

# Preparation of Sulfur-Modified Powdered Polychloroprene Rubber by Inverse Coagulation

Anqiang Zhang, Lianshi Wang, Yaling Lin

Department of Polymer Material Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

Received 15 July 2004; accepted 6 March 2005

DOI 10.1002/app.22256

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

**ABSTRACT:** Sulfur-modified powdered polychloroprene rubber (PCR-121) was prepared by inverse coagulation. A new coating agent (SN) was developed that could generate *in situ* the coating layer by inverse coagulation. The results show that this is a low-cost, stable technology for the production of powdered rubber with a very low coating agent content. A powdering model based on the liquid–liquid stirring theory of noncoalescing, liquid–liquid dispersion was proven with uniform design testing. According to this model, the mass fraction of medium-scale particles (1–3 mm) was only related to the agitation speed in the experimental range. Scanning electron microscopy (SEM) analysis showed that the PCR-121 particles were single continuous particles coagulated from single chloroprene rubber latex drops. En-

ergy spectrum analysis showed that a layer with higher Ca content was coated at the surface of PCR-121 particles, which made PCR-121 a free-flowing powdered rubber. The results show that the variation of Mooney viscosity ( $ML_{1+4}$  100°C) from 30 to 130 had no obvious effect on the mechanical properties of PCR-121. Compared with bale CR121, PCR-121 had better mechanical properties. SEM analysis and energy spectrum analysis on the tensile fracture surfaces showed that the dispersion of compounding agents in PCR-121 was better than that in bale CR121, which resulted in better mechanical properties in PCR-121. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2109–2115, 2005

**Key words:** fracture; particle size distribution; surfaces

## INTRODUCTION

Polychloroprene rubber (CR) has conventionally been available in the solid state in the form of bales or relatively large size pellets, but the powdered form is rarely supplied.<sup>1–4</sup> From the 1960s to the 1980s, some articles and patents were published on the preparation of powdered PCR from rubber latex with spray drying or coagulation.<sup>5–14</sup> To prevent reagglomeration in the powdered particles, a large number of separating agents or coating agents, such as calcium carbonate, talcum, silica, various silicates, modified forms of starch, or polymer coating resins, have been added into the rubber latex or the powdered rubber products.<sup>5–14</sup> The content of such additives in rubber powder has been more than 10 phr, and they did not have similar natures to the rubber and could not be used by

the rubber compounding designer. More unfortunately, some of these conventional methods are expensive and, in some cases, detrimental to the rubber properties.<sup>3</sup> Thus, a free-flowing powdered PCR with less additives is needed for the rubber industry. In this article, a new preparation method with a lower coating agent content was developed to meet this requirement.

## EXPERIMENTAL

### Materials

A commercially available grade of unpeptized sulfur-modified PCR latex [CR121 latex, solid content = 33.4% (w/w), pH = 10.5 at 25°C; Chongqing Changshou Chemical Industry Co., Ltd., Chongqing, China] was used to prepare the sulfur-modified powdered PCR (PCR-121). Bale sulfur-modified CR (grade CR1211, similar to Neoprene GN, Mooney viscosity ( $ML_{1+4}$  100°C) = 30–40; Chongqing Changshou Chemical Industry) was used for comparison. The SN coating agent, a mixture of fatty acid soaps, including potassium stearate, sodium stearate, sodium laurate, and potassium oleate,<sup>15</sup> used for the preparation of PCR-121, was prepared in the laboratory. The other agents were all common, commercially available materials and were used as purchased.

Correspondence to: L. Wang (wanglianshi@126.com).

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

Contract grant sponsor: Guangdong Province Natural Science Foundation; contract grant numbers: 031366 and 04300069.

Contract grant sponsor: Natural Science Foundation of South China University of Technology.

Contract grant sponsor: Chongqing Changshou Chemical Industry Co., Ltd., China.

