The Reinforcement of Red Clay on Natural Rubber and Its Reinforcing Mechanism

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ABSTRACT: Three kinds of red clay were fractionated according to the particle size using ultrasonic and centrifugal method. The mechanical properties of the clay-rubber composite with various clay fractions were determined. At the same time, both the content of the metal components in the clay and the affect to the aging properties were determined. The result shows that within a certain range, the clay particle size only affects some of the mechanical properties of clay-rubber composite. The characteristic morphological structure of the clay provides a significant reinforcing action on clay-rubber composite. We speculate that mechanism of the reinforcement of clay on rubber is that the clay forms a rigid or semi-rigid chain aggregation structure in rubber. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3418–3422, 2009

Key words: red clay; clay-rubber composite; reinforcing; mechanism

INTRODUCTION

Because of the continuous rising of the price of carbon black, research workers had been looking for other inexpensive reinforcing fillers. The previous research work showed that the red clay could be used as reinforcing filler to replace the carbon black such as high abrasion furnace black (HAY), general purpose furnace black (GPF), and semi reinforcing furnace black (SRF). It can be made into the clay-rubber composite with rubber for producing the bicycle tire, tube, and sole.[1] In general, it is recognized that the main factors influencing the reinforcement of filler are size, distribution, morphology, and surface chemical properties of its particles.[2–7] As for the clay, its structure and chemical properties are very complex owing to the difference forming conditions in nature.[8–11] Therefore, up to now, no comprehensive introduction and general consideration are formed. In this article, three sorts of clay were graded into four grades according to the particle size by supersonic wave and concentration method, and their particle size, structure, and chemical composition were determined. The physical properties and structure of vulcanizates, after prepared into composite with natural rubber latex were also determined.

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EXPERIMENTAL

The red clays are bought from Nanguang farm and Nanhua farm in Guangdong province and Qianjin farm in Hainan province. The NR latex we used is the fresh NR latex bought from Qianjin farm in Guangdong province. Its physical and chemical properties are as follow: dry rubber content (DRC) 25%; alkalinity (ammonia) 0.03%; sludge content 0.02%; volatility 0.38%; and plasticity retention index (PRI) 72.

The raw clay samples and graded clay samples are prepared according to the method described in reference.[12] The clay particle size and structure are determined by JEM-100CXII transmission electronic microscope, Nicolet 5DX Fourier Infrared Spectrometer, and Riguku D/max-1200 X-ray diffraction meter. The chemical composition of clay was determined by EPM-8100 electronic probe. By statistics, we get the D_N, D_W, and F. D_N is number-average diameter and D_W is weight-average, F is polydispersed index ($F = D_W/D_N$).

The composite were prepared by coagulating the clay with fresh NR latex, sheeting, and drying. The physical properties of vulcanizates were determined according to Chinese Standards concerned (GB 528-1998). The distribution structure of clay in rubber was determined by TEM.

RESULTS AND DISCUSSION

Effects of clay particle size on reinforcement of clay

Table I shows the particle size of four grades of three sorts of clay. It can be seen that the particle

TABLE I
Particle Size of Different Grades of Three Sorts of Clay

	Clay A					Clay B					Clay C				
Grades	1	2	3	4	5 (raw clay)	1	2	3	4	5 (raw clay)	1	2	3	4	5 (raw clay)
D_N (μm)	0.072	0.14	0.27	1.2	0.11	0.10	0.12	0.24	1.4	0.12	0.10	0.11	0.14	0.19	0.11
D_W (μm)	0.12	1.6	1.1	3.6	2.5	0.20	1.1	2.7	7.9	2.3	0.27	0.92	1.2	2.6	0.71
F	1.7	11	4.1	3.0	22	2.0	9.2	11	5.6	19	2.7	8.4	8.6	14	6.5

may be graded into four grades effectively by supersonic wave and concentration method. Figures 1–6 shows the physical properties of vulcanizates of composite prepared form three sorts of clay.

