# Mechanical Properties and Crosslink Density of Rare Earth-Modified High-Abrasion Furnace-Filled Powdered Natural Rubber

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Received 8 December 2005; accepted 2 March 2006
DOI 10.1002/app.24407

**ABSTRACT:** High-abrasion furnace-filled powdered natural rubber [P(NR/HAF)] has more advantages than traditional HAF-filled bale NR (NR/HAF) because of its better environmental performance and easier processing quality, but its lower mechanical properties are disadvantageous. To improve the mechanical properties, rare earth-modified HAF-filled powdered NR [P(NR/HAF-Ln)] (Ln = Sm,La,Pr) was prepared by means of coacervation–coprecipitation, using rare earth-modified HAF as separant and filler. The effect on mechanical properties of P(NR/HAF-Ln) vulcanizate exerted by the emulsifier/HAF ratio, powdering temperature, Ln/HAF ratio and type of Ln, and HAF content were studied. The results indicated that when optimum formulation, the mechanical properties of P(NR/HAF-Ln) vulcanizate were better than P(NR/HAF) vulcanizate. In addition, the relationship of the apparent crosslink density and HAF content of P(NR/HAF-Ln), P(NR/HAF), NR/HAF vulcanizates was also investigated, along with their SEM microphotographs of tensile fracture surface, which indicated that the excellent mechanical properties of P(NR/HAF-Ln) vulcanizate was attributed to correct amount of Ln that could increase crosslink density and reinforce the interface structure of NR matrix/HAF-Ln particle. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1755–1762, 2006

**Key words:** rare earth-modified HAF; powdered natural rubber; mechanical property; crosslink density; SEM

## INTRODUCTION

Filled powdered rubber means powdered raw rubber filled with carbon black, $CaCO_3$, clay, $SiO_2$, or other fillers. Carbon black has small particle size and high surface activity; among all these fillers, carbon black has the most prominent effect on rubber reinforcement,[1] which makes it the most important reinforcing filler. Filled powdered rubber is prepared by means of coacervation–coprecipitation[2] after rubber latex and filler emulsion are evenly mixed. Its particle diameter is less than 1.0 mm, and the particles have good flowing property,[3,4] without contact-contamination also. The powdered rubber can be processed by plastic process technique such as extrusion, injection, and die processing, as well as traditional rubber process techniques. This filled powdered rubber has advantages of simple process, energy saving, timesaving, lower manufacturing cost, excellent dispersion of filler in rubber, and good vulcanizate mechanical properties. Filled powdered rubber, especially carbon black-filled powdered rubber, has no fluffy black, which can usually make black environmental contamination when processing.

Non contact-contamination HAF-filled powdered natural rubber [P(NR/HAF)] has been prepared successfully by means of coacervation–coprecipitation, but found that its vulcanizates has lower mechanical properties when compared to that of traditional HAF-filled bale NR (NR/HAF), especially the 300% modulus. That is because, in the powdering system, made up of rubber latex and carbon black emulsion, the surface activity of carbon black particles can be damaged by water and impurities in rubber latex, which weakens the combining power between the carbon black particles and rubber, and results in the damage of vulcanizate mechanical properties. To compensate for the lost surface activity, the surface of carbon black particles must be modified. Rare earth is an important ingredient when producing luminescent, electric, and magnetic materials[5–7] because of its special electronic structure. In the synthesis field of polymer, the compound of rare earth can be used as catalyzer of olefin monomer polymerization.[8] In recent years, it was reported that the crystallization behavior of crystalline polymer can be improved by rare earth oxide powder

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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 number: 031366.

Journal of Applied Polymer Science, Vol. 102, 1755–1762 (2006)

and crystalline polymer compounds, so as the processing ability and mechanical properties.[9] Few studies were published on rare earth application in rubber but accelerating vulcanizate as accelerant.[10] The reinforcement of rare earth to HAF-filled natural rubber has not been reported by now. The atomic orbital of rare earth might have some reaction with double bonds in natural rubber. In this article, rare earth compound was used to modify carbon black particles surface in emulsion, and rare earth-modified HAF-filled powdered NR [P(NR/HAF-Ln)] (Ln = Sm, La, Pr) has been prepared to raise the interface combining power between molecular chains of natural rubber and carbon black particles, and so as the mechanical properties of the vulcanizates. The regularity of crosslink density[11,12] and interface structure of the vulcanizates were also discussed.

## EXPERIMENTAL

### Materials

NR latex (Malaysia, 1#; solid content, 60 wt %) was supplied by Guangzhou No.11 Rubber Factory (Guangzhou, China). High-abrasion furnace black (HAF, grade N330) was supplied by Shanghai LIDE Chemical (Shanghai, China). Bale NR (Hainan, Standard 5#, Hainan, China), 10 wt % $CaCl_2$ water solution was prepared in the laboratory and used as a coagulation agent. Rare earth oxide (product purity, 99.99 wt %) was supplied by Guangdong Zhujiang Rare Earths (Guangzhou, China). Toluene (AR) was supplied by Guangzhou Chemical Reagent Factory (Guangzhou, China). The other agents were all common commercially available materials.

