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Preparation and Properties of Natural Rubber/Palygorskite Composites by Co-Coagulating Rubber Latex and Clay Aqueous Suspension

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Abstract

Natural rubber (NR)/Palygorskite composites were prepared by co-coagulating rubber latex and clay aqueous suspension. Org-palygorskite was attained by using cetyltrimethylammonium bromide (CTAB) and the four factors influencing the average diameter of palygorskite were discussed. Four optimal conditions of preparing minimum average diameter were determined which included the concentration of palygorskite, the concentration of sodium polyacrylate, ultrasonic time and ultrasonic power. Mechanical properties suggested that composites using modified palygorskite which were dispersed by ultrasonic wave were the best, the tensile strength, tear strength, 300% modulus and shall hardness increased by 77.14%, 118.18%, 242.86% and 65.2%, respectively. Modified palygorskite was shown by FTIR spectrogram and observed by ESEM. Modified palygorskite dispersed by ultrasonic wave were dispersed into the rubble uniformly, some stick particles inserted into the rubber and it is difficult to find stick shape, and there were 20% particles belonging to nanomaterials and 80% micromaterials.

Introduction

Rubber/clay nanocomposites, compared with their micron or macrocomposites due to the ultra fine phase dimensions and special phase structure involved, exhibit new and improved properties which have attracted great interest of researchers in the world both in industrial and in scientific field. The nanoconcept is highly relevant and more advantageous for rubber composites, and nanoreinforcement has been proved to be an extremely effective and necessary way for rubber application. Nowadays, carbon black and silica are two main nanofillers as rubber reinforcement due to their huge specific area, nanosize and certain of active functional groups on the surface [1, 2]. Technologies for synthesis of rubber/clay nanocomposites focus mainly on rubber melt or solution intercalation of organoclay [3–6] and latex route using pristine clay [7]. Compared with the melt or solution method, the approach of co-coagulating rubber latex and clay aqueous suspension [7], where pristine clay (non-organoclay) is employed, is promising for industrialization due to the low cost of pristine clay, simplicity of preparation process and superior cost/performance ratio [8].

Some clays are suitable additives for latex, provided that they can form dispersions adequate for latex compounding [9]. With the help of ultrasonic, the clay can be dispersed into the latex evenly. In this study, the approach of co-coagulating rubber latex and clay aqueous suspension was employed to produce NR/palygorskite nano/micro composites, and then to improve the mechanical properties of NR.

Experimental procedure

Materials

Palygoprskite was purified by high speed centrifugal technique. Its chemical compositions are shown in Table 1. NR (solid content 60%) was provided by Hainan Chemical Company (China); CTAB (purity of 99.8%) was purchased from Tianjin Chemical Company and used without further purification. Sodium polyacrylate and Sodium Hexametaphosphate were provided by China Medicine Shanghai Chemical Reagent Corporation. Sulfur, stearic acid, zinc oxide and so on were employed.

Preparation of composites

Co-coagulating rubber latex and clay aqueous suspension method was used to prepare the composites. Purified palygorskite was dispersed into deionized water with an ultrasonic cell pulverizer and an aqueous suspension of clay was obtained. CTAB was added into the suspension with another ultrasonic dispersal to get modified clay suspension. Natural rubber latex mixed uniformly with the suspension. Finally, the mixture was coagulated by coagulating agent (hydrochloric acