Dispersion of Carbon Black in High-Abrasion Furnace Black Filled Nonsulfur Modified Powdered Polychloroprene Rubber

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ABSTRACT: High-abrasion furnace black (HAF, grade N330) filled nonsulfur modified powdered polychloroprene rubber [P(CR231/HAF)] was prepared with the method of carbon black–rubber latex coagulation using CR231 latex as raw rubber material, HAF as reinforcing filler, and polymeric resin as coating resin. The influence of the content of dispersing agent and coating resin on contact staining and dispersion properties of carbon black in P(CR231/HAF) were investigated. The results show that the addition of dispersing agent and coating resins can decrease the contact staining level of carbon black effectively. When the dispersing agent/HAF (w/w) ratio was 0.12 or 0.1, 10 phr coating resin was added, and P(CR231/HAF) without contact staining can be prepared. The analysis on scanning electron microscopy and surface energy spectrum showed that free carbon black crumb on the surface and inner of P(CR231/HAF) particles causes its contact staining. The well dispersion of carbon black in the P(CR231/HAF) can eliminate contact staining effectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 192–196, 2006

Key words: carbon black filled powdered rubber; nonsulfur modified polychloroprene rubber; coating resin; contact staining; dispersions

INTRODUCTION

Carbon black is widely used in rubber industry as reinforcing filler. When carbon black was mixed with rubber by rolling mills or internal mixer, carbon black moves upward and induces serious environmental pollution.[1–5] The application of carbon black filled powdered rubber could effectively reduce dust emissions and energy consumed during mixing.[1–9] What's more, the quality of dispersion of carbon black into rubber matrix is one of the most important factors affecting the physical properties of the resulting compounds.[3–5,10–14] Also, former studies showed that carbon black filled powdered rubber could not only improve the dispersion of carbon black in the rubber matrix but also improve the processibility of carbon black filled rubber.[10–13,15–18] In recent years, a number of articles were published concerning the preparation and properties of filler-filled powdered rubber using various methods,[19–28] while few articles discussed the dispersion of carbon black in carbon black filled powdered rubber.[18] However, the dispersion of carbon black in carbon black filled powdered rubber will influence the processibility, contact staining, and subsequent application of carbon black filled powdered rubber.[13,18,29]

The present article studies the influence of preparation technology on contact staining and dispersion property of carbon black in P(CR231/HAF). The relationship between contact staining and dispersion property of carbon black in P(CR231/HAF) was also discussed.

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EXPERIMENTAL

Materials

A commercially available grade of nonsulfur modified polychloroprene rubber latex (CR231 latex; solid content, 32.0 wt %), supplied by Chongqing Changshou Chemical Industry Co. (People's Republic of China), was used for preparing carbon black filled powdered CR231. High-abrasion furnace black (HAF, grade N330) was supplied by Shanghai LIDE Chemical Co. (People's Republic of China). The coating resins used in the production of carbon black filled powdered CR231 were prepared in the laboratory by emulsion polymerization.[10–13,18] 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 commercially.

Sample preparation and physical testing

The preparation of P(CR231/HAF)

P(CR231/HAF) was prepared as follows:

1. Distilled water and dispersing agent were charged to a container, and the mixture was stirred for 15 min to make dispersing agent solution.
2. Carbon black (HAF) was added to the dispersing agent solution prepared earlier, and stirred for 20 min to form carbon black emulsion.
3. CR231 latex and coating resin (If the recipe calls for coating resin) were added to the carbon black emulsion prepared earlier, 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. A 10% $CaCl_2$ water solution was added to the mixture under high-speed agitation, with continuous stirring for 20 min.
5. 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.

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

The powdered rubber product, prepared using the technology described earlier, is high-abrasion furnace black filled powdered CR231 [P(CR231/HAF)].

Contact staining of P(CR231/HAF) particles

Contact staining is the pollution that occurs when carbon black filled powdered rubber comes into contact with the environment.[18] For example, when the P(CR231/HAF) particles come into contact with white paper (where friction is applied several times) and 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 five grades, ranging from zero to four. Zero means noncontact staining, while four means the most serious contact staining. When we rubbed some P(CR231/HAF) particles with white paper, if the paper was stained to very dark, then we consider the contact staining level is four, while if the paper remains white as before, then we consider the contact staining level is zero. This regularity is analogized to other levels.

Scanning electron micrograph studies and surface energy spectrum analysis

Scanning electron micrographs (SEM) were taken in a Philips XL30 FEG SEM (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. Surface energy spectrum analysis was carried using the EDAX DX4I attached to the SEM.