### Sample preparation and physical testing

P(NR/HAF-Ln) was prepared as follows:

1. Distilled water and emulsifier were charged to a flask, and the mixture was stirred for 15 min to make emulsifier solution.
2. Carbon black was added to the emulsifier solution, and stirred for 30 min to form a carbon black emulsion.
3. Water solution of rare earth salt was added to the carbon black emulsion, and stirred for 20 min, and then ammonia water was added to adjust PH scale to 9.0–10.0, and stirred for 30 min with low-shear agitation.
4. NR latex was added and stirred for 30 min to form a "powdering system."
5. 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.
6. Antiaging agent 264 was added, and stirred for 15 min.
7. A 10% $CaCl_2$ water solution was added to the mixture at 85°C under high-speed agitation, and stirred for 20 min. Powered sediment appeared in the powdering system.
8. The powdered rubber products were filtered and washed with water, sieved by boult, and dried on trays in a forced draft oven at 85°C for about 2 h until the water content was below 1%. Thus, the rare earth-modified HAF-filled powdered rubber product, P(NR/HAF-Ln), was obtained.

**TABLE I**
**Formulation of NR Compound**

| Ingredient | Composition (phr)[a] |
|---|---|
| NR (powder or bale) | 100 |
| Zinc oxide | 4.17 |
| Stearic acid | 1.67 |
| Sulfur | 1.5 |
| Accelerator TT | 0.13 |
| Accelerator DM | 1.08 |
| Antiaging agent 264 | 2 |
| Carbon black (HAF, N330) | Variable |
| Rare earth | Variable |

[a] phr, parts per hundred parts NR.

P(NR/HAF) was prepared using the same preparation process but omitting the step 3.

### Preparation of vulcanizates and physical testing

The blend composition of P(NR/HAF-Ln), P(NR/HAF), and NR/HAF were listed in Table I. The compounds were blended using a 6-inch two-roll blender mill till banding, and after 10 times of triangle mixing, the rubber compounds were prepared. After 24 h of storage, the rubber compounds were vulcanized into 2-mm thick test specimens at 145°C according to their cure times ($t_{90}$), after GB9869–88, determined by the disk oscillating vulkameter (LH-II; Shanghai Rubber Machinery Works No. 1). The tensile and tear testing specimens were cut into dumbbell shape and right-angle shape, respectively.

The tensile and tear testing procedure was carried out in accordance with GB/T 528–92 and GB/T 529–91, respectively. An DXLL-2500 electronic tension machine (Shanghai No. 4 Chemical Machinery Factory, China), operating at 500 mm/min, was used to determine the tensile and tear properties of the vulcanizate. Readings of tensile strength, tensile modulus, M100 (modulus at 100% elongation), M300 (modulus at 300% elongation), percentage elongation at break, and tensile strength 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

**TABLE II**
**Influence of Emulsifier/HAF Ratio on the Mechanical Properties of P(NR/HAF-Ln)[a] Vulcanizate**

| | Emulsifier/HAF ratio (%) | | | |
|---|---|---|---|---|
| Property | 4 | 6 | 8 | 10 |
| Tensile strength (MPa) | 24.2 | 26.3 | 27.0 | 24.5 |
| 100% modulus (MPa) | 2.4 | 2.4 | 1.9 | 1.9 |
| 300% modulus (MPa) | 10.8 | 11.8 | 11.0 | 10.0 |
| Elongation-at-break (%) | 490 | 510 | 510 | 540 |
| Permanent set (%) | 40 | 30 | 40 | 40 |
| Tear strength (kN/m) | 68.2 | 69.3 | 81.8 | 82.7 |
| Hardness (Shore A) | 56 | 59 | 57 | 56 |

[a] $Ln_2O_3$/HAF ratio = 1%, (Ln = Sm); HAF, 50 phr.

(XY-1; Shanghai No. 4 Chemical Machinery Factory, China) according to GB/T 531–92. All tests were conducted at room temperature (23–25°C).

### Crosslink density testing

Swelling index (SI) was used to indicate apparent crosslink density in this article.

