Rare Earth Compounds Modified Carbon Black Filled Powdered Natural Rubber: Preparation, Morphology and Properties

Yaling Lin,[1] Anqiang Zhang,[2] Lianshi Wang[2]

[1]Department of Pharmaceutical Engineering, College of Resources and Environment, South China Agriculture University, Guangzhou 510642, China
[2]Department of Polymer Material Science & Engineering, College of Material Science and Engineering, South China University of Technology, Guangzhou 510641, China

ABSTRACT: Ten types of rare earth (RE) compounds modified carbon black (HAF-RE) were prepared using chemical-deposit method, then HAF-RE were mixed with natural rubber latex to prepare HAF-RE filled powdered natural rubber [P(NR/HAF-RE)] by a carbon black/rubber latex coagulation method. It is found that most of the P(NR/HAF-RE) vulcanizates showed better mechanical properties, especially higher tensile modulus, and tensile strength, compared with none-rare earth modified carbon black filled powdered natural rubber [P(NR/HAF)]. Dysprosium (Dy) modified carbon black (HAF-Dy) filled powdered natural rubber [P(NR/HAF-Dy)] was chosen for intensive investigation because of its better comprehensive mechanical properties. It is found that the adding of Dy compounds could help to get smaller particles with narrower particle size distribution, and results from the SEM analysis show that carbon black has been dispersed in rubber matrix uniformly with diameter of 50–150 nm. The TEM analysis showed that Dy compounds could obviously reduce the aggregation of primary particles of carbon black, and promote the dispersion of carbon black in P(NR/HAF-Dy) particles. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1393–1401, 2008

Key words: dysprosium modified carbon black; powdered natural rubber; particle size distribution; mechanical properties, carbon black dispersion

INTRODUCTION

Rare earth (RE) was widely used in the preparation of functional materials for its special electronic structure and character, and polymer modification by REs is a new field of research. In the last few years, a number of articles were published concerning REs modified polymer, such as natural rubber (NR)[1,2] and polypropylene (PP).[3] It was shown that REs had a very strong inductive effect on polymers, and some properties of polymers are enhanced by the addition of REs.

Guo[4] prepared lanthanum (La) modified nano calcium carbonate (nCaCO$_3$-La) using the method of chemical-deposit, and modified polypropylene (PP) with nCaCO$_3$-La. The results showed that nCaCO$_3$-La could improve the impact strength and crystallization temperature of the PP/nCaCO$_3$-La composites, compared with virgin PP and unmodified nCaCO$_3$ filled PP composites (PP/nCaCO$_3$). It was found that La compounds deposited on the surface of nCaCO$_3$ particles could enhance the dispersion of nCaCO$_3$ in PP matrix and at the same time increase the reactivity of nCaCO$_3$ particles, thus contribute to better mechanical properties.

However, the reinforcement of RE modified inorganic fillers to rubbers has rarely been reported. In our past work,[5] RE modified nano calcium carbonate (nCaCO$_3$-RE) filled natural rubber composites (NR/nCaCO$_3$-RE) were prepared using chemical deposit and rubber latex/filler coagulation. The studies based on SEM, DMA, and mechanical properties showed that REs, including lanthanum (La), samarium (Sm), cerium (Ce), praseodymium (Pr), holmium (Ho), and ytterbium (Yb), can effectively enhance the interaction between nCaCO$_3$ and rubber matrix, which resulted in higher 300% modules and better tensile properties.

Carbon black is the most widely used filler in rubber industry. However, carbon black tends to aggregate and cannot disperse well in the rubber matrix.

Much research[6–8] have been reported about the surface modification of carbon black to reduce the aggregation of carbon black, increase the activity of carbon black surface, and thus enhance the interaction between carbon black and rubber matrix.

There are two key points lying in the carbon black/rubber composite, i.e., the dispersion of carbon black in rubber matrix and the interaction between carbon black and rubber chains. For the first point, the former studies[9–15] showed that it was an effective way to improve the dispersion of filler in rubber using the filler-rubber latex coagulation method, which has a lot of advantages such as elimination free filler, reduction the energy consumed during mixing, and improvement of mechanical properties. While for the second point, since RE can increase the surface activities of filler and enhance the interaction of filler (such as $CaCO_3$) and rubber chain, the application of RE in the modification of carbon black would be a novel method to enhance the interaction of rubber matrix and carbon black particles. We noticed that there had been no study so far on the modification of carbon black particles covered with RE compounds using the method of chemical deposit.

