

# CaCO<sub>3</sub>/Natural Rubber Latex Nanometer Composite and Its Properties

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**ABSTRACT:** Calcium carbonate/natural rubber (NR) latex nanometer composites were prepared by adding nanometer CaCO<sub>3</sub> whose surface had been treated to natural rubber latex (NRL) before sulfuration. The physical, thermooxidative aging, and thermal degradation properties and the ultra-microstructure were analyzed with a multipurpose material testing meter, a thermal analysis meter and a Philips XL-30 SEM, respectively. The results showed that the structures and properties of nanometer composites could be clearly improved by NRL mixed with surface-treated nano-

meter CaCO<sub>3</sub>. The physical properties of the nanometer composites were best when the content of surface treatment agent was 2.5% (to nanometer CaCO<sub>3</sub>), the nanometer CaCO<sub>3</sub>/NRL content was 3:100, and the stirring time for treating the surface of the nanometer CaCO<sub>3</sub> was 20 min. Simultaneously, the thermooxidative aging resistance of the nanometer composites also was significantly improved. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3442–3447, 2006

**Key words:** nanometer CaCO<sub>3</sub>; rubber; composites

## INTRODUCTION

Nanometer material is material smaller than 100 nm in size in at least one dimension.<sup>1–4</sup> It has unique properties because of its small size, leading to surface, volume, and quantum size effects and so on. If this type of nanometer granule is applied to NR modification, NR nanometer composites<sup>5–9</sup> with excellent properties can be produced. Nanometer CaCO<sub>3</sub> (NCa) is a new type of ultrafine solid material developed in 1980s. It is low in toxicity, less polluting, and whiter. It does not react to any toxicity or biological incompatibility brought by other mixtures. NRL has good processing properties, and products made from it have a smooth texture, are very elastic, and have unique physical properties. Although a great amount of research has been done in the field of NR nanometer composites, there have been few reports on NRL nanometer composites. In the present study, NCa/NRL nanometer composites with excellent properties were produced by mixing surface-treated NCa with NRL and its properties and ultra-microstructure studied.

## EXPERIMENTAL

### Materials

Natural concentrated rubber latex was supplied by the Zhanjiang Medical Latex Product Factory (Guangdong Province, China); Nanometer CaCO<sub>3</sub> (NCa), with an average grain diameter of 80 nm, and the other raw materials were of CP and AR grade; The surface treatment reagent of nanometer CaCO<sub>3</sub> (STA) was a compound of phosphatidate and many other types of chemical agents, produced on site.

### Test sample preparations

The ingredients used for preparing the test samples were: 100 NRL (based on dry rubber), 1.2 sulfur, 0.7 oxidized zinc, 0.7 zinc diethyl dithiocarbamate (promoter ZDC), 0.4 zinc ethyl phenyl dithiocarbamate (promoter Px), and an appropriate quantity of stabilizer. For the NCa modification, NCa and STA were mixed evenly at 35°C.

### Preparation of pre vulcanized latex

A mixture of NRL with NCa was modified evenly first. Then it was evenly blended with other mixtures and a pre vulcanizate in a water bath for 25 min at 60°C.

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**Preparation of vulcanized latex**

The film of the test sample was prepared by using the ion deposition gelatinization method (the coagulating solution was CaCl<sub>2</sub> solution). The vulcanizing condition lasted 6 h at 100°C.

**Properties test**

Physical properties were investigated on a Instron 3365 multipurpose material testing meter according to Chinese Standard GB/T528-1998 (equivalent to ISO 37 : 1994). Hardness was tested according to Chinese Standards GB/T531-1999 (equivalent to ISO 7619 : 1986) on a Model Share A hardness meter. Analyses of the ultra-microstructure of the samples were performed on a Philips XL-30 SEM.

Thermooxidative aging property was carried out according to Chinese Standard GB3512-2001(equivalent to ISO 188-1982). The thermooxidative aging conditions of the test sample in air were 24 and 36 h, both at 100°C.

The thermooxidative properties of the test sample were expressed by the variation ratios of the physical properties before and after aging, as  $(O - A)/O \times 100\%$ , where  $O$  and  $A$  are the properties of the samples after and before aging separately.

Thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out in a TGA-7 Perkin Elmer thermoanalyzer in an air atmosphere with the temperature increasing at a rate of 10°C/min and an air flow rate of 50 mL/min.