SI was tested as follows. The rubber compounds were vulcanized into 0.5-mm thick test specimens at 145°C in a flat slab vulcanizer, which provide pressure of 25 MPa according to their cure times ($t_{90}$). Test specimen (30–40 mg) was taken (error range is 0.1 mg) and put into a brown ground glass stoppered bottle, then 50 mL toluene was added into the bottle, and sealed it with ground glass stopper. After 24 h, the specimen was quickly removed from the bottle onto a clean and dry filter paper, then the paper was folded to absorb toluene on specimen's surface and the specimen was weighted with torque balance (JN-A), $W_b$ represents this weight. $W_a$ is the dry specimen weight after drying the specimen in an oven at 60°C for 24 h, both error rage is 0.1 mg. Use the following equation to calculate SI.

$$SI = W_b / W_a$$

where, $W_a$ is the dried specimen weight after swelling test (in grams) and $W_b$ is the specimen weight after swelling (in grams).

### Scanning electron micrograph studies

Scanning electron micrographs (SEMs) were taken using 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

### Influence of mechanical properties of P(NR/HAF-Ln) vulcanizate

#### Influence of emulsifier/HAF ratio

The mechanical properties of P(NR/HAF-Ln) vulcanizate, with different emulsifier/HAF ratios, are presented in Table II. With increasing emulsifier content, tensile strength reached maximum value when emulsifier/(HAF-Ln) ratio is 8%. That is because when emulsifier content is suitable, emulsifier was only distributed on the surface of HAF-Ln cluster, which make the emulsifier easier to wash out to let NR molecular chain combine with the activity point of HAF-Ln particles directly, and form a tight interface and increase the tensile strength. When emulsifier content increases more, hard-washed-out residual emulsifier in HAF-Ln cluster would damage the combination of NR molecular chain and cluster.

The tear strength increase with increasing emulsifier content, and reach above 81 MPa when the emulsifier/HAF ratio is 8–10%. It is because with the increase of emulsifier content, although the size of the HAF-Ln clusters became smaller, its quantity increases, therefore tear cracks get more chances to encounter the cluster and to be terminated, deflected, branched or to form shorter cracks, which are propitious to improve tear strength of the vulcanizates. The other mechanical properties are relatively unchanged when emulsifier content increase. Thus the optimum emulsifier/HAF ratio is 8%.

#### Influence of powdering temperature

Powdering temperature is the heating-up and agglomeration temperature of powdering system. The mechanical properties of P(NR/HAF-Ln) vulcanizate, with different powdering temperature, are presented in Table III. Tensile strength, elongation at break, and tear strength increase with increasing temperature. The other mechanical properties are relatively un-

**TABLE III**
**Influence of Powdering Temperature on the Mechanical Properties of P(NR/HAF-Sm)[a] Vulcanizate**

| | Powdering temperature (°C) | | |
|---|---|---|---|
| Property | 20 | 60 | 85 |
| Tensile strength (MPa) | 20.8 | 25.7 | 26.6 |
| 100% modulus (MPa) | 3.5 | 3.3 | 2.6 |
| 300% modulus (MPa) | 12.2 | 12.5 | 11.8 |
| Elongation-at-break (%) | 420 | 480 | 510 |
| Permanent set (%) | 30 | 35 | 35 |
| Tear strength (kN/m) | 65.8 | 66.4 | 73.1 |
| Hardness (Shore A) | 63 | 58 | 59 |

[a] $Ln_2O_3$/HAF ratio = 1%, (Ln = Sm); HAF, 50 phr.

**TABLE IV**
**Influence of $Sm_2O_3$/HAF ratio on the Mechanical Properties of P(NR/HAF-Sm)[a] Vulcanizate**

| | $Sm_2O_3$/HAF ratio (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Property | 0.25 | 0.5 | 0.75 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 0 |
| Tensile strength (MPa) | 26.2 | 25.4 | 24.0 | 26.0 | 26.2 | 23.5 | 24.8 | 27.5 | 24.6 |
| 100% modulus (MPa) | 2.8 | 3.0 | 3.0 | 2.6 | 3.0 | 3.0 | 2.2 | 3.1 | 2.4 |
| 300% modulus (MPa) | 11.6 | 12.3 | 12.9 | 11.8 | 12.2 | 10.4 | 9.6 | 10.8 | 9.1 |
| Elongation-at-break (%) | 510 | 490 | 470 | 510 | 500 | 520 | 570 | 560 | 560 |
| Permanent set (%) | 40 | 35 | 30 | 35 | 40 | 30 | 30 | 35 | 30 |
| Tear strength (kN/m) | 69.8 | 85.9 | 72.3 | 65.9 | 79.4 | 78.4 | 80.0 | 98.2 | 77.8 |
| Hardness (Shore A) | 60 | 60 | 56 | 59 | 59 | 52 | 51 | 54 | 52 |

[a] NR, 100 phr; HAF, 50 phr.

changed. Generally, the optimum powdering temperature is 85°C.