In this paper, 10 kinds of RE oxide, including lanthanum oxide (La_2O_3), samarium oxide (Sm_2O_3), dysprosium oxide (Dy_2O_3), cerium oxide (CeO_2), praseodymium oxide (Pr_6O_{11}), holmium oxide (Ho_2O_3), ytterbium oxide (Yb_2O_3), europium oxide (Eu_2O_3), thulium oxide (Tm_2O_3) and erbium oxide (Er_2O_3), used as the modifier of carbon black (HAF) to prepare compound modified HAF (HAF-RE). Then HAF-RE were mixed with natural rubber latex to prepare HAF-RE filled powdered natural rubber [P(NR/HAF-RE)] by a carbon black/rubber latex coagulation method. Dysprosium compounds were chosen from the above 10 types of oxide for intensive study. The morphology of carbon black particles, distribution of carbon black in rubber matrix, particle size distribution and morphology of powdered rubber particles, mechanical properties, dynamic properties, and tensile fracture surfaces of powdered rubber vulcanizates were studied.

EXPERIMENTAL

Materials

Dysprosium oxide (Dy_2O_3), lanthanum oxide (La_2O_3), samarium oxide (Sm_2O_3), cerium oxide (CeO_2), praseodymium oxide (Pr_6O_{11}), holmium oxide (Ho_2O_3), ytterbium oxide (Yb_2O_3), europium oxide (Eu_2O_3), thulium oxide (Tm_2O_3) and erbium oxide (Er_2O_3), all with purity of 99.9%, were supplied by Pearl River Smelting Plant (Guangzhou, China), was used for preparing 0.5 mol/L RE chloride ($RECl_3$) water solution. High-abrasion furnace

TABLE I
Formulation of NR Compound

Ingredient	Composition, phr[a]
NR	100
HAF-Dy	50+[b]
Zinc oxide	5
Stearic acid	2
Sulfur	2.25
Accelerator NS (*N-tert*-butyl-2-benzothiazolesulfenamide)	0.7

[a] Parts per hundred rubber, phr.
[b] The effective HAF content was remained constant at 50 phr, so the HAF-Dy content would be more than 50 phr.

black (HAF, grade N330) was supplied by Shanghai Lishi Chemical Co., Ltd. (Shanghai, China). A commercially available grade of natural rubber latex (NR latex, solid content 60 wt %), made in Malaysia and supplied by Guangdong Guangtaihe Rubber Co., Ltd. (Guangzhou, China), was used for preparing P(NR/HAF-Dy). $CaCl_2$ (chemical pure) was supplied by Guangdong Guanghua Chemical Co., Ltd. (Shantou, China), and a 10 wt % $CaCl_2$ water solution was prepared in the laboratory and used as a coagulation agent. The other agents were all industrial grades and used as purchased commercially.

Sample preparation and testing

The preparation of P(NR/HAF) and P(NR/HAF-RE)

Rare earth modified HAF filled powdered NR, P(NR/HAF-RE), based on 100 g natural rubber, was prepared as follows:

1. Five hundred milliliter of distilled water and emulsifier of HAF were charged to a container, and the mixture was stirred for 5 min to make emulsifier solution.
2. Fifty gram of HAF was added to the solution prepared above, and stirred for 10 min with high speed to form HAF emulsion.
3. Rare earth oxide was dissolved using 10% HCl solution to get 1 mol/L $RECl_3$ solution, and was added to HAF emulsion at room temperature under agitation. Then ammonia water ($NH_3 \cdot H_2O$) was added to adjust pH of the mixing system more than 9, then $RECl_3$ would transform to $RE(OH)_3$ and deposit on the surface of HAF particles. After stirring for 10 min, RE modified HAF (HAF-RE) was obtained. In this step, varied volume of 1 mol/L rare earth were added to the HAF emulsion to prepare HAF-RE with varied contents of rare earth, such as 0.5/100, 1/100, 2/100, 3/100, and 5/100 (wt/wt).

TABLE II
The Mechanical Properties of P(NR/HAF) and P(NR/HAF-RE)

Mechanical properties	Rare earth type										
	Blank	La	Ce	Pr	Sm	Eu	Dy	Ho	Tm	Er	Yb
100% modulus (MPa)	1.9	2.8	2.2	2.7	2.8	2.4	2.7	2.2	2.5	2.5	2.9
300% modulus (MPa)	9.4	12.3	9.0	12.2	10.4	12.8	12.6	9.3	10.5	11.3	10.0
Tensile strength (MPa)	21.6	22.9	22.0	24.5	24.0	27.5	29.5	26.8	25.1	25.7	25.3
Elongation at break (%)	518	490	595	460	520	562	556	508	536	519	510
Permanent set (%)	44	30	36	36	30	40	28	40	28	32	40
Tear strength, (kN/m)	56.9	77.7	63.1	71.2	78.1	69.6	82	88	80.8	71.4	76.2
Hardness (Shore A)	63	57	60	60	58	59	58	58	57	59	59

4. One hundred sixty-seven gram NR latex (60 wt %) was added to HAF-RE prepared above, with low-shear agitation to form a NR latex/HAF-RE mixture, i.e., the powdering system. Distilled water were added to the mixture to adjust the solid content of the powdering system to about 10 wt %. Heating was carried out in a water bath, and maintained for 30 min after the temperature of the powdering system reached 85°C.