It can be seen that the tensile strength, the elongation at break, and tear strength of clay-rubber composite increased obviously with the decrease of particle size, but wear has little difference in the scope of small particle size. Besides, the particle size has no effect on the modulus of composite. The Shore hardness also increased with the decrease of particle size except clay B. It also shows that although the distribution of particle size of raw clay is wide, it has a good comprehensive property. According to B. Wijayarathna, the smaller the particle size of filler, the more increase the composite's mechanical properties. But we found the clay does not follow the principles. Our result is obviously different from the previous result on carbon black and silicon oxide.[13] In addition, there is no relevant relationship between the particle size and properties of different sorts of clay, which indicates that the determinative factor that affects on the reinforcement is not particle size.

Effect of morphological structure of clay on reinforcement of clay

The results from TEM show that three sorts of clay are consisted of four kinds of basic particle with different morphological structure (see Fig. 7). The highest content of the particles in clay is the smallest one called particle a, its particle size in the range of 0.03–0.15 μm. The particle sizes of other three basic particles (b, c, and d) are in the range of 0.1 to several μm, but their content (quantity) in clay is low. It, in the same time, is observed that there are caves on the surfaces of particles, and different clay has different content of caves. The morphological structure and caves have no positive effects on the properties of clay-composite.

Effects of chemical composition on reinforcement of clay

Figures 8–10 is the content of the metal components in the three clay particles. And the metal components which the content less than 1% does not show in the picture, such as Cr_2O_3, Na_2O, K_2O, MgO, CdO, CuO, ZnO, CaO, and MnO. It can be seen that in the relevant grades with similar particle size and morphological structure of three sorts of clay some chemical elements such as kalium, manganese, copper, and cobalt have no positive effect on the reinforcement of clay. Whereas the increase of iron content has a harmful effect on the tensile strength, elongation at break, tear strength, and wear of composite. It is observed from FTIR results that there are no other organic groups on clay particle surface

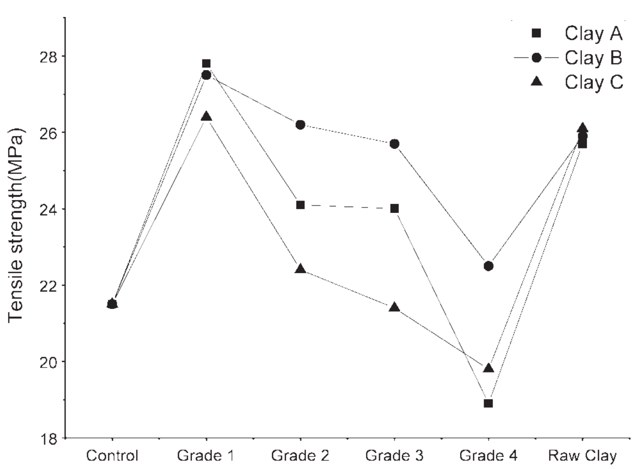

Figure 1 Effects of three kinds of clay use as filler in the natural rubber on the tensile strength.

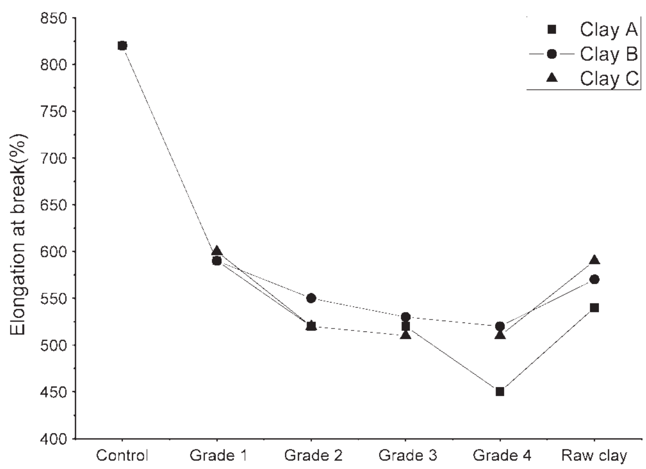

Figure 2 Effects of three kinds of clay use as filler in the natural rubber on the elongation at the break.