## Influence of $Sm_2O_3$/HAF ratio

The mechanical properties of P(NR/HAF-Sm) vulcanizate, with different $Sm_2O_3$/HAF ratio, are shown in Table IV. With the increase of $Sm_2O_3$/HAF ratio, tensile strength shows little fluctuation, 300% modulus are relatively unchanged when $Sm_2O_3$/HAF ratio is between 0.25 and 1.5%, but lower when $Sm_2O_3$/HAF ratio is between 2.0 and 3.0%. Elongations at break has a minimum value, and tear strength increases. Compared to P(NR/HAF), tensile strength and 300% modulus of the vulcanizates increase remarkably.

## Influence of $La_2O_3$/HAF ratio

The mechanical properties of P(NR/HAF-La) vulcanizate, with different $La_2O_3$/HAF ratio, are presented in Table V. Tensile strength and tear strength increase with increasing $La_2O_3$/HAF ratio, the other mechanical properties are relatively unchanged.

## Influence of $Pr_6O_{11}$/HAF ratio

Table VI presents the mechanical properties of P(NR/HAF-Pr) vulcanizate with different $Pr_6O_{11}$/HAF ratio, tear strength achieves a maximum value of 93.9 KN/m with $Pr_6O_{11}$/HAF ratio of 2.5%. The other mechanical properties are relatively unchanged.

## Influence of HAF contents

"1Sm" in P (NR/HAF-1Sm) means the $Sm_2O_3$/HAF ratio is 1%. "3Sm" in P (NR/HAF-3Sm) means the $Sm_2O_3$/HAF ratio is 3%.

Figure 1(a) shows the tensile strength of P(NR/HAF-3Sm), P(NR/HAF-1Sm), P(NR/HAF), and NR/HAF with different HAF contents. As shown in Figure 1(a), tensile strength of P(NR/HAF-3Sm) was remarkably higher than the other three vulcanizates when HAF content was the same. Tensile strength of P(NR/HAF-3Sm) and P(NR/HAF-1Sm) vulcanizates started from the highest tensile strength and simply decrease with increasing HAF content, whereas the other two vulcanizates has maximum value with HAF content of 25 and 30 phr. With the increase of HAF content, tensile strength of the four vulcanizates all decrease when HAF-Sm content is between 10 and 100 and HAF content is between 30 and 100, respectively. Generally, the tensile strength of the four vulcanizates are P(NR/HAF-3Sm) > P(NR/HAF-1Sm)≈P(NR/HAF) > NR/HAF.

The 100% modulus of the four vulcanizates with increasing HAF contents are plotted in Figure 1(b). Hundred percent modulus of the four vulcanizates increase with increasing HAF content, when HAF con-

**TABLE V**
**Influence of $La_2O_3$/HAF ratio on the Mechanical Properties of P(NR/HAF-La)[a] Vulcanizate**

| | $La_2O_3$/HAF ratio (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| Property | 0.25 | 0.5 | 0.75 | 1.0 | 1.5 | 2.0 | 2.5 |
| Tensile strength (MPa) | 22.8 | 22.6 | 21.9 | 25.3 | 23.2 | 24.1 | 25.7 |
| 100% modulus (MPa) | 3.2 | 3.3 | 2.9 | 3.3 | 3.4 | 3.4 | 3.4 |
| 300% modulus (MPa) | 12.6 | 13.9 | 12.5 | 12.8 | 12.7 | 13.4 | 13.1 |
| Elongation-at-break (%) | 430 | 400 | 440 | 470 | 450 | 470 | 480 |
| Permanent set (%) | 30 | 30 | 25 | 30 | 30 | 30 | 35 |
| Tear strength (KN/m) | 63.2 | 68.7 | 76.5 | 76.9 | 71.4 | 78.0 | 83.3 |
| Hardness (Shore A) | 59 | 60 | 57 | 56 | 55 | 57 | 55 |

[a] NR, 100 phr; HAF, 50 phr.

**TABLE VI**
**Influence of $Pr_6O_{11}$/HAF ratio on the Mechanical Properties of P(NR/HAF-Pr)[a] Vulcanizate**

| | $Pr_6O_{11}$/HAF ratio (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| Property | 0.25 | 0.5 | 0.75 | 1.0 | 1.5 | 2.0 | 2.5 |
| Tensile strength (MPa) | 23.4 | 23.8 | 23.8 | 22.9 | 22.6 | 23.1 | 24.6 |
| 100% modulus (MPa) | 2.7 | 3.0 | 2.5 | 2.8 | 2.7 | 2.8 | 2.8 |
| 300% modulus (MPa) | 11.4 | 12.9 | 12.2 | 11.8 | 11.1 | 12.2 | 13.0 |
| Elongation-at-break (%) | 490 | 480 | 470 | 460 | 470 | 450 | 460 |
| Permanent set (%) | 35 | 30 | 30 | 30 | 30 | 40 | 30 |
| Tear strength (kN/m) | 78.7 | 81.3 | 65.3 | 70.7 | 78.1 | 91.8 | 93.9 |
| Hardness (Shore A) | 58 | 59 | 59 | 59 | 58 | 59 | 60 |

[a] NR, 100 phr; HAF, 50 phr.

tent is more than 60 phr, their increase speed up synchronously. Hundred percent modulus of P(NR/HAF-3Sm) is 1 MPa higher than that of the other three vulcanizates.