5. Twenty milliliter 10 wt % $CaCl_2$ water solution was poured into the powdering system under high-speed agitation and the powdering system would transfer to a water/rubber slurry mixture, then with continuous stirring for 20 min.

6. The powdered rubber products were hot-filtered, washed with cold water, dewatered with centrifugal machine, 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 step (1)–(6) would be repeated. Here, the W_c includes the following: solid contents in NR latex, carbon black, and $RE(OH)_3$ added to the mixture.

The powdered rubber product, prepared using the technology described above, is P(NR/HAF-RE), which contain 50 phr efficient carbon black (HAF). If the rare earth oxide used in step (3) is dysprosium oxide (Dy_2O_3), the product can be expressed as P(NR/HAF-Dy), the others are analogized as this.

P(NR/HAF) was prepared as a control using the same procedure listed above except that none rare earth were added in step (3).

Particle size distribution and powdering index (PI) of P(NR/HAF-RE) 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 the following:

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

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 D3184-01 and ASTM D3192-02 using a 6-inch two-roll mill (XK-160, Zhanjiang, China).

The rubber compounds were compression molded into test specimens at 145°C according to the respective cure times (t_{90}) determined by the Monsanto Moving Die Rheometer (MDR 2000, Monsanto, St. Louis, MO). 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, Shimadzu, Kyoto, Japan) operating at 500 mm/min was used to determine the tensile properties of the vulcanizates. Readings of tensile strength, tensile modulus, M100 (modulus at 100% elongation) and M300 (modulus at 300% elongation), and percentage

TABLE III
Calculated and Measured Dy^{3+} Content in Varied HAF-Dy

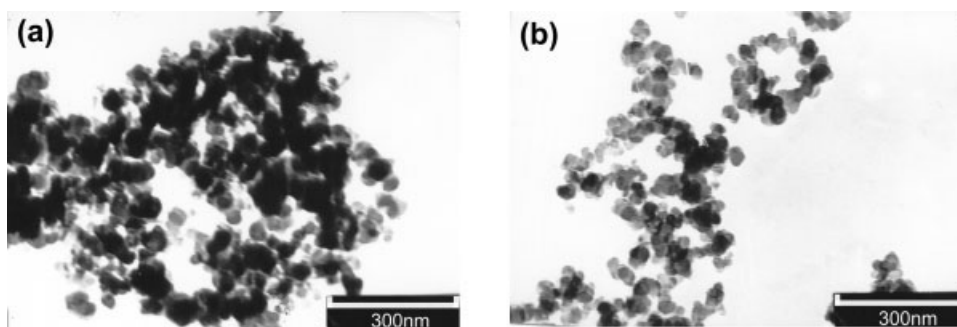| Sample	Calculated Dy^{3+}/HAF ratio (wt/wt, %)	Measured Dy^{3+}/HAF ratio by ICP (wt/wt, %)	Loss ratio (%)
HAF-0.5Dy	0.49	0.47	4.08
HAF-1Dy	0.99	0.96	3.03
HAF-2Dy	1.96	1.92	2.04
HAF-3Dy	2.91	2.88	1.03
HAF-5Dy	4.76	4.73	0.63

Figure 1 TEM photos of the morphology of HAF particles: (a) HAF without modification; (b) HAF-Dy.

elongation at break were recorded directly from the digital displays at the end of each test, the final results were obtained from the mid-value of the five tested pieces of each sample. The test for hardness was carried out using a Shore A type durometer (Shanghai No.4 Chemical Machinery Plant, Shanghai, China) according to ASTM D 2240-02. All tests were conducted at room temperature (23–25°C).

Scanning electron micrograph studies (SEM)

Scanning electron micrographs (SEM) were taken in a PHILIPS XL30 FEG scanning electron micrograph (Philips, Eindhoven, 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.

Transmission electron microscope studies (TEM)

About 0.1 mL water slurry of unmodified HAF and dysprosium compounds modified carbon black (HAF-Dy) prepared according to the preparation of P(NR/HAF) and P(NR/HAF-RE) section (step 3) were dispersed in 20 mL distilled water using an ultrasonic dispersion machine, then drop the diluted carbon black slurry on the wire screen and send for natural drying before the observation of TEM. The micrographs were obtained by a JEM100-CXII transmission electron microscope (Tokyo, Japan).