RESULTS AND DISCUSSION

Influence of content of dispersing agent and coating resins on contact staining of P(CR231/HAF) particles

Contact staining may happen when carbon black filled powdered rubber comes into contact with the environment. Contact staining can macroscopically characterize the dispersion properties of carbon black filled powdered rubber. The contact staining of carbon black filled powdered rubber can not only induce the flying of free carbon black during mixing, but also damage the mechanical properties of vulcanized rubber.

It was found that carbon black would agglomerate into particles about 1 mm in the water without the dispersing agent, which caused poor dispersion in water. The addition of the dispersing agent (such as some kinds of nonionic surfactants, e.g., Triton X-100) can improve the dispersion of carbon black in water and form a stable carbon black emulsion. As shown in Table I, with the increasing content of the dispersing agent, the contact staining level of P(CR231/HAF) decreased. When the dispersing agent/carbon black (w/w) ratio reaches 0.12, noncontact staining P(CR231/HAF) particles can be obtained, but the particle size is not uniform, ranging from 0.5 to 6 mm.

To get P(CR231/HAF) particles with proper particle size and narrow particle size distribution, we choose two kinds of coating resins with T_g of 55.3°C (abbreviation, M7) and 84.2°C (abbreviation, M8), respectively, according to prior study.[10,30]

When the dispersing agent/carbon black ratio is 0.1, noncontact staining P(CR231/HAF) with narrow particle size distribution can be obtained with the addition of 10 phr M7 or M8, and the increase of coating resin content would reduce the mean particle size of the product, as shown in Table I. So the addition of coating resins can not only help to get P(CR231/HAF) particles with proper particle size and narrow particle size distribution, but also helps to reduce the contact staining level of P(CR231/HAF) particles.

TABLE I
Influence of Dispersing Agent/Carbon Black Ratio and Coating Resin Contents on the Contact Staining Level and Particle Size Distribution of P(CR231/HAF) Particles

Sample no.	Al	A2	A3	A4	A5	A6	A7	B1	B2	Cl	C2
Dispersing agent/carbon black ratio (wt %)[a]	0	2	4	6	8	10	12	10	10	10	10
Coating resin content (phr)	0	0	0	0	0	0	0	10[b]	15[b]	10[c]	15[c]
Contact staining leve1[d]	4	4	4	3	2	1	0	0	0	0	0
2.0–6.0 mm	100	89.4	85.3	80.0	75.1	70.2	64.6	0	0	0	0
0.9–2.0 mm	0	10.6	14.7	17.0	19.5	24.3	24.9	90.7	5.6	92.1	7.2
Particle size distribution											
0.45–0.9 mm	0	0	0	3.0	5.4	5.0	9.5	9.3	88.0	7.9	89.4
<0.45 mm	0	0	0	0	0	0.5	1.0	0	6.4	0	3.4

[a] Carbon black (FIAF) content, 50 phr.
[b] Coating resin, M7.
[c] Coating resin, M8
[d] The contact staining level was divided into five grades, ranging from zero to four. Zero means non-contact staining, while four means the most serious contact staining. This regular can be analogized to other levels.

SEM studies and surface energy spectrum analysis on P(CR231/HAF) particles

P(CR231/HAF) particles with contact staining

As shown in Figure 1, both the surface and cross section of the P(CR231/HAF) particles with contact staining are very coarse. The prominent sphere with diameter about 100–150 μm on the particle surface [as marked by the arrows shown in Fig. 1(a) and (b)] was analyzed with surface energy spectrum analysis. It was found that the content of carbon is very high and is up to 95.3%, while the content of chlorine is only 2.8%, as shown in Table II. So these spheres can be judged as nondispersed carbon black agglomerates. It was also found that there are plenty of small cavities on the cross section of the P(CR231/HAF) particle, as shown in Figure 1(c) and (d), and this honeycombed structure gave P(CR231/HAF) a good drying prop-