The plot of 300% modulus of the four vulcanizates versus HAF content is shown in Figure 1(c). Three hundred percent modulus of the four vulcanizates all increase with increasing HAF content. But when HAF content is the same, 300% modulus of P(NR/HAF-3Sm) vulcanizate is obviously higher than the other two powdered NR, which prove that optimum Sm content can remarkably improve 300% modulus of P(NR/HAF) vulcanizate. Yet, 300% modulus of NR/HAF increase faster with increasing HAF content, and exceeds the other three vulcanizates when HAF content is about 25 phr.

Figure 1(d) shows the curves of tear strength of the four vulcanizates versus HAF content. All the vulcanizates have the maximum value, tear strength of the three powdered NR vulcanizates is obviously higher than that of NR/HAF. Among the three powdered NR vulcanizates, tear strength of P(NR/HAF-3Sm) vulcanizate is highest when HAF content is between 10 and 80 phr. Although NR/HAF vulcanizate achieve a maximum value when HAF content is 60, powdered NR vulcanizate reach its crest value when HAF con-

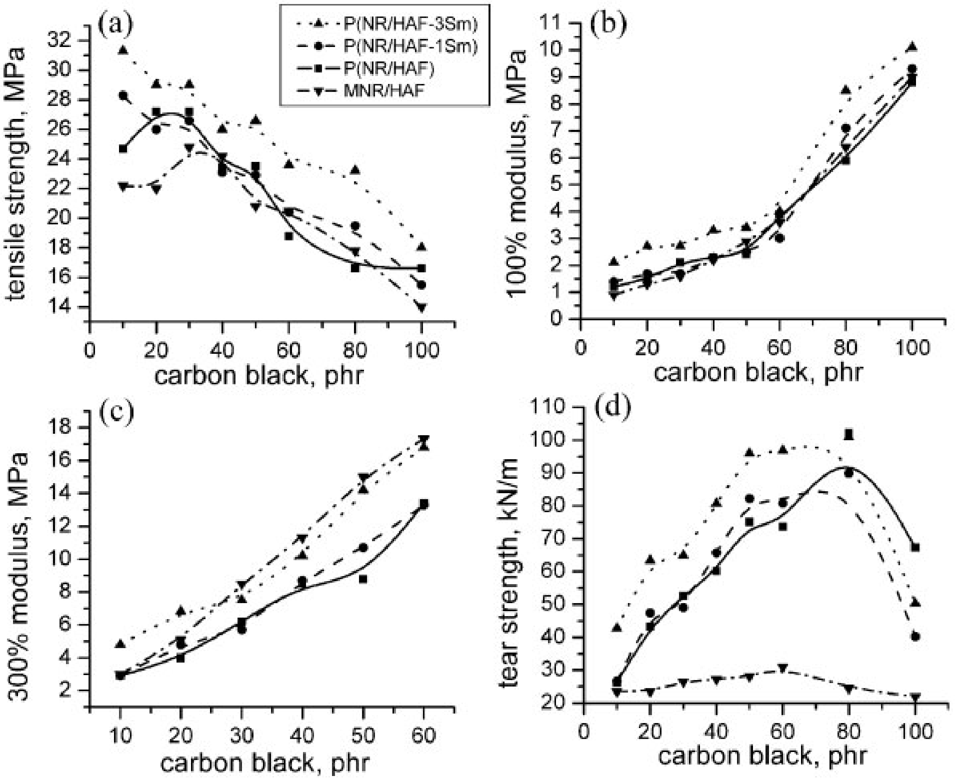

**Figure 1** (a) Tensile strength versus carbon black content, (b) 100% modulus versus carbon black content, (c) 300% modulus versus carbon black content, (d) tear strength versus carbon black content for P(NR/HAF-3Sm), P(NR/HAF-1Sm), P(NR/HAF), and NR/HAF vulcanizates.