Inductively coupled plasma-atomic emission spectrometer analysis (ICP-AES)

About 10 mL water slurry of unmodified HAF and HAF-Dy prepared according to the preparation of P(NR/HAF) and P(NR/HAF-RE) section (step 3) were washed with distilled water in a filter bowl for five times to make sure most of the soluble agents were washed. The washed samples were dried, incinerated in a muffle furnace at 500°C. The residues were digested by concentrated HNO_3 and sent to measure the Dy contents using inductively coupled plasma-atomic emission spectrometers (ICP-AES, type CIROS[CCD], supplied by SPECTRO, Germany) according to GB/T 10725-1989.

Dynamic mechanical properties analysis (DMA)

Dynamic mechanical properties were measured over a wide temperature range from −110°C to 100°C using a dynamic mechanical analyzer (NETZSCH DMA242, NETZSCH Gerätebau GmbH, Germany) with a tension clamp. The width, length, and thick of sample were about 3.5, 15, and 1.0 mm, respectively. The frequency was set to 10 Hz and the temperature rising rate was 3°C/min.

RESULTS AND DISCUSSION

Effect of rare earth type on the mechanical properties of P(NR/HAF-RE)

Ten kinds of rare earth were chosen to modify carbon black (RE/HAF = 2/100, wt/wt) and prepare

TABLE IV
The Influence of Dy/HAF Ratio on the Particle Size Distribution of P(NR/HAF-Dy)

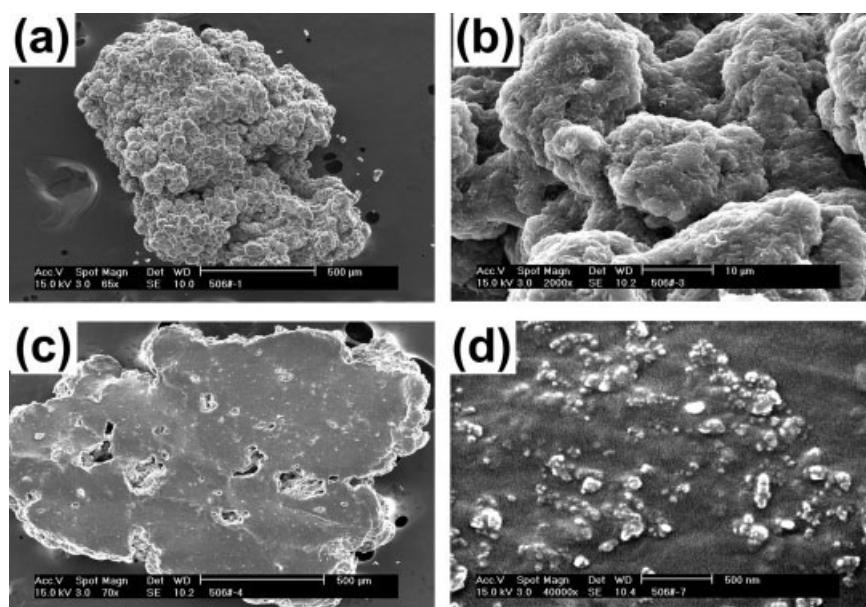| Dy/HAF (wt/wt)	Particle size distribution, wt %				Powdering index (PI)
	>2.0 mm	0.9–2.0 mm	0.45–0.9 mm	<0.45 mm	
0/100	14.1	33.1	50.5	2.3	52.8
0.5/100	0	0	92.7	7.2	100
1/100	0	0	83.5	16.5	100
2/100	0	0	52.7	47.3	100
3/100	0	0	47.6	52.4	100
5/100	0	0	0	100	100

Figure 2 SEM morphology of P(NR/HAF-Dy) particle: (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(NR/HAF-RE), as shown in Table II. The results showed that most of the P(NR/HAF-RE) vulcanizates showed better tensile properties, including higher modules and tensile strength, compared with control, i.e., P(NR/HAF), the blank. The P(NR/HAF-Dy) vulcanizates showed better comprehensive mechanical properties, and were chosen for intensive studies, as shown below.

Analysis of HAF-Dy

As described in the preparation of P(NR/HAF) and P(NR/HAF-RE) section, when ammonia water ($NH_3 \cdot H_2O$) was added to $HAF/DyCl_3$/water mixture to adjust pH of the mixing system more than 9, Dy^{3+} would react with OH^- and transform to $Dy(OH)_3$ and deposit on the surface of HAF particles. Table III exhibits the measured Dy^{3+} contents
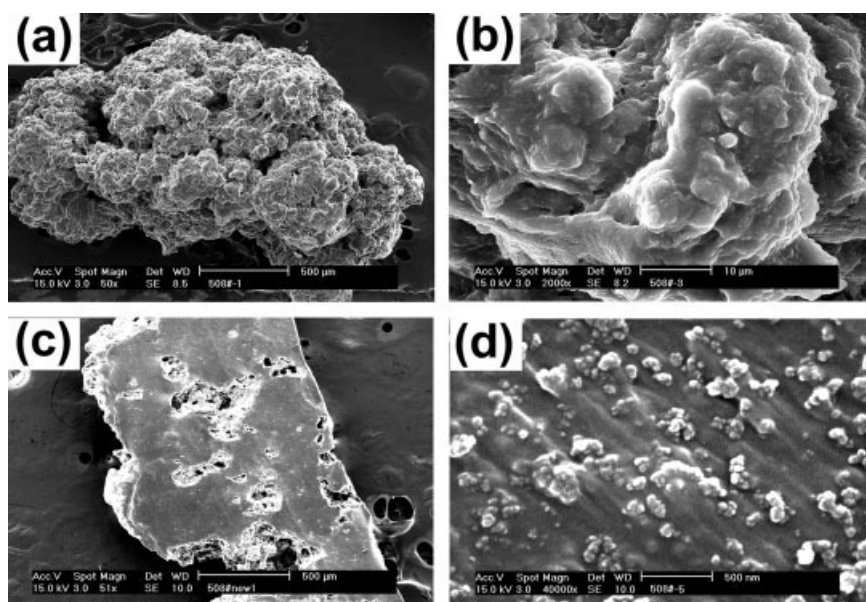

Figure 3 SEM morphology of P(NR/HAF) particle: (a) individual particle; (b) detail view of surface of the particle; (c) the cross-section through a particle; (d) detail view of the section through a particle.

TABLE V
The Influence of Dy/HAF Ratio on the Mechanical Properties and Curing Characteristics of P(NR/HAF-Dy)

Properties	Dy/HAF ratio (wt/wt)					
	0/100	0.5/100	1/100	2/100	3/100	5/100
Scorch time, t_{10} (min)	3.9	5.2	5.3	5.5	5.4	5.2
Optimized curing time, t_{90} (min)	12.6	14.5	13.7	12.8	11.8	11.6
Minimize torque, M_L (dNm)	1.3	1.1	1.1	1.2	1.1	1.1
Maximize torque, M_H (dNm)	33.2	38.4	38.7	39.4	38.2	37.7
Tensile strength (MPa)	21.6	25.5	28.0	29.5	27.8	26.6
100% modulus (MPa)	1.9	2.7	2.7	2.7	2.7	2.9
300% modulus (MPa)	9.4	11.2	11.5	12.6	11.4	11.7
Elongation at break (%)	518	515	537	556	545	520
Permanent set (%)	44	32	32	28	28	26
Tear strength (kN/m)	56.9	90.3	81.9	82.0	85.6	76.6
Hardness (Shore A)	63	60	61	58	60	61

of HAF-Dy using inductively coupled plasma-atomic emission spectrometers (ICP-AES), which showed that more than 95% of the Dy added to the HAF slurry was mixed with HAF to form HAF-Dy.

Figure 1(a,b) shows the TEM morphologies of HAF without modification and HAF-Dy, respectively. As shown in Figure 1(a), for the unmodified carbon black, the primary particles (about 50 nm) of carbon black aggregated to form a typical spherical secondary particle. While for HAF-Dy, the aggregation of primary particles was reduced effectively, and a botryoidal secondary particle was obtained. This shows that the existence of Dy can improve the stability and reduce the aggregation of the primary particles of carbon black in water.

Particle size distribution and morphology of P(NR/HAF-Dy)

The particle size and particle size distribution, i.e., powdering index (PI) of the product are the concerned problems during the preparation of powdered rubber. As shown in Table IV, the particle size of all P(NR/HAF-Dy) is less than 0.9 mm. When Dy/HAF ratio is 0.5/100, all of the particles can pass the 0.9 mm screen, i.e., powdering index (PI) is 100. With the increasing of Dy/HAF ratio, the ratios of particle size smaller than 0.45 mm (pass the 40-mesh screen) increase remarkably. When Dy/HAF ratio is 5/100, the product with diameter less than 0.45 mm can be prepared. Thus, the addition of Dy can help to prepare powdered rubber with smaller particle size and narrower particle size distribution.

Figure 2(a) exhibits the SEM morphology of P(NR/HAF-Dy) particle without contact staining, which shows that a typical P(NR/HAF-Dy) particle, with a diameter about 0.9 mm, is irregular in shape. The P(NR/HAF-Dy) particle was bonded by several small granules with diameters between 20 and 100 μm, and no free carbon black particles were observed in the surface of the particle, as shown in Figure 2(b).

Figure 2(c) is the cross-section of a typical P(NR/HAF-Dy) particle without contact staining. As shown in Figure 2(c), carbon black and rubber matrix have formed a macro-homogenous, and none free carbon black particles can be seen in the section of P(NR/HAF-Dy) particle. Carbon black dispersed well in the rubber matrix with size of 50 to 150 nm, as the bright particles shown in Figure 2(d). As we know, fine filler dispersion could effectively enhance the reinforcement effect of carbon black on rubber. It was also noticed that a number of small cavities were found at the surface and cross-section of the P(NR/HAF-Dy) particle, which makes it easy to be dried during the drying process.

As a comparison, the SEM morphology of P(NR/HAF) particle were also shown in Figure 3, which is almost the same as that of P(NR/HAF-Dy) particle, except the detail view of cross-section, as shown in Figure 3(d). By comparing Figures 3(d) and 2(d), it could be found that the adding of Dy can improve the dispersibility of carbon black on P(NR/HAF-Dy) and reduce the agglomeration of carbon black. Figure 2(d) showed that the carbon black particles are dispersed in P(NR/HAF) with diameter about 50 to 300 nm, which means that carbon black can be dispersed in natural rubber matrix very well using the preparation technology of P(NR/HAF-Dy) with very low shear rate and low energy consuming. The well dispersion of carbon black cannot only reduce energy consuming during mixing, but also improve the mechanical properties of vulcanizates.

Mechanical properties of P(NR/HAF-Dy)

As shown in Table V, scorch time (t_{10}) of P(NR/HAF-Dy) is longer than that of P(NR/HAF), so the adding of Dy can help to provide a safe processing
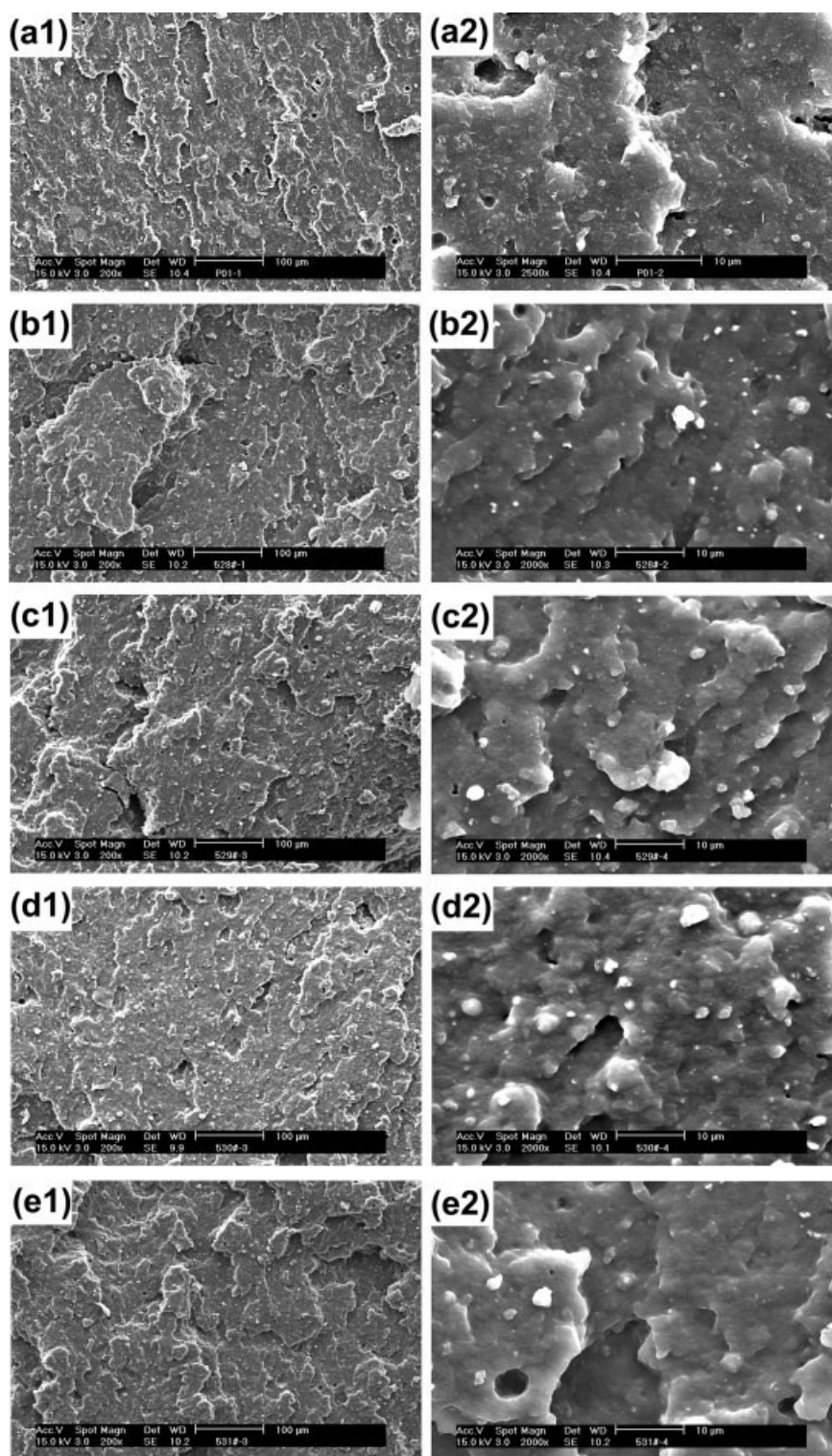
Figure 4 SEM microphotographs of tensile fracture surfaces of P(NR/HAF-Dy) with different Dy/HAF ratios: (a) 0/100, (b) 0.5/100, (c) 1/100, (d) 2/100, (e) 3/100.