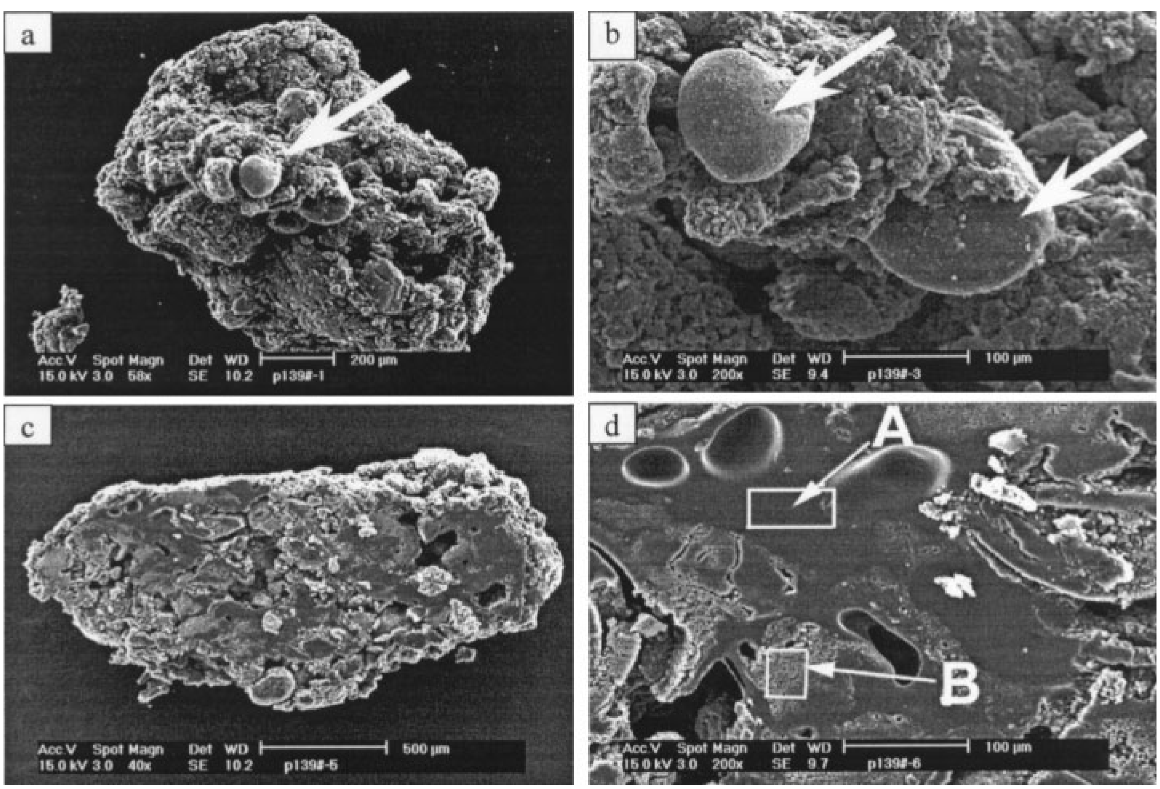

Figure 1 SEM morphology of a P(CR231/HAF) particle with contact staining: (a) individual particle; (b) detail view of surface of the particle; (c) the cross section through a particle; (d) detail view of the section through a particle.

TABLE II
Surface Energy Spectrum Analysis of a P(CR231/HAF) Particle with Contact Staining

Analysis area	Element content (wt %)			Composition
	C	C1	Ca	
The whole surface of particle	50.6	38.9	3.6	Rubber matrix
The prominent sphere on the surface	95.3	2.8	1.8	Carbon black agglomerates
Region A (deep color region)	52.7	39.0	1.3	Rubber matrix
Region B (light color region)	92.6	4.0	3.4	Carbon black agglomerates

erty. The surface energy spectrum analysis on region A (deep color region) and region B [light color region, as shown in Fig. 1(d)] showed that there was a higher carbon content in the region B, as shown in Table II. This means that B region is rich in carbon black, i.e., many nondispersing carbon black agglomerates exist in B region. The interface of regions A and B is clear. For P(CR231/HAF) particles with contact staining, the existence of free carbon black agglomerates in the surface and inner of the particles is the main reason of the contact staining.

P(CR231/HAF) particles with noncontact staining

It was found that the Ca content on the outside surface of P(CR231/HAF) particles was higher than that on the inner of P(CR231/HAF) particles, as shown in Table III. This means that a layer with higher Ca content was coated at the surface of P(CR231/HAF) particles, after the P(CR231/HAF) particles was coagulated. This coating layer contributes to alleviate contact staining, keep the powdered rubber free flowing, and separate the particles to individual particle even though the powdered particles were impacted under high pressure.

Compared with the P(CR231/HAF) particles with contact staining, both the surface and cross section of P(CR231/HAF) particles with noncontact staining are slippery. None of the free carbon black agglomerates were found on the surface, as shown in Figure 2(a) and (b). The surface energy spectrum analysis on region A and region B [as shown in Fig. 2(c)] showed that the content of carbon black of region B was slightly higher than that of region A. And so, none of the carbon black agglomerates or free carbon black particles can be found in the surface and inside of the powdered rubber particles. The interface of regions A and B is blurry. In P(CR231/HAF) particles with noncontact staining, the carbon black was dispersed well in the rubber matrix [Fig. 2(d)] and formed macroscopic homogeneous rubber–carbon black composite. The absence of free carbon black and the good rubber–carbon black interaction were the main genesis of noncontact staining of P(CR231/HAF).

CONCLUSIONS

High-abrasion furnace black filled nonsulfur modified powdered polychloroprene rubber was prepared using the method of carbon black–rubber latex coagulation. The influence of the content of dispersing agent and coating resin on contact staining and dispersion properties of carbon black in P(CR231/HAF) were studied. It was found that

1. The addition of the dispersing agent is effective to reduce the contact staining level of P(CR231/HAF) particles. When the dispersing agent/carbon black (w/w) ratio is 0.12, noncontact staining P(CR231/HAF) products can be obtained.
2. The addition of coating resin (M7 or M8) can not only help to get P(CR231/HAF) particles with proper particle size and narrow particle size distribution, but also helps to reduce the contact staining level of P(CR231/HAF) particles.
3. SEM studies and surface energy spectrum analysis on P(CR231/HAF) particles show, for P(CR231/HAF) particles with contact staining, the poor interaction of carbon black and rubber matrix and the free carbon black existing in the surface is the main reason of the contact staining. While both the surface and the cross section of

TABLE III
Surface Energy Spectrum Analysis of a P(CR231/HAF) Particle without Contact Staining

Analysis area	Element content (wt %)			Composition
	C	C1	Ca	
The whole surface of particle	51.8	37.1	4.1	Rubber matrix
Region A (deep color region)	37.7	53.1	2.2	Rubber matrix
Region B (light color region)	62.5	29.0	1.5	Rubber matrix withrich carbon black

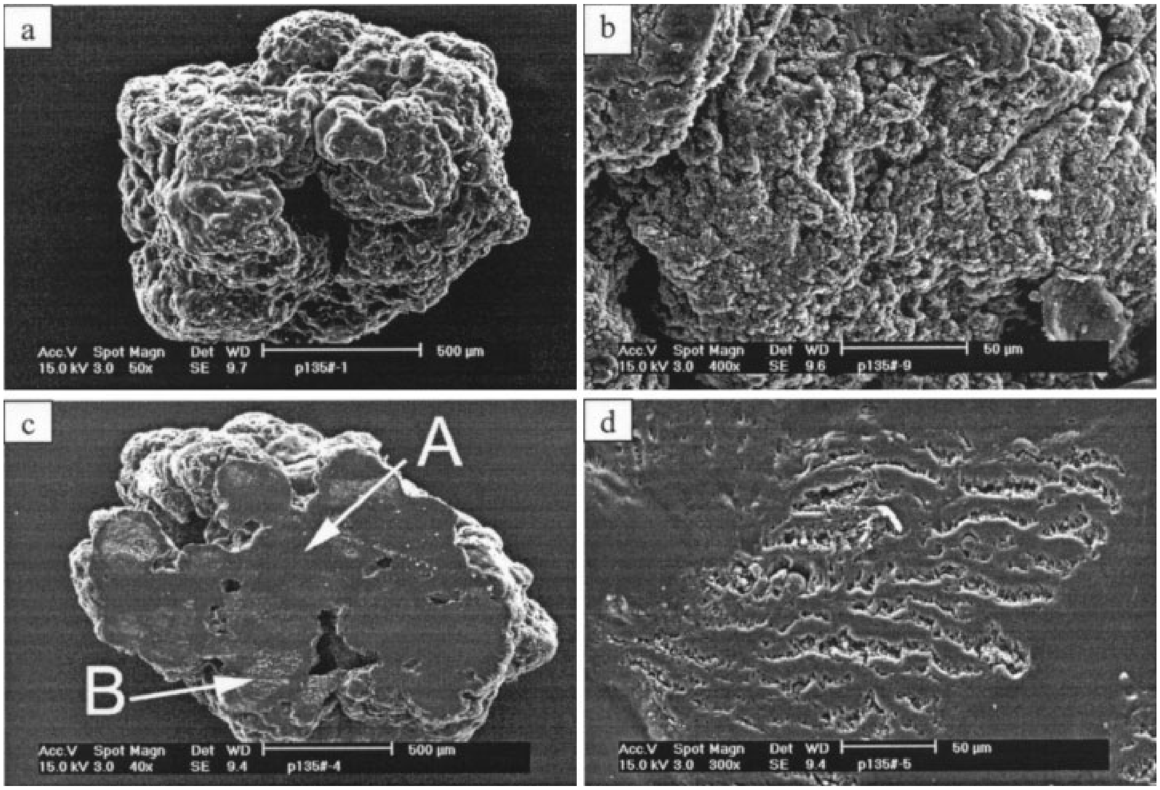

Figure 2 SEM morphology of a P(CR231/HAF) particle with noncontact staining: (a) individual particle; (b) detail view of surface of the particle; (c) the cross section through a particle; (d) detail view of the section through a particle.

P(CR231/HAF) particles with noncontact staining are slippery and none of the free carbon black was found. The carbon black was dispersed well in the rubber matrix and was embedded by the rubber. The absence of free carbon black and the good rubber–carbon black interaction were the main genesis of noncontact staining of P(CR231/HAF).

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