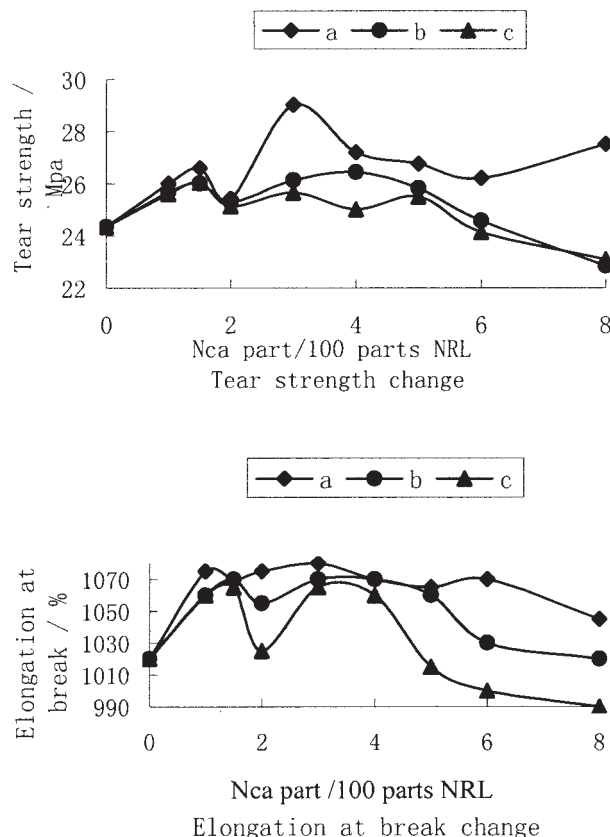
**Determination of degradation activation energy**

The TG data of the test samples were processed with a method of integration according to the Coats-Redfern<sup>10</sup> equation in order to find the corresponding data of the reaction kinetics of the test sample. The reaction kinetics equation,  $da/dt = k(1 - a)^n$ , and the Arrhenius equation,  $k = Ae^{-E/RT}$ , were used.

The following equation was obtained after mathematical processing:

$$\ln\{[1 - (1 - a)^{1-n}]/[T^2(1 - n)]\} = \ln[(1 - 2RT/E)AR/\beta E] - E/RT(n \neq 1)$$

where  $n$  is the reaction order,  $a$  is the reaction degree,  $T$  is the absolute temperature,  $\beta$  is the rate of temperature increase,  $E$  is the activation energy of the reaction,  $R$  is the gas constant, and  $A$  is the frequency factor. When  $n \neq 1$ , a straight line was obtained from the diagram by using  $\ln\{[1 - (1 - a)^{1-n}]/[T^2(1 - n)]\}$  and  $1/T$  as coordinates, and the intercept of the line was  $\ln[(1 - 2RT/E)AR/\beta E]$ . When the maximum correlation coefficient,  $r$ , was obtained by use of the least-squares fit method with different  $n$  values, then  $n$  was



**Figure 1** Effect of dosage of STA and NCa powder on the sample properties (a) STA dosage (to NCa) is 2.5%; (b) STA dosage (to NCa) is 3.5%; (c) STA dosage (to NCa) is 4.5%.

the reaction order sought, and the corresponding  $E$  was the activation energy of reaction sought.

**RESULTS AND DISCUSSION**

**Physical properties of CaCO<sub>3</sub>/NRL nanometer composite**

The surface of NCa was treated with different dosages of STA of 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, and 4.5% relative to the NCa dosage. The test samples were prepared by adding 0, 1, 1.5, 2, 3, 4, 5, 6, or 8 parts NCa (to 100 parts NR) to NRL separately.

STA acted as a bridge when NCa was linked to NR molecules. It strengthened the combination between the NCa and NR molecules and at the same time weakened the ability of agglomeration of NCa. STA could not fully act on NCa when its dosage was too small, as the inertial NCa could not combine with the NR molecules organically. Also, NCa would not have a reinforcing function because of losing its nanoeffect. When the dosage of STA was too large to be separated effectively, all the NCa would become purely filler. The experimental results indicated that STA did not play a part in the surface treatment if its dosage was lower than 2.5%. Figure 1 shows the physical perfor-

**TABLE I**  
Effect of Stirring Times on Sample Properties When NCa Surface Was Modified

Time (min)	5	10	15	20	25	30	35
Hardness, Shore A (degree)	37	37	37	37	37	37	37
300% Tensile strength (Mpa)	1.79	1.80	1.74	2.00	1.83	1.70	1.71
Elongation at break (%)	1050	1060	1040	1080	1015	1055	1035
Tear strength (Mpa)	27.82	25.17	25.05	29.01	24.57	24.94	24.50

mance of the samples when the dosage of STA was 2.5%, 3.5%, or 4.5%, indicating that the best results were with the 2.5% dosage.

As can be seen in Figure 1, the properties of the samples increased gradually as the dosage of NCa increased when the dosage of NCa was under 3 parts and the properties were best at about 3 parts. After that, the properties of the samples declined as the dosage of NCa increased. This explains that there is a balanceable state of saturation for the NCa function on the NR basic body. Before the balanceable state, the more NCa dosage, the better the functioning. But after the balanceable state, the greater the NCa dosage, the greater was the possibility that NCa would gather in the second structure. Afterward, the stress concentration produced had a negative effect on the properties of the samples.

Table I shows the effect of stirring time on the sample properties when NCa surface had been modified. It could be demonstrated from Table I that at first the properties of the test samples increased along with longer stirring time lengthening. The maximum properties of the test samples appeared at 20 min. From then on, every property of the test samples declined as stirring time increased. When the NCa surface was treated, stirring is good for keeping the NCa in full touch with STA and mixing completely.<sup>11-13</sup> Meanwhile, the NCa particles became slighter. However, if the stirring time was too long, the NCa particles would frequently have contact and get closer to each other. In addition, the heat

effect from electric stirring would make STA break away from the NCa surface and finally cause the properties of the samples to decline.

#### Thermooxidative aging properties of the CaCO<sub>3</sub>/NRL nanometer composite

The test samples were prepared after putting NCa treated with STA (2.5% to NCa) into NRL separately according to different NCa dosages of 0, 1, 1.5, 2, 3, 4, 5, 6, or 8 parts (to 100 parts NR). The corresponding serial numbers of the test samples were I, II, III, IV, V, VI, VII, VIII, and IX. The thermooxidative aging properties of every test sample are shown in Table II, which has the thermo-oxidative aging conditions for 24 h at 100°C and for 36 h at 100°C. The thermooxidative aging properties of the samples are expressed as:  $(O - A)/O \times 100\%$ , where  $O$  and  $A$  are the properties of the samples after and before aging, respectively.

From Table II, it can be seen that after 24 h of aging, the thermooxidative aging properties of the samples modified by NCa were better than those of the samples not modified by NCa. Among them, the thermooxidative aging properties of sample V (which had 3 parts NCa) were remarkable. A comparison of samples V and I showed that the ratio of hardness (shore A) was reduced from 5.71% in sample I to 2.78% in sample V, the ratio of elongation at break was reduced from 16.58% in sample I to 6.30% in sample V, the ratio of tear strength was reduced from 44.11% in sample I to 21.60% in sample V, the ratio of 300% tensile

**TABLE II**  
Thermo-oxidative Aging Properties of Test Samples

Project	Dosages of NCa modified parts								
	I	II	III	IV	V	VI	VII	VIII	IX
Sample properties after 24 h of thermo-oxidative aging at 100°C									
Ratio of hardness, Shore A (%)	5.71	5.41	2.86	2.78	2.78	8.11	10.8	2.78	2.71
Ratio of elongation at break (%)	16.58	13.71	10.61	13.70	6.30	11.80	11.00	7.64	13.1
Ratio of tear strength (%)	44.11	41.28	37.78	35.40	21.60	24.80	38.50	30.00	30.70
Ratio of 300% tensile strength (%)	16.41	12.74	9.13	7.15	6.08	6.86	13.18	19.49	14.78
Sample properties after 36 h of thermo-oxidative aging at 100°C									
Ratio of hardness, Shore A (%)	11.43	8.11	8.57	11.10	5.56	13.50	16.20	5.56	5.41
Ratio of elongation at break (%)	18.31	15.02	13.84	16.60	13.70	12.28	13.19	8.92	14.60
Ratio of tear strength (%)	45.60	44.65	44.43	42.29	35.30	34.30	42.00	43.90	41.60
Ratio of 300% tensile strength (%)	25.34	24.11	22.68	19.67	14.18	18.62	22.25	27.28	20.50

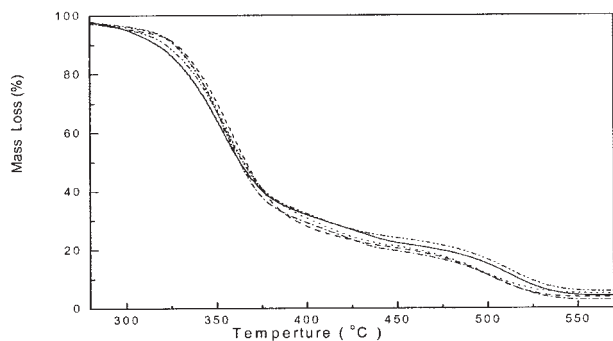


Figure 2 TG curve of the natural rubber latex glue film.

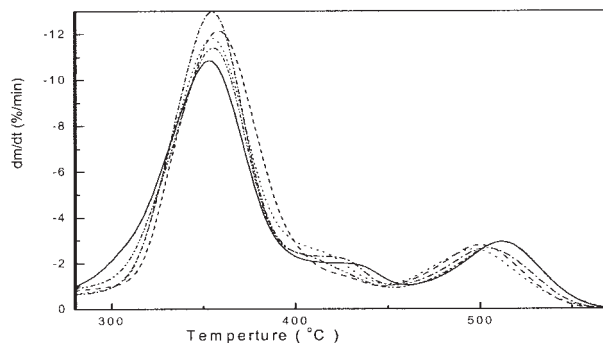


Figure 3 DTG curve of the natural rubber latex glue film.

strength was reduced from 16.41% in sample I to 6.08% in sample V. The thermooxidative properties of the samples modified by NCA were also better than those of the samples not modified with NCA after 36 hours of aging.

During aging, NR hydrocarbons produce free radicals as a result of the action of oxygen. These free radicals would be oxidized into hydrogen peroxide and decomposed into oxides and new free radicals further, which would cause the constant fractures from NR hydrocarbon strand. Then samples were so destroyed that thermooxidative aging appeared. However, some free radicals would combine with NCA when present, which would reduce the fractures from the NR hydrocarbon strand and improve the thermooxidative aging resistance properties of the samples. But when the NCA dosage was more than 3 parts, the reunion of NCA increased as NCA dosage increased, which would increase the infiltration of oxygen and cause the thermooxidative aging properties of the samples to decrease to some extent.

**Thermooxidative degradation properties of the CaCO<sub>3</sub>/NRL nanometer composite**

To investigate the thermooxidative degradation properties of NRL modified by NCA, the samples were prepared as follows: sample 1, NRL not modified by NCA; samples 2, 3, and 4, the addition of 1, 3, or 5 parts NCA (which had been treated with STA the dosage is 2.5%), respectively, to NR; sample 5, NRL added to 1 part antioxidant 264 (2,6-di-*tert*-butyl-4-methyl-phenol). The TG and DTG curves of the five samples were analyzed, and the experimental results are shown in Figures 2 and 3.

Figures 2 and 3 show that the thermooxidative degradation processes of the five samples had two stages: the main degradation stage and a secondary degradation stage. In this article only the study of the main degradation stage is reported. The TG curves were processed with the pairs of tangent line law; then the initial temperature,  $T_0$ , and the final temperature,  $T_f$  of

the thermooxidative degradation stage of the samples could be obtained. The main degradation peak temperature,  $T_p$ , could be obtained from the DTG curve, and the activation energy of the degradation reaction could be obtained from the Coats-Redfern equation. The results are listed in Table III.

It can be seen from Table III that the  $T_0$ ,  $T_p$  and  $T_f$  of the samples increased when NCA, with which the surface had been treated, was added. Compared with sample 5, to which a share of the antioxidant 264 was added, the degradation speed of sample 3, which had 3 parts NCA added, was smaller; the initial degradation temperature,  $T_0$ , was lower than that of sample 5 by about 4°C, the main degradation peak temperature,  $T_p$ , was the same; and the final temperature,  $T_f$ , was higher than that of sample 5 by about 7°C. Table III also shows that sample 5 had the highest thermooxidative degradation activation energy as well as the best thermooxidative stability. Then the activation energy of the thermooxidative degradation reaction of sample 3 was close to that of sample 5, differing by only 3.44 kJ/mol. This proves that the two samples had very similar thermooxidative degradation ability, that is, close to raising the antioxidant ability by joining 3 parts surface-treated NCA to 1 part antioxidant 264.

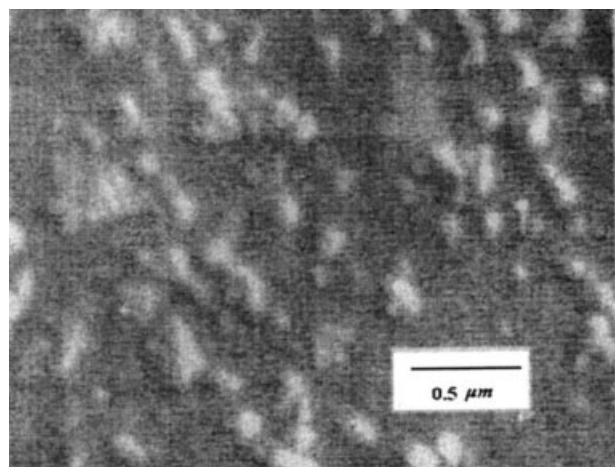
**Ultra-microstructures of the CaCO<sub>3</sub>/NRL nanometer composites**

Figures 4–6 are the SEM ultra-micrographs of the cross sections of the samples. The sections of the sam-

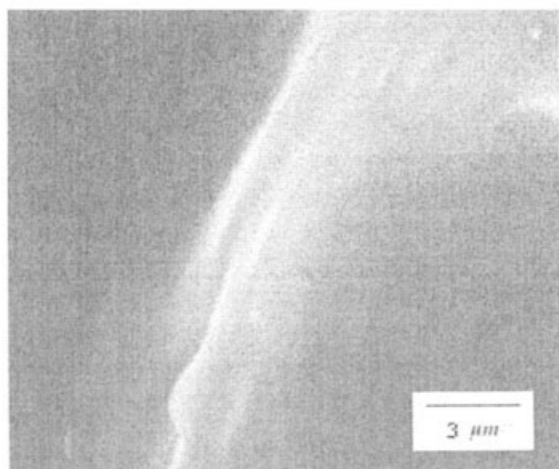
**TABLE III**  
Thermo-oxidative Degradation Temperature and Degradation Activation Energy of Samples

Sample	$T_0$ (K)	$T_p$ (K)	$T_f$ (K)	$E$ (kJ/mol)
1	316.8	352.5	535.0	148.06
2	318.7	357.5	536.0	165.81
3	321.8	354.0	537.5	173.76
4	319.0	354.5	534.5	157.67
5	325.7	354.2	530.3	177.20

Thermo-oxidative degradation reaction order is  $n = 2$ .



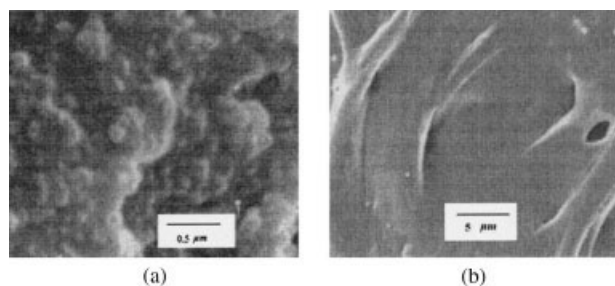
(a)



(b)

**Figure 4** SEM ultra-micrographs of the cross sections of (a) sample 3<sup>#</sup> and (b) sample 0<sup>#</sup>.

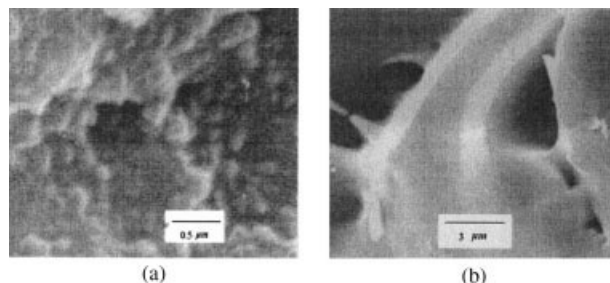
ples were obtained by using freeze-peeling treatment with liquid nitrogen. Both sample 3, mentioned above, and sample 0 without NCA were applied here. The SEM ultra-micrographs of the cross sections of samples 3 and 0 are shown before aging in Figure 4, after aging for 24 h in Figure 5, and after aging for 36 h in Figure 6. It can be seen from the SEM ultra-micro-



(a)

(b)

**Figure 5** SEM ultra-micrographs of the cross sections of (a) sample 3<sup>#</sup> and (b) sample 0<sup>#</sup> after 24 hours aging.



(a)

(b)

**Figure 6** SEM ultra-micrographs of the cross sections of (a) sample 3<sup>#</sup> and (b) sample 0<sup>#</sup> after 36 hours of aging.

graphs of the cross sections of the sample that NCA dispersed more evenly in the NR basic bodies [Fig. 4(a)]. From Figure 5(a), it can be seen that the section of the sample that had had NCA added appeared slightly uneven after thermooxidative aging for 24 h but still showed organic integration between the NCA and the NR basic bodies. Figure 5(b) shows that the part of the sample without NCA had obvious holes and cracks, with the interfaces between the hole and layer clearly apparent. A comparison of the corresponding samples shows that the structures shown in Figure 6 were slightly worse than those shown in Figure 5. It can also be seen from Figure 6 that the structures of samples without NCA [Fig. 6(b)] were destroyed more seriously than those of samples with NCA [Fig. 6(a)]. It is obvious that the structures of samples with NCA were protected more perfectly<sup>14</sup> during thermooxidative aging, indicating that NCA was combined with NR base bodies so tight that the thermomovement of NR molecule strands were blocked effectively. That would cause the structure of NR molecules to be protected and the thermooxidative aging resistance properties of the samples to be improved.

## CONCLUSIONS

1. NCA was able to improve the physical properties of nanometer NRL composites. The best prescription was: STA dosage of 2.5% (to NCA), stirring time of 20 min when the NCA surface was activated, and a dosage of 3 parts NCA (to 100 parts NR).
2. NCA was able to improve the thermooxidative aging resistance properties of the nanometer NRL composites. When 3 parts NCA joined with STA (2.5% to NCA), the thermooxidative aging resistance properties of the nanometer composites were best. The thermooxidative aging resistance ability was comparable to that of 1 part the antioxidant 264.
3. SEM ultra-micrographs of the cross sections of the nanometer NRL composites showed that

NCA dispersed evenly in the NR basic bodies and combined well with the NR molecules, so that the structures of the NR molecules were effectively protected.

## References

1. Zhang, L.-Q.; Wu, Y.-P.; Wang, Y.-Q. *J China Synth Rubber Ind* 2000, 23, 71.
2. Ishida, H.; Campbell, S.; Blackwell, J. *J Chem Mater* 2000, 12, 1260.
3. Hu, J. *J Henan Chem Ind* 2001, 5, 1.
4. Gubin, S. P.; Ross Khim, Z. *Rossiiskoe Khimicheskoe Obshchestvo im D. I. Mendeleeva* 2000, 44, 23.
5. Chen, M.; Ao, N.-J.; Zhou, H.-L.; Qu, J. L.; Wang, H.-W. *J Chin Electron Microsc Soc* 2002, 21, 199.
6. Ao, N.-J.; Chen, M.; Zhou, H.-L.; Wang, H.-W. *J Chinese Electron Microscopy Soc* 2002, 21, 203.
7. Wang, L.-S.; Zhou, Y.-Y.; Yang, C.-L. *J China Rubber Ind* 2000, 47, 530.
8. Avella, M.; Errico, M. E.; Martelli, S.; Martuscelli, E. *J Appl Organomet Chem* 2001, 15, 435.
9. Baker Crispin, S. L. *Plast Eng* 2001, 61, 61.
10. Coats, A. W.; Redfern, J. P. *J Nature* 1964, 201, 68.
11. Lu, X.-C. *The Intensity and Destruction of the Polymer Material*. ChengDu: Sichuan Province, China 1998, 319.
12. Wang, X.-T.; Hu, L.-M. *J Chem Reports* 1995, 5, 13.
13. Wang, X.; Huang, R.; Jin, C.-H.; Chen, H.-T. *Beijing Suliao Yanjiuso* 2000, 29, 32.
14. Chen M.; Ao, N.-J.; Chen, Y.; Qu, J.-L.; Yu, H.-P.; Wang, C.; Zhou, H. L.; Qian, H.-L. *J Rubber Res* 2003, 6, 164.