time. Compared with P(NR/HAF), P(NR/HAF-Dy) shows better mechanical properties. Max torque (M_H), tensile strength, M100, M300, and tear strength improve remarkably, and permanent set decreases effectively with the adding of Dy. Tensile strength and tear strength achieve maximum values when Dy/HAF ratios are 2/100 and 0.5/100, respectively.

It was also noticed that the mechanical properties were almost stable with the increase of Dy compounds, which mainly due to the effective contents

Properties	Dy$_2$O$_3$/HAF (wt/wt)					
	0/100	0.5/100	1/100	2/100	3/100	5/100
Scorch time, t_{10} (min)	3.9	4.4	4.5	4.5	4.5	4.4
Optimized curing time, t_{90} (min)	12.9	13.5	12.8	13.0	13.5	14.0
Minimize torque, M_L (dNm)	1.3	1.2	1.2	1.2	1.2	1.2
Maximize torque, M_H (dNm)	33.2	34.7	34.4	35.1	34.6	34.7
Tensile strength (MPa)	21.6	23.2	23.9	23.8	22.2	22.4
100% modulus (MPa)	1.9	2.5	2.4	2.5	2.5	2.4
300% modulus (MPa)	9.4	10.4	10.2	10.8	10.1	10.1
Elongation at break (%)	518	522	534	544	544	538
Permanent set (%)	44	32	36	28	30	32
Tear strength (kN/m)	56.9	76	73	77	74	75
Hardness (Shore A)	63	59	61	60	60	60

of Dy compounds, i.e., 0.5/100 of Dy/HAF is enough for Dy compounds to form a coating layer on the surface of carbon black, further increase of Dy contents might not enhance the interaction between carbon black and rubber effectively. Which could also be seen from the tensile fracture surface of P(NR/HAF) and P(NR/HAF-Dy), as shown in Figure 4, Dy/HAF ratios of Figure 4(a1,a2), Figure 4(b1,b2), Figure 4(c1,c2), Figure 4(d1,d2), and Figure 4(e1,e2) are 0/100, 0.5/100, 1/100, 2/100, and 3/100, respectively. There are lots of cracks on the tensile fracture surfaces of all P(NR/HAF-Dy) vulcanizates, and uncovered carbon black agglomeration could also be seen on the surface. With the adding of Dy, the number of cracks increases and more energy is consumed when tensiled, so tensile strength of P(NR/HAF-Dy) vulcanizates increases, and the number of uncovered carbon black agglomeration were decrease, which indicate stronger interaction between carbon black and rubber matrix, thus contribute to higher modulus. With the increasing of Dy/HAF ratio, uncovered carbon black agglomeration on the tensile fracture surface slightly decreases, as shown in Figure 4(a2), Figure 4(b2), Figure 4(c2), Figure 4(d2), and Figure 4(e2). Thus, the modulus and tensile strength of P(NR/HAF-Dy) vulcanizates were almost stable.

As a comparison, the mechanical properties of P(NR/HAF) and Dy$_2$O$_3$ powder blends, i.e., P(NR/HAF)-Dy$_2$O$_3$ blends, via dry mixing with varied Dy$_2$O$_3$ contents were also studied, as shown in Table VI. It was found that the Dy$_2$O$_3$ powder incorporated with P(NR/HAF) by dry mixing showed few improvements on the mechanical properties of P(NR/HAF)-Dy$_2$O$_3$ blends, compared with that of P(NR/HAF-Dy), for the reason that most of Dy$_2$O$_3$ powder was just dispersed in the rubber matrix, and few Dy$_2$O$_3$ could cover at the surface of carbon black, thus the activities of carbon black particles could not be enhanced effectively, which result in

lower M_H, M300, and tensile strength. This also showed that the method of chemical deposit is a proper method to prepare HAF-Dy, and the surface activity of carbon black could be increased only when the most of the Dy compounds were deposited on the surface.