TABLE I  
Formulation of the PCR Compound

	Composition (phr)
PCR	100.0
Zinc oxide	5.0
Magnesium oxide	4.0
Stearic acid	0.5

### Sample preparation

PCR-121 was prepared as follows:<sup>16</sup>

1. The chloroprene rubber (CR) latex was put into a container, and the pH was adjusted to 11.0–11.5 with 5% NH<sub>4</sub>OH. The palpitation agent [(tetraethyl thiuram disulfide (TETD))] was then added into the container with low-speed agitation, and the contents were allowed to react at 30°C for 1–4 h until the Mooney viscosity (ML<sub>1+4</sub> 100°C) reached the expected value.
2. The SN coating agent was added into the latex mixture prepared in the previous step with medium agitation, and the mixture was heated to 85°C with a water bath and then kept at 85°C for 10–30 min.
3. The previously prepared latex was added into a 80°C coagulation solution (a 0.5% CaCl<sub>2</sub>-water solution) with high-speed agitation, and the mixture was stirred for 20 min at medium speed.

TABLE II  
Influence of the Heat-Treating Process and Coating Agent on the Powdering of PCR-121

Experiment	Heat-treating process	SN content	Assessment of particle formation
A	None	0	Very tacky, rapid agglomeration, no powders obtained
B	85 ± 5°C	0	Tacky, some agglomeration, no powders obtained
C	85 ± 5°C	1	No agglomeration, good particulate with very light tack
D	85 ± 5°C	2	No agglomeration, free-flowing powders
E	85 ± 5°C	3	No agglomeration, free-flowing powders
F	85 ± 5°C	5	No agglomeration, free-flowing powders

TABLE III  
U<sub>8</sub>\*(8<sup>5</sup>) Uniform Design Table

Level	Test				
	1	2	3	4	5
1	1	2	4	7	8
2	2	4	8	5	7
3	3	6	3	3	6
4	4	8	7	1	5
5	5	1	2	8	4
6	6	3	6	6	3
7	7	5	1	4	2
8	8	7	5	2	1

4. The powdered rubber-water slurry was hot-filtered and washed with cold water, and the slurry was dehydrated with a centrifuge. Then, the dehydrated slurry was dried on trays in a forced draft oven at 85°C for about 2 h; the particle size of the PCR-121 was determined with standard mesh screens.

### Physical testing

The Mooney viscosity (ML<sub>1+4</sub> 100°C) of PCR-121 and bale CR121 was determined with a Monsanto Mooney viscosity rheometer (MV2000) (Monsanto, St. Louis, MO) according to ASTM D 1646-1998.

The composition of the compounds is given in Table I. The mixing procedure was carried out in accordance with ASTM D 3190-2000 with a two-roll open mill (XK-160) maintained at 50 ± 5°C.

The rubber compounds were compression-molded into test specimens at 150°C according to their optimum cure times (*t*<sub>90</sub>'s), as determined by a rubber processing analyzer (RPA 2000) (Alpha Technologies, Akron, OH) according to ASTM D 5289-1995. Dumb-bell samples were cut from a 2 mm thick molded sheet.

The tensile testing procedure was carried out according to test method A of ASTM D 412-1998. A Shimadzu testing machine (AG-1) (Shimadzu, Kyoto, Japan) oper-

TABLE IV  
Arrangement for the Factors and Levels of the U<sub>8</sub>\*(8<sup>5</sup>) Uniform Design Table

Level	Factor	
	<i>N</i> (t/min)	<i>Q</i> (L/min)
1	260	0.3
2	290	0.5
3	320	0.7
4	350	0.9
5	380	1.1
6	410	1.3
7	440	1.5
8	470	1.7

**TABLE V**  
**Factor Distribution and Particle Size Distribution for the Test Arrangement of  $U_8^*(8^5)$**

Sample no.	Test arrangement		Particle size distribution			
	$N$ (r/min)	$Q$ (L/min)	$Y_1$	$Y_2$	$Y_3$	$Y_4$
A1	260 (1)	0.9 (4)	0.623	0.332	0.045	2.74
A2	290 (2)	1.7 (8)	0.598	0.378	0.024	2.73
A3	320 (3)	0.7 (3)	0.408	0.461	0.131	2.20
A4	350 (4)	1.5 (7)	0.495	0.473	0.032	2.54
A5	380 (5)	0.5 (2)	0.278	0.559	0.163	1.94
A6	410 (6)	1.3 (6)	0.377	0.593	0.030	2.35
A7	440 (7)	0.3 (1)	0.165	0.667	0.168	1.75
A8	470 (8)	1.1 (5)	0.245	0.715	0.040	2.11

ating at 500 mm/min was used to determine the tensile properties of the rubber blends. Readings of 500% modulus, tensile strength, and percentage elongation at break were recorded directly from the digital displays at the end of each test. A test for hardness was carried out with a Shore A type durometer (Shanghai No. 4 Chemical Machinery Plant, Shanghai, China) according to ASTM D 2240-2002. All tests were conducted at room temperature (23–25°C).

**Scanning electron microscopy (SEM) studies**

SEM was obtained on a Philips XL30 FEG scanning electron microscope (Philips, Eindhoven, the Netherlands). The samples were covered with a layer of AuPd by a sputtering treatment. The surface images were obtained with the scanning electron microscope at an acceleration voltage of 15 keV. Surface energy spectrum analysis was carried out with an ED AX DX4I instrument (EDAX, AMETEK Co., Ltd., Mahwah, NJ) attached to the scanning electron microscope.

**RESULTS AND DISCUSSION**

**Particle size distribution of the PCR-121 particles**

Influence of heat treatment and coating agent content

As mentioned in some published articles about the preparation of powdered rubber with the method of

latex coagulation, heat-treatment processes and coating agents are two key technologies.<sup>16–19</sup> To evaluate these two points, six comparison experiments were put forward to show the influence of heat-treatment processes and coating agent contents. The results are shown in Table II.

In experiment A, the untreated CR121 latex was extruded into the coagulation solution with high-speed agitation; both the latex and the coagulation solution were at room temperature, and no coating agents were added into the latex.

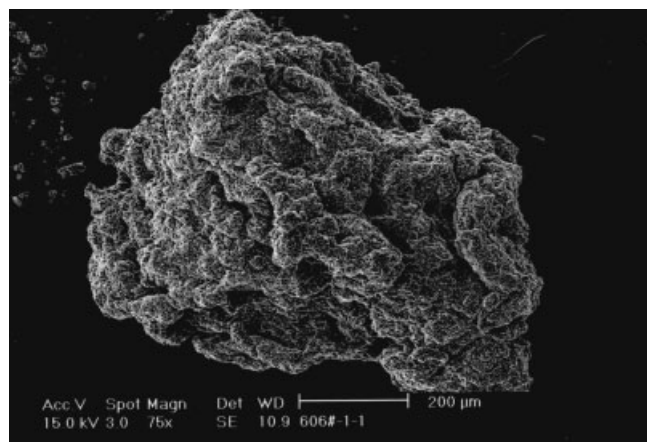
In experiment B, both the latex and the coagulation solution were kept at  $85 \pm 5^\circ\text{C}$ , and no coating agents were added into the latex during the heat-treatment process.

In experiments C, D, E, and F, the contents of the SN coating agent added into the latex during heat-treatment process were 1, 2, 3, and 5 phr, respectively.

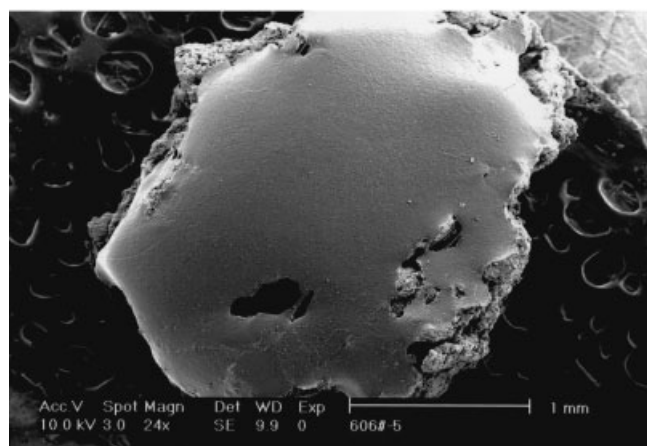
Because the SN coating agent could be dissolved in hot water above  $60^\circ\text{C}$ , heat treatment could help to disperse the SN coating agent uniformly into the CR latex. Although the CR latex drops were conglomerated by the coagulation solution, the SN coating agent at the surface and inside of the latex drops reacted *in situ* with  $\text{Ca}^{2+}$  to generate an undissolved coating layer at the surface of powdered rubber particles. This coating layer helped to keep the powdered rubber free flowing and to separate the individual particles, even

**TABLE VI**  
**Proofed Test for the Preparation of PCR by the Inverse Coagulation Method**

	Test sample no.					
	A9		A10		A11	
$N$ (r/min)	275		440		465	
$Q$ (L/min)	1.5		0.35		0.45	
Particle size distribution	Predicted value	Measured value	Predicted value	Measured value	Predicted value	Measured value
$Y_1$	0.688 (0.590–0.803)	0.642	0.184 (0.158–0.215)	0.171	0.187 (0.160–0.218)	0.183
$Y_2$	0.359 (0.338–0.381)	0.348	0.660 (0.622–0.701)	0.698	0.709 (0.668–0.733)	0.732
$Y_3$	0.030 (0.016–0.054)	0.018	0.193 (0.105–0.355)	0.131	0.139 (0.076–0.256)	0.085
$Y_4$	3.12 (2.92–3.35)	3.27	1.85 (1.72–1.98)	1.97	1.89 (1.76–2.02)	2.01



(a)



(b)

**Figure 1** SEM photo of PCR prepared by the inverse coagulation method: (a) overview; (b) cross section.

though the powdered particles were impacted under high pressure.

The particle size of PCR-121 in experiments D, E, and F were similar, which showed that 2–3 phr was the optimum content of coating agent for the preparation of PCR-121.

#### Inverse coagulation model of CR121 latex

There are two typical coagulation processes for the coagulation of rubber latex: one is normal coagulation, and the other is inverse coagulation. For the former,

the coagulation solution is added into the rubber latex; for the latter, rubber latex is extruded into the coagulation solution. Because the coagulation agent was normally greatly locally excessive to the rubber latex drops in inverse coagulation, a coagulation model of CR121 latex with the existence of the SN coating agent is put forward to explain the powdering process of inverse coagulation. Usually, the powdering process would comprise the three stages described next.<sup>16,20</sup>

First, the coagulation solution is simply agitated before the rubber latex is added.

Second, when the rubber latex is extruded into the coagulation solution with high-speed stirring, the latex stream is broken up into small drops by the high-speed flowing coagulation solution, and the small latex drops may be cut into smaller drops before they coagulate into small solid particles. In this stage, the rubber latex and the coagulation solution form a liquid–liquid agitation system.<sup>21–26</sup>

Third, after a very short time, the small latex drops generated in the second stage coagulate into small solid particles, and these solid particles are neither cut into smaller particles nor tacked with the other particles to form bigger particles.

On the basis of this three-stage coagulation model, the particle size distribution of PCR-121 could be expressed by the liquid drop size distribution of the CR latex in the coagulation solution. According to the second stage of the model, the liquid drop size distribution of the CR latex in the coagulation solution could be calculated on the basis of the liquid–liquid agitation theory of noncoalescing, liquid–liquid dispersion.<sup>21–26</sup> According to the powdered model of PCR latex in the inverse coagulation process by Lin et al.,<sup>20</sup> the drop size of the CR latex drops could be expressed by the following equation:

$$D_0 = C_0 N^a Q^b \quad (1)$$

where  $D_0$  is the mean drop size of the latex,  $N$  is the agitation speed,  $Q$  is the latex extruding speed, and  $a$ ,  $b$ , and  $C_0$  are constants. This means that the particle size of PCR-121 was only related to  $N$  and  $Q$ .

