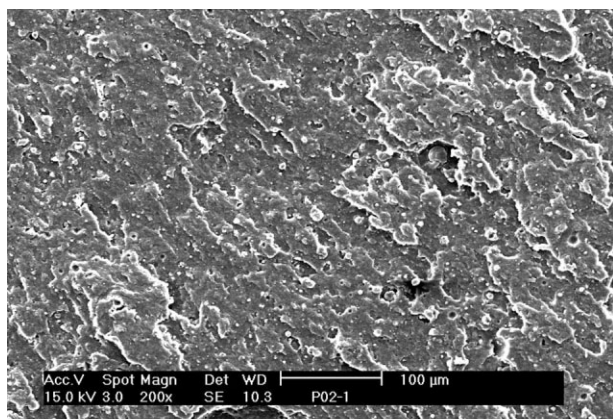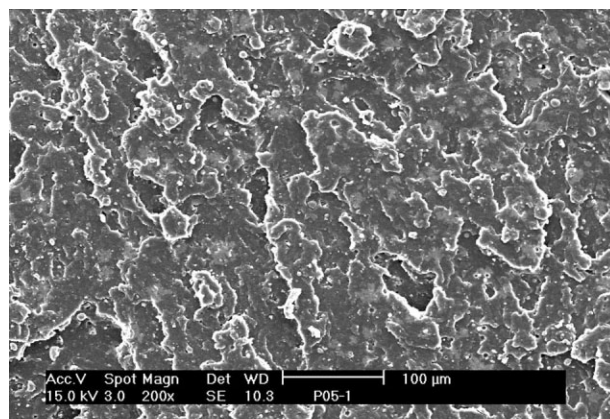
(b)

Figure 5 The SEM morphology of tensile fracture surface of NR/HAF with 70 phr carbon black: (a) ×200, (b) ×2500.

(a)

(b)

Figure 6 The SEM morphology of tensile fracture surface of P(NR/HAF) with 70 phr carbon black: (a) ×200, (b) ×2500.

Compared with NR/HAF and NRL/HAF, P(NR/HAF) vulcanizate showed better mechanical properties, which depends primarily upon the absence of free carbon black, the fine dispersion of filler on the rubber matrix, and the better interaction of carbon black and rubber matrix due to the proper preparation condition of noncontact staining carbon black filled powdered NR.

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