Dynamic mechanical properties of P(NR/HAF-Dy)

The temperature dependence of loss factor (tan δ) for polymer can be got by dynamic mechanical analysis (DMA). Temperature corresponding to the maximum of tan δ is corresponding to the glass transition temperature (T_g) of polymer. T_g is a useful physical criterion reflecting fairly well the molecular movements. The less mobility of rubber chain, the higher the T_g.

The temperature dependence of tan δ for P(NR/HAF-Dy) containing various proportions of Dy/
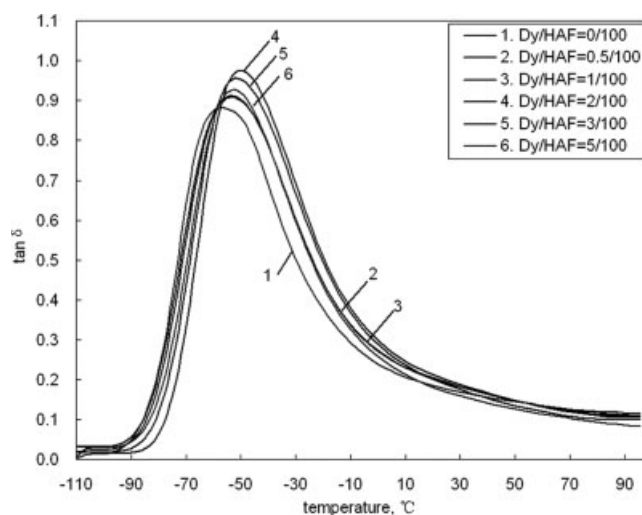

Figure 5 Loss factor (tan δ) versus temperature for P(NR/HAF-Dy) containing various proportions of Dy/HAF.

TABLE VII
The Influence of Dy/HAF Ratio on the Dynamic
Mechanical Properties of P(NR/HAF-Dy)

Dy/HAF (wt/wt)	T_g (°C)	Tan δ at 0°C	Tan δ at 70°C
0/100	−57.0	0.239	0.127
0.5/100	−53.3	0.272	0.125
1/100	−53.4	0.273	0.122
2/100	−50.0	0.299	0.119
3/100	−51.4	0.289	0.108
5/100	−52.6	0.258	0.103

HAF is given in Figure 5. The value of T_g and tan δ corresponding to the temperature at 0°C and 70°C are listed in Table VII. As shown in Figure 5 and Table VII, T_g increases with the adding of Dy, and gets the maximum value at Dy/HAF ratio of 2/100.

Since the carbon black filled natural rubber may be used in tire tread rubber compound, the rolling resistance and wet grip of the vulcanizates are two important factors. It is known that in case of rolling resistance and wet grip there is a correlation with the loss factor tan δ. High values for tan δ at low temperatures (∼ 0°C) lead to an improvement of wet grip whereas low values at elevated temperatures (∼ 70°C) favor a reduced rolling resistance.[16,17]

According to Table VII, tan δ at 0°C increases and tan δ at 70°C decreases with the adding of Dy. So, the modification of HAF with Dy cannot only increase the wet grip but also reduce the rolling resistance of vulcanized rubber effectively. T_g, tan δ at 0°C and tan δ at 70°C reach peak values when Dy/HAF ratios are 2/100, 2/100, and 5/100, respectively. Thus for preparing rubber with higher wet grip and lower rolling resistance, there is an optimal Dy/HAF ratio.

CONCLUSIONS

Ten type of rare earth modified carbon black (HAF-RE) filled powdered natural rubber [P(NR/HAF-RE)] were prepared by chemical deposit method and carbon black/rubber latex coagulation method, most of the P(NR/HAF-RE) vulcanizates showed higher tensile modulus and tensile strength, compared with P(NR/HAF). In which P(NR/HAF-Dy) vulcanizates showed better comprehensive mechanical properties and chosen for detail studies.

It was found that Dy can help to get smaller P(NR/HAF-Dy) particles with narrower particle size distribution, improve the modulus, tensile strength and tear strength of P(NR/HAF-Dy) vulcanizates, and at the same time, reduce the permanent set.

The TEM and SEM analysis shows that Dy can obviously reduce the aggregation of primary particles of carbon black, and promote the dispersion of carbon black in P(NR/HAF-Dy) particles.

Compared with unmodified carbon black filled powdered natural rubber [P(NR/HAF)], P(NR/HAF-Dy) shows higher tan δ at 0°C and lower tan δ at 70°C, which shows that the tire tread containing P(NR/HAF-Dy) would get higher wet grip and lower rolling resistance.

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