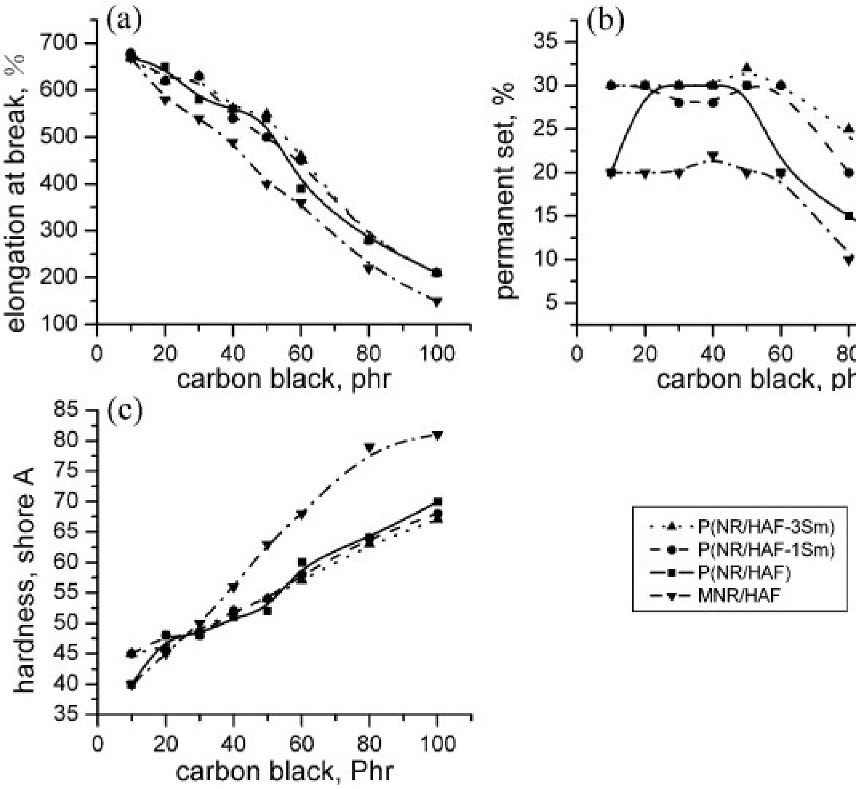

**Figure 2** (a) Permanent set versus carbon black content, (b) elongation at break versus carbon black content, (c) hardness versus carbon black content for P(NR/HAF-3Sm), P(NR/HAF-1Sm), P(NR/HAF), and NR/HAF vulcanizates.

tent is just 80 phr, P(NR/HAF-3Sm) vulcanizate even reaches 100.9 kN/m.

Figures 2(a)–2(c) show the curves of elongation at break, permanent set and hardness of the four vulcanizates versus HAF content, respectively.

As shown in Figure 2(a), elongations of all vulcanizates decrease with increasing HAF content. When HAF content is the same, the elongation degree of the four vulcanizates are P(NR/HAF-3Sm) > P(NR/HAF-1Sm)≈P(NR/HAF) > NR/HAF.

Figure 2(b) shows that with increasing HAF content, almost all the four permanent set has a flat curve first, and then decrease. When HAF content is the same, permanent set of P(NR/HAF-3Sm) vulcanizate is the highest and that of NR/HAF vulcanizate is the lowest.

As known from Figure 2(c), hardness of all vulcanizates increase with the increase of HAF content. When HAF content is the same, hardness of P(NR/HAF-3Sm) have little differences with the other two powdered NR, but all of them are lower than NR/HAF vulcanizate when the HAF content more than 25 phr.

### Influence of black carbon content on the crosslink density

Figure 3 shows the curves of crosslink density of the four vulcanizates versus HAF content. When NR/vulcanized agent ratio is constant, SI of all the four vulcanizates gradually decrease with increasing HAF content, in other words, apparent crosslink density gradually increase. Therefore, the increase of HAF content can obviously raise apparent crosslink density. When HAF content is the same, the SI of the four