#### Influence of $N$ and $Q$

To study the relationship among the particle size distribution of PCR-121,  $N$ , and  $Q$ , a  $U_8^*$  ( $8^5$ ) uniform

**TABLE VII**  
Spectrum Analysis on the Surface of PCR-121

Analysis zone	Main element content (wt %)		
	C	Cl	Ca
Outside surface of a PCR-121 particle	49.5	37.4	4.97
Cross-section surface of a PCR-121 particle	51.6	38.5	0.84

**TABLE VIII**  
**Mechanical Properties of PCR-121 and Bale CR**

Property	PCR-121 <sup>a</sup>						Bale CR121	CR121–alcohol
	B1	B2	B3	B4	B5	B6		
Peptisation time (min)	160	120	100	80	40	30	—	—
ML <sub>1+4</sub> 100°C	30	42	53	66	123	131	33	71
Mooney scorch (min)	25	40	>60	43	60	37	25	18.5
Scorch time (min)	9.5	11	11.5	10.5	12	11	9.5	8.5
t <sub>90</sub> (min)	21.5	22	24.5	22	23.5	21	19	17
500% modulus (MPa)	3.0	4.0	3.8	3.5	3.3	3.1	4.8	5.2
Tensile strength (MPa)	23.0	26.1	23.7	26.6	24.2	23.3	24.3	19.0
Elongation at break (%)	980	910	880	990	960	940	880	850
Permanent set (%)	16	14	16	18	16	14	20	14
Shore A hardness	46	47	47	47	47	47	45	44
Tear strength (N/m)	23.5	22.3	26.5	24.2	22.3	25.3	24.6	22.1

<sup>a</sup> SN content = 2.5 phr.

design table<sup>27</sup> was chosen to arrange the two influence factors *N* and *Q*. The uniform design is shown in Table III, and the variable levels of these two factors are listed in Table IV. The test results are shown in Table V.

The particle size distributions and the mean particle sizes were determined by standard mesh. Four dependent variables (*Y*<sub>1</sub>–*Y*<sub>4</sub>) were chosen as evaluation indicators, where *Y*<sub>1</sub>, *Y*<sub>2</sub>, and *Y*<sub>3</sub> are the mass fractions of particles 3–5, 1–3, and less than 1 mm in size, respectively, and *Y*<sub>4</sub> is the arithmetical mean particle size and is calculated with the following expression:

$$Y_4 = Y_1 \cdot 4.0 + Y_2 \cdot 2.0 + Y_3 \cdot 0.5 \quad (2)$$

The test result data were processed with step regression analysis by Statistic Analysis System software (SAS Institute Inc., Cary, NC) to reject the nonsignificant variable, with a variable selected level of 0.05; the following expressions were determined:

$$Y_1 = e^{(8.301 \pm 0.154)} N^{-1.573} Q^{0.398} \quad (3)$$

$$Y_2 = e^{(-8.304 \pm 0.060)} N^{1.296} \quad (4)$$

$$Y_3 = e^{(-3.000 \pm 0.610)} Q^{-1.289} \quad (5)$$

$$Y_4 = e^{(3.947 \pm 0.069)} N^{-0.514} Q^{0.195} \quad (6)$$

Equation (4) shows that the mass fraction of the middle-size particles (*Y*<sub>2</sub>) had a nonsignificant relationship with *Q*, whereas the mass fraction of the

small particles (*Y*<sub>3</sub>) was just related to *Q*. With increasing *N* and decreasing *Q*, the mean particle size (*Y*<sub>4</sub>) was reduced.

To verify the expressions put forward in eqs. (3)–(6), three additional tests were carried out, and the test results are shown in Table VI.

A comparison between the predicted and measured values showed that eqs. (3)–(6) predicted the particle size distribution of PCR-121 in the experimental range.

As shown in Figure 1, the PCR-121 particle was almost an irregular sphere with an irregular surface, and the section morphology showed that the PCR-121 particle was not a particle agglomerated from a lot of smaller particles but a continuous intact particle, which confirmed that the PCR-121 particles were coagulated from single CR latex drops. The particle size of PCR-121 particles was determined by the CR latex drop size.