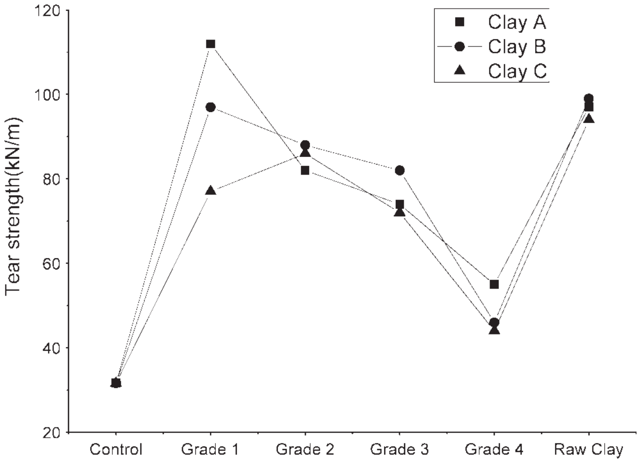

Figure 3 Effects of three kinds of clay use as filler in the natural rubber on the tear strength.

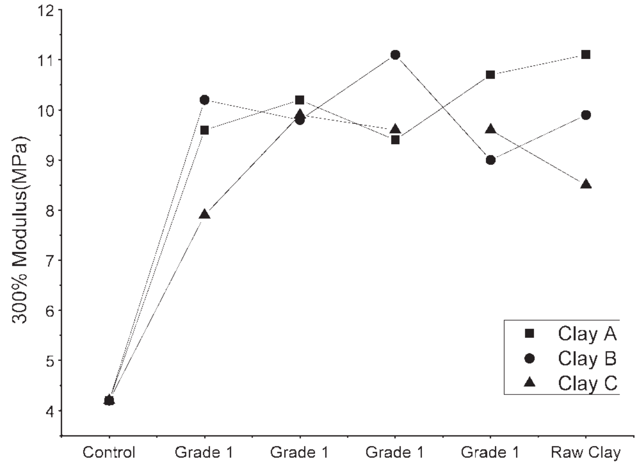

Figure 5 Effects of three kinds of clay use as filler in the natural rubber on the 300% modulus.

except hydroxyl groups (see Fig. 11), and the number of hydroxyl groups increase with the decrease of particle size. Heating the clays at 650°C, the hydroxyl groups on particle surface can be removed, the particle size and morphology don't change obviously, but the properties of composite become worse. It indicates that the hydroxyl groups on particle surface have an important effect on the reinforcement of clay to rubber.

The reinforcing mechanism of red clay on natural rubber

With further studies on distribution of clay in rubber by TEM, we found that in the grades of clay with small particles, which lent the composite better physical properties, the clay particles formed a kind of chain structure with limited length, which distributed evenly in the rubber phase (see Fig. 12). The composite prepared with raw clay shows the similar structure.

In the previous works, it is said that the reinforcing effects obtained were found to depend strongly on the extent of the dispersion of the clay into the rubber matrices. Clay can preventing coalescence of rubber domains, arisen in decreasing of rubber particle size, as the clay and rubber contents are high; the blocking effect on the overlap of stress volume around rubber matrices caused broadening of the brittle ductile transition region and decrease of toughness, and the effective stress transfer leading a better reinforcement when the interpretable distance is smaller than the critical value.[14–19]

Hence, we speculate that mechanism of the reinforcement of clay on rubber is that the clay forms a rigid or semi-rigid chain aggregation structure in

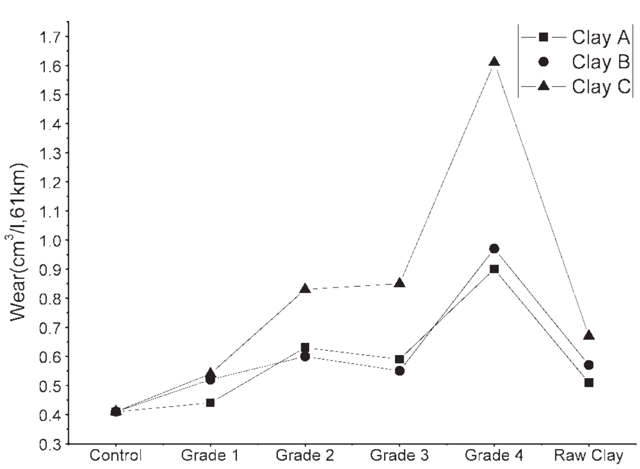

Figure 4 Effects of three kinds of clay use as filler in the natural rubber on the wear.