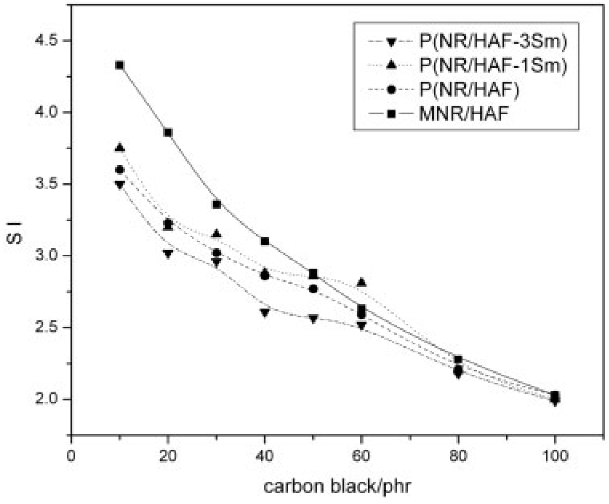

**Figure 3** Swelling index versus carbon black content for MNR/HAF, P(NR/HAF), and P(NR/HAF-Sm) vulcanizates.

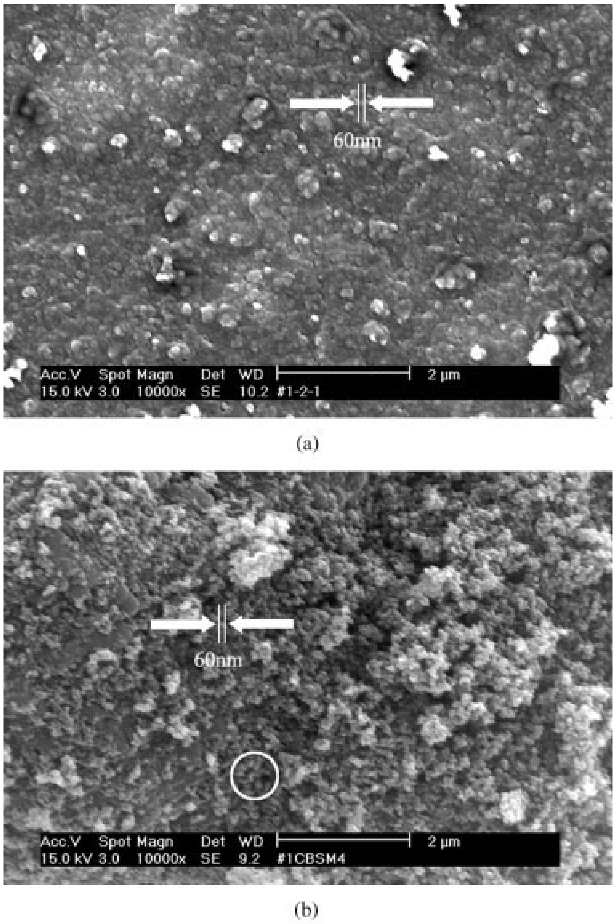

**Figure 4** SEM microphotographs of (a) HAF (×10,000); (b) HAF-2Sm (×10,000).

vulcanizates are P(NR/HAF-3Sm) < P(NR/HAF-1Sm)≈P(NR/HAF) < NR/HAF. SI of the four vulcanizates are almost the same when HAF content is 100 phr. The results show that apparent crosslink density of P(NR/HAF-3Sm) vulcanizate is obviously higher than the other three vulcanizates when HAF content is the same. This proves that HAF-3Sm cluster can remarkably increase apparent crosslink density of vulcanizate, which results in improved tensile strength and tear strength, moreover, 100% modulus and 300% modulus are distinctly higher than that of P(NR/HAF) either.

## SEM analysis

### Surface of HAF and HAF-Sm

Figure 4(a,b) shows scanning election micrographs of HAF and HAF-Sm, and $Sm_2O_3$/HAF ratio is 2%. As shown in Figure 4(a), carbon black particles size are about 60 nm before being modified, and presents close packing structure. When $Sm_2O_3$/HAF ratio is 2%, particle size of carbon black did not change, whereas HAF-Sm particles began to adhere to each other and fluffy structure of HAF-Sm particles is observed, circled by a white ring as shown in Figure 4(b), which demonstrates that carbon black has been modified. Spaces inside HAF-Sm provided by this fluffy structure are propitious to be infiltrated by NR latex particles.