Energy spectrum analysis showed that the Ca element content at the surface of the PCR-121 particles was higher than that of the section of the PCR-121 particles (i.e., the inner part of the PCR-121 particles), as shown in Table VII. After the CR latex drops were coagulated as solid, the SN coating agent at the surface of the solid continue to react *in situ* with the Ca ions in the coagulation solution, as shown in eq. (7), which resulted in the surface calcification of the PCR-121 particles. A high Ca content layer then coated the surface of the PCR-121 particles, which contributed to the separation of the PCR-121 particles:



TABLE IX  
Spectrum Analysis of the Tensile Fracture Surface of the PCR Vulcanizate

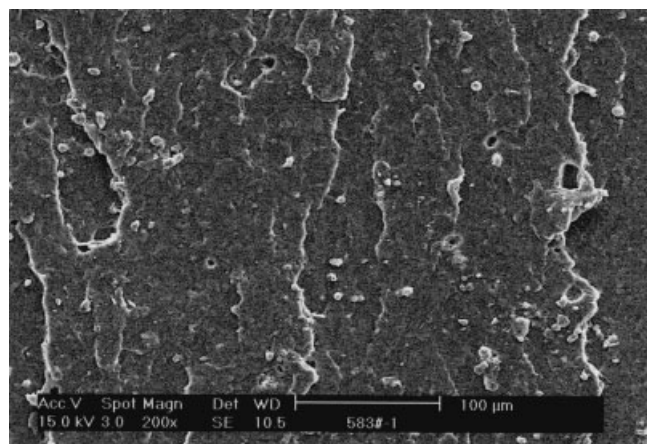
Sample	Analysis zone	Main element contents (wt %)				Inferred material
		C	Cl	Mg	Zn	
Bale CR 121	A	18.0	13.5	39.9	24.9	Rich ZnO and MgO particles
CR121-alcohol	B	33.6	25.7	2.67	31.8	Rich ZnO particles

### Mechanical properties of PCR

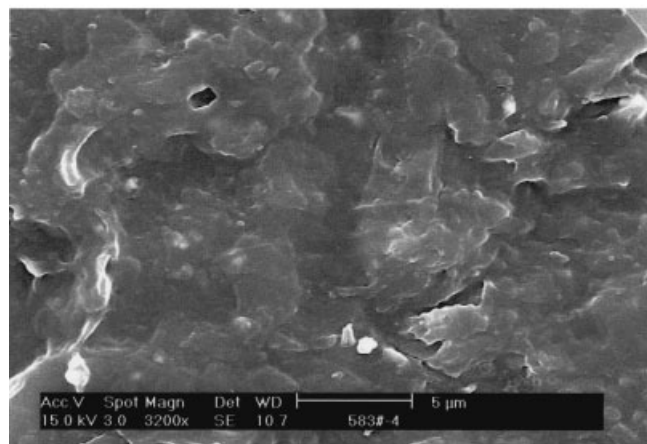
Because the molecular weight of the sulfur-modified PCR was adjusted by the peptizing agent (TETD), the main influence factors included the peptization temperature, peptization time, and peptizing agent content. In practice, peptization time is usually chosen to adjust the molecular weight, that is, the Mooney viscosity of the sulfur-modified PCR. In this study, a series of peptization times was selected to obtain different Mooney viscosities, as shown in Table VIII.

Although as a comparison, the mechanical properties of bale sulfur-modified PCR (bale CR121) and the bale rubber coagulated from peptized sulfur-modified PCR latex with ethyl alcohol (CR121-alcohol) are also listed in Table VIII.

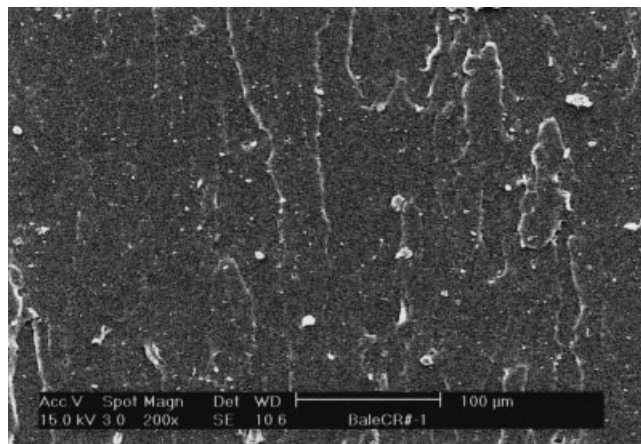
At a wide Mooney viscosity range of 30–130, PCR-121 showed better mechanical properties, especially better scorch properties, than the comparison sample of CR121-alcohol and bale CR121. Although the processing properties of PCR-121 were better than those of bale rubber, it was easier for PCR-121 to form a



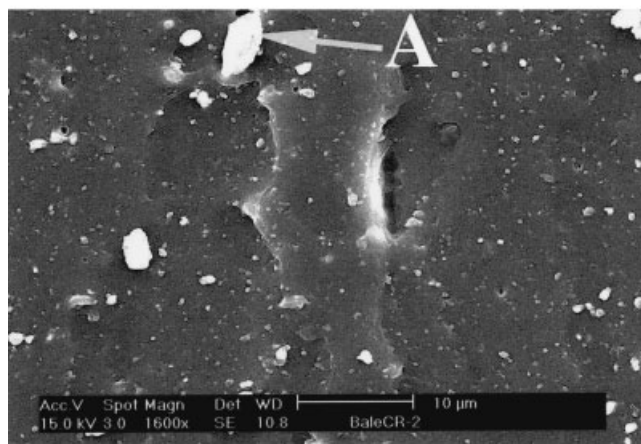
(a)



(b)



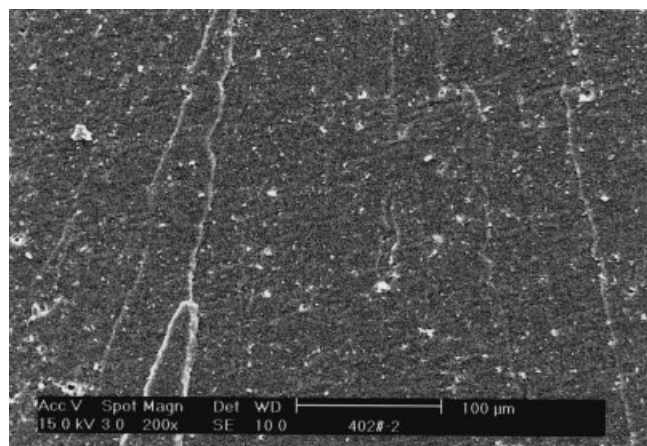
(a)



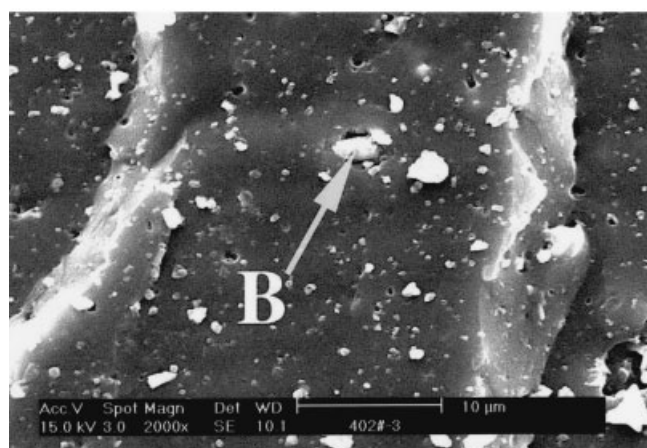
(b)

Figure 2 SEM photo of the tensile fracture surface of PCR prepared by the inverse coagulation method: (a)  $\times 200$ ; (b)  $\times 3200$ .

Figure 3 SEM photo of the tensile fracture surface of bale CR121 prepared by the conventional method: (a)  $\times 200$ ; (b)  $\times 1600$ .



(a)



(b)

**Figure 4** SEM photo of the tensile fracture surface of CR121-alcohol: (a)  $\times 200$ ; (b)  $\times 2000$ .

band around the mixing roll even with a higher Mooney viscosity. As the SN coating agent was similar to wax with a low molecular weight, it helped with the lubrication of polymer chains and the dispersion of filler in the rubber.

The tensile fracture surfaces of PCR-121, bale CR121, and the CR121-alcohol vulcanizate are shown in Figures 2–4. Many small particles with diameters of 0.5–5  $\mu\text{m}$  were found in the fracture surfaces of bale CR121 and the CR121-alcohol vulcanizate, whereas the fracture surface of the PCR-121 vulcanizate was somewhat smooth with no obvious similar particles. Energy spectrum analysis showed that these small particles were nondispersed agglomerated particles of magnesium oxide or zinc oxide, as shown in Table IX. So the dispersion of processing agents and fillers in PCR-121 was better than that of bale CR121.

## CONCLUSIONS

A powdering model was developed based on the liquid-liquid stirring theory of noncoalescing, liquid-liquid dispersion, which was proven with uniform design testing. According to this model, the mass fraction of medium-scale particles (1–3 mm) was only related to  $N$  in the experimental range.

SEM analysis showed that the PCR-121 particles were single continuous particles coagulated from single CR latex drops. Energy spectrum analysis showed that a layer with higher Ca content coated the surface of the PCR-121 particles.

The results showed that the variations in Mooney viscosity ( $ML_{1+4}$  100°C) between 30 and 130 had no obvious effect on the mechanical properties of PCR-121. Compared with bale CR121 and CR121-alcohol, PCR-121 showed better mechanical properties, which benefited from the better filler dispersion in PCR-121.

## References

- Murray, R. M.; Thompson, D. C. *The Neoprenes*; DuPont de Nemours: Wilmington, DE, 1963.
- Johnson, P. R. *Rubber Chem Technol* 1976, 49, 650.
- Evans, C. W. *Powdered and Particulate Rubber Technology*; Applied Science: London, 1978.
- Widmer, H. *Rubber Age* 1974, 106, 185.
- Yacoe, J. C. U.S. Pat. 2,879,173 (1959).
- Hedberg, Y. G. U.S. Pat. 3,194,781 (1965).
- Conley, J. B. U.S. Pat. 3,311,601 (1967).
- Turner, N. L. U.S. Pat. 3,988,306 (1976).
- Turner, N. L. U.S. Pat. 4,098,989 (1978).
- Shimizu, A. U.S. Pat. 3,969,334 (1976).
- Nothen, K.; Creixell, F. B.; Ehrig, B. U.S. Pat. 4,127,945 (1978).
- Bice Archie, R.; Burchett, D. K. U.S. Pat. 4,136,251 (1979).
- Musech, R.; Gobel, W.; Muller, E.; Konter, W. U.S. Pat. 4,452,947 (1984).
- Musech, R.; Gobel, W.; Muller, E.; Konter, W. U.S. Pat. 4,482,676 (1984).
- Wang, L.; Zhang, A.; Zhou, Y. China Pat. 02134362 (2003).
- Zhang, A. Ph.D. Dissertation, South China University of Technology, 2003.
- Wang, L.; Hu, H.; Zhou, Y. *Hecheng Xiangjiao Gongye/China Synth Rubber Ind* 2003, 26, 5.
- Wang, L.; Hu, H.; Zhou, Y. *Hecheng Xiangjiao Gongye/China Synth Rubber Ind* 2003, 26, 212.
- Zhou, Y.; Xu, T.; Wang, L. *Hecheng Xiangjiao Gongye/China Synth Rubber Ind* 2003, 26, 288.
- Lin, Y.; Zhang, A.; Wang, L.; Zhou, Y. *J Chem Eng Chinese Univ* 2005, 19, 486.
- Ali, A. M.; Yuan, H. H. S.; Dickey, D. S. *Chem Eng Commun* 1981, 4, 205.
- Calabrese, R. V.; Chang, T. P. K.; Dang, P. T. *AIChE J* 1986, 32, 657.
- Wang, C. Y.; Calabrese, R. V. *AIChE J* 1986, 32, 667.
- Calabrese, R. V.; Wang, C. Y.; Bryner, N. P. *AIChE J* 1986, 32, 677.
- Chen, H. T.; Middleman, S. *AIChE J* 1967, 13, 989.
- Brown, D. E.; Pitt, K. *Chem Eng Sci* 1972, 27, 577.
- Fang, K. *Uniform Design and the Uniform Design Table*; China Science: Beijing, 1994.