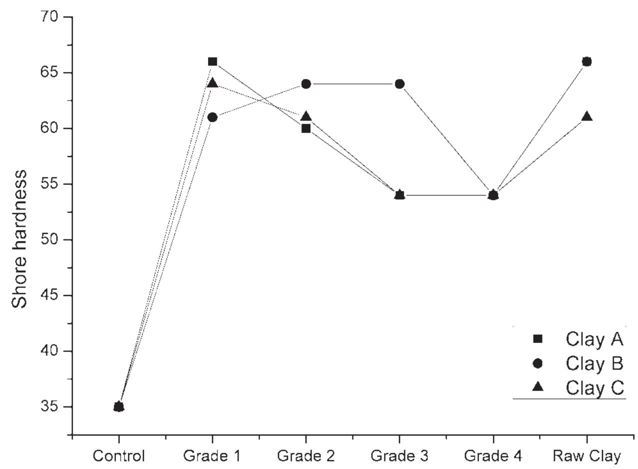

Figure 6 Effects of three kinds of clay use as filler in the natural rubber on the shore hardness.

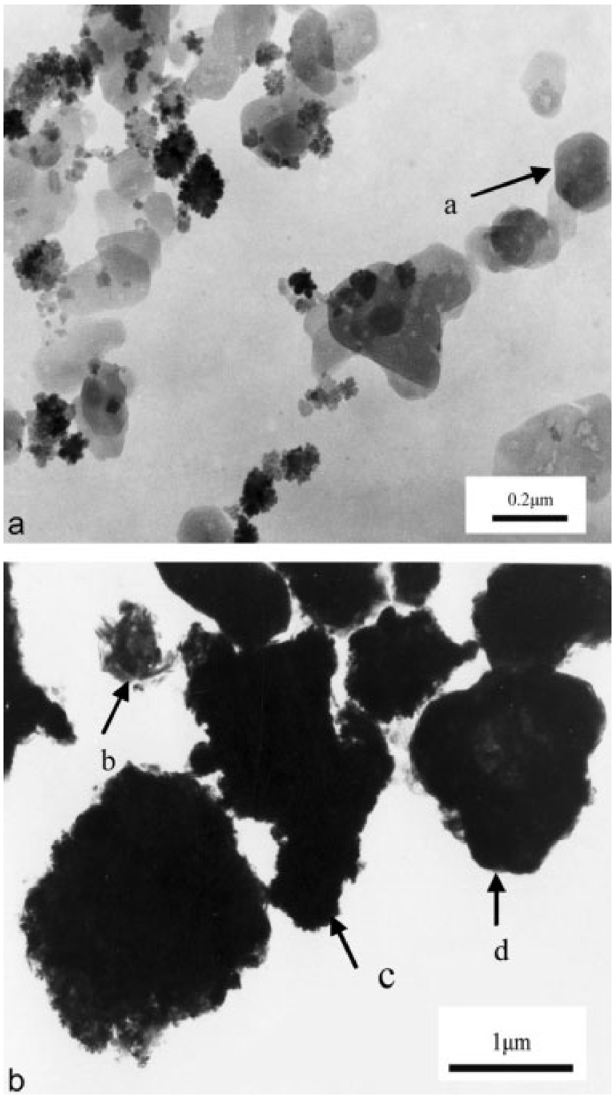

Figure 7 TEM micrographs of a, b, c, and d particle in clay.

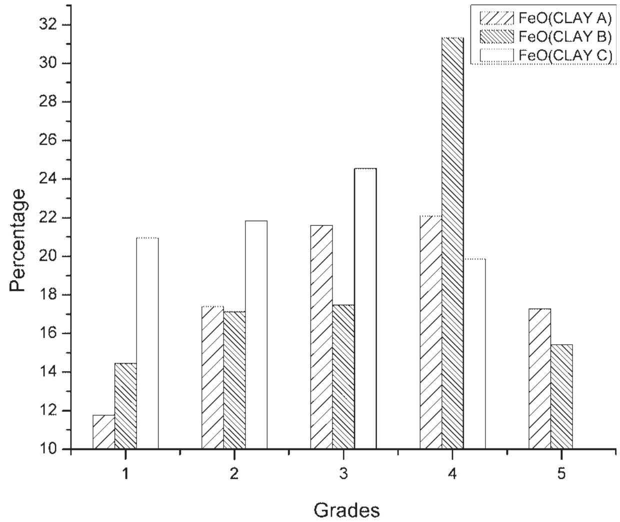

Figure 9 The percentage of FeO in the three clay particles.