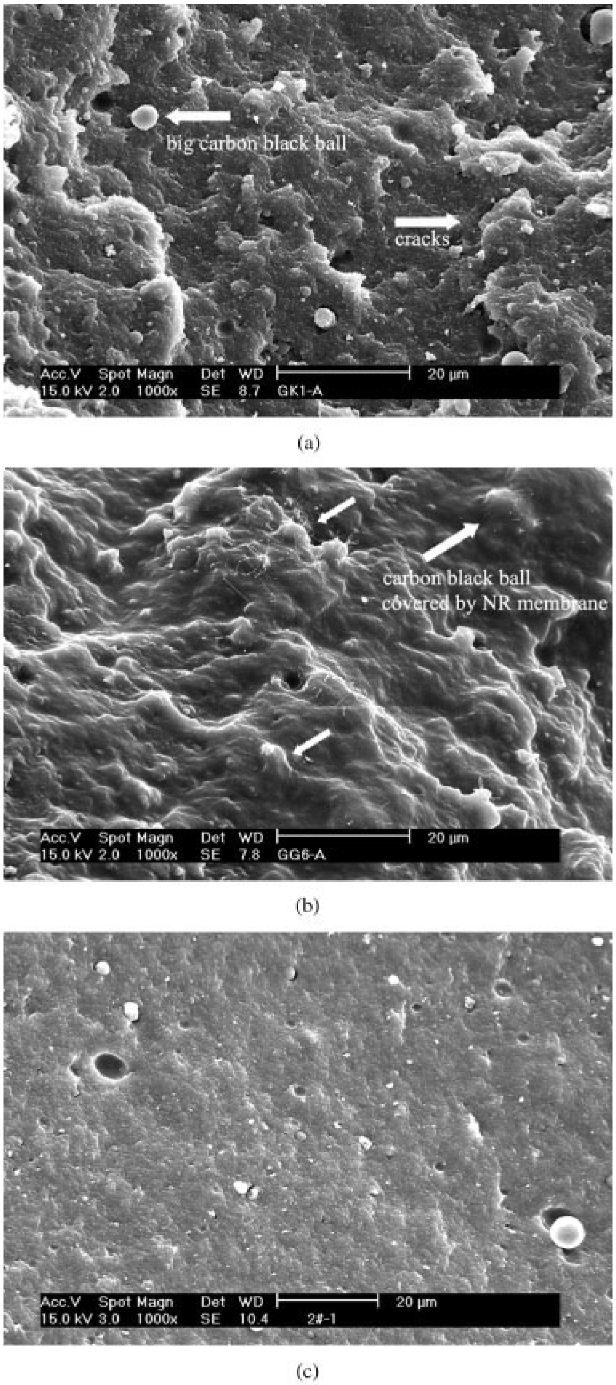

**Figure 5** SEM microphotographs of tensile fracture surface of (a) P (NR/HAF) (×1000); (b) P (NR/HAF-2La) (×1000); (c) P (NR/HAF-5La). HAF, 50 phr.

### Tensile fracture surface morphology of P(NR/HAF), P(NR/HAF-La)

Figure 5(a–c) illustrate the morphology of the tensile fracture surface of P(NR/HAF) and P(NR/HAF-La) vulcanizates, HAF content is 50 phr, and $La_2O_3$/HAF ratios are 0, 2, and 5%, respectively. The gray particles on microphotographs are carbon black clusters, and the darker background is NR matrix. Figure 5(a) is a photograph of the tensile fracture surface of P(NR/HAF) vulcanizate, it can be observed that when HAF is not modified, cracks are presented on the tensile fracture surface and large numbers of carbon black balls are exposed. Besides, a few of big carbon black ball sized 1.5–6.0 $\mu$m are desquamated from the surface, which demonstrated that the adhesion between unmodified carbon black particles and NR matrix is too loose to avoid separating when stretched, thus mechanical properties of P(NR/HAF) vulcanizate are poorer. As shown in Figure 5(b), when $La_2O_3$/HAF ratio is 2%, the tensile fracture surface of vulcanizate presents to be fluctuant, with no cracks and no exposed carbon black particles on the surface, although there is some big size carbon black ball, their surface are covered by NR membrane, which indicates that HAF-La particles and NR matrix had firm interface adhesion. Therefore, when vulcanizate is stretched, crack can not cross through the interface but only around the NR matrix near the interface, and tensile strength of vulcanizate rises. When $La_2O_3$/HAF ratio is 5%, as shown in Figure 5(c), most of carbon black particles are dispersed well in NR matrix, but the surface of vulcanizate is flat and rigid, which indicates that NR molecular chains become more rigid with the increasing $La_2O_3$/HAF ratio, and the molecular chain orientation in tension has been damaged, thus the tensile strength of vulcanizate decrease. SEM demonstrates optimum $La_2O_3$/HAF ratio, which can enhance the interface adhesion degree between carbon black particles and NR matrix, and improve the mechanical properties of vulcanizate remarkably.

## CONCLUSIONS

The general mechanical properties of P(NR/HAF-Ln) vulcanizate are optimum when emulsifier/HAF ratio is 8% and powdering temperature is 85°C. $Sm_2O_3$, $La_2O_3$, and $Pr_6O_{11}$ modified HAF have good reinforcement effect, with $Sm_2O_3$ and $La_2O_3$ being preferred. Compared to P(NR/HAF), general mechanical properties of P(NR/HAF-Ln) increases remarkably, especially the 300% modulus.

Tensile strength, 100% modulus, and tear strength of P(NR/HAF-3Sm) vulcanizate were significantly higher than that of P(NR/HAF-1Sm), P(NR/HAF), and NR/HAF vulcanizates, which indicates that HAF-3Sm has reinforcement effect on P(NR/HAF-3Sm) vulcanizate. Three hundred percent modulus of P(NR/HAF-3Sm) vulcanizate was remarkably higher than that of P(NR/HAF) vulcanizate when HAF content was the same, and approached to that of NR/HAF vulcanizate, which indicates HAF-3Sm distinctly improves the low 300% modulus of P(NR/HAF).

With the increase of HAF content, the SI of the four vulcanizates are P(NR/HAF-3Sm) $<$ P(NR/HAF-1Sm)$\approx$P(NR/HAF) $<$ NR/HAF when HAF content was the same, which proves HAF-3Sm cluster can remarkably increase apparent crosslink density of vulcanizate, which results in improved tensile strength and tear strength. SEM micrographs demonstrate that correct $La_2O_3$/HAF ratio can strengthen the interface bonding force between HAF-La particles and NR matrix, and improve the mechanical properties of vulcanizate remarkably.

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