rubber. This kind of structure is formed by the presentation of the hydroxyl groups on particle surface, which forms strong hydrogen bond and makes the particles attracted one another. The number of hydroxyl groups determines the attractive force between particles affects the strength of chain structure and also affects the linkage between and rubber hydrocarbon ruptured during milling and vulcanization. When the clay consists mainly of the small particles with adequate and dispersive in rubber, it forms a rigid chain network (see Fig. 13) distributing evenly in rubber owing to the absorption aggregation caused by the hydroxyl groups no the clay particle surface, which not only makes the rubber

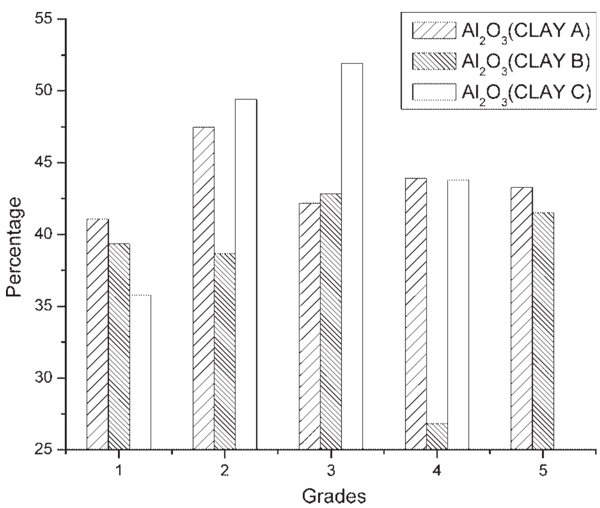

Figure 8 The percentage of Al_2O_3 in the three clay particles.

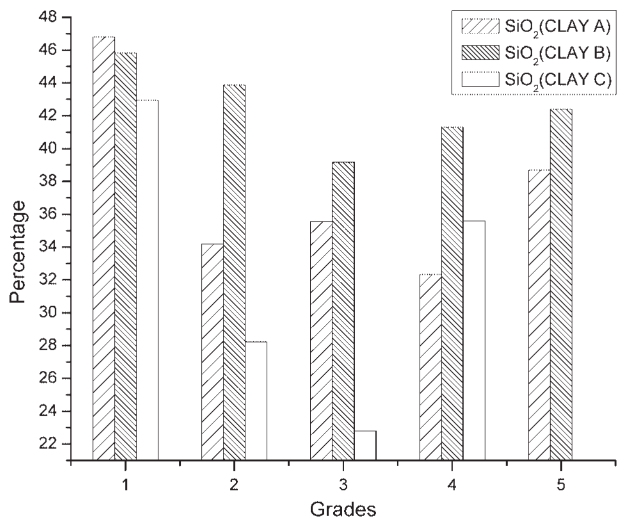

Figure 10 The percentage of SiO_2 in the three clay particles.

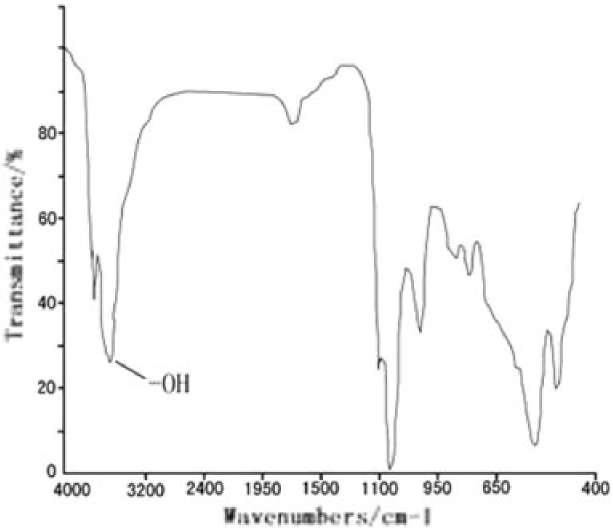

Figure 11 FTIR spectrum of clay.

Figure 13 Clay chain network in composite (R is rubber chain and C is clay).

hydrocarbon produce Van der Waals absorption or crosslinkage, but also makes the rubber molecular chains tangled on the clay chains, resulting in the dispersion of stress and showing an excellent reinforcement, and further verification of this proposed mechanism is awaited.

CONCLUSION

The main drawback of filler in general is expensive; therefore, clay was added to the NR latex. Within a certain range, the clay particle size only affects some of the mechanical properties of clay-rubber composite. The characteristic morphological structure of the clay provides a significant reinforcing action on clay-rubber composite. The unique nanocompounding mechanism can provide rubber/clay nanocomposites with the rigid or semi-rigid chain aggregation structure, which makes them different from intercalated and exfoliated polymer/clay nanocomposites prepared by melt blending.

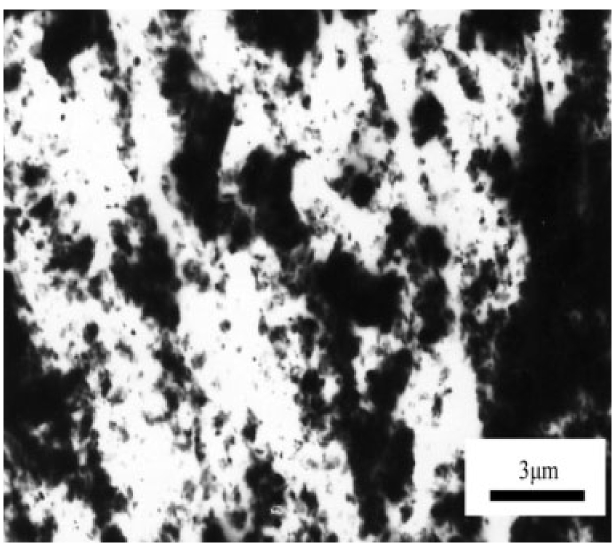

Figure 12 TEM micrograph of composite.

References

1. Meng, Q. Y.; Li, Z. P.; Deng W. Y. Synth Rubber Ind 1993, 16, 137.
2. Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; et al. Macromolecules 1997, 30, 6333.
3. Liu, L.; Qi, Z.; Zhu, X. J. J Appl Polym Sci 1999, 71, 1133.
4. Liang, Y. R.; Cao, W. L.; Zhao, Z. et al. Polym Test 2008, 27, 270.
5. Cho, J. W.; Paul, D. R. Polymer 2001, 42, 1083.
6. Hasegawa, N.; Okamoto, H.; Kato, M. et al. Polymer 2003, 44, 2933.
7. Wang, Y. Q.; Zhang, H. F.; Wu, Y. P.; et al. Eur Polym J 2005, 11, 2776.
8. Mathew, G.; Rhee, J. M.; Lee, Y. S.; et al. J Ind Eng Chem 2008, 14, 60.
9. Karger Kocsis, J.; Wu, C. W. Polym Eng Sci 2004, 44, 1083.
10. Chen, M.; Ao, N. J.; Liao, Y. Y.; et al. J Appl Polym Sci 2006, 100, 3809.
11. Li, W.; Huang, W. D.; Ahmadi, S. J. J Appl Polym Sci 2004, 94, 440.
12. Wang, S. X.; Ao, N. J.; Li, Z. P. Polym Sci Technol 1995, 51, 94.
13. Wijayarathna, B. Rubber Chem Technol 1978, 51, 1006.
14. Dasari, A.; Yu, Z. Z.; Mai, Y. W. Polymer 2005, 46, 5986.
15. Chiu, F. C.; Lai, S. M.; Chen, Y. L.; Lee, T. H. Polymer 2005, 46, 11600.
16. Krikorian, V.; Kurian, M.; Galvin, M. E.; et al. J Polym Part B 2002, 40, 2579.
17. Yen, T. V.; James, E. M.; Ly, H. P.; et al. J Polym Sci 2001, 82, 1391.
18. Zita, M.; Dirk, K.; Ralf, T.; et al. Polym Adv Technol 2005, 16, 362.
19. Wang, K.; Wang, C.; Li, J.; et al. Polymer 2007, 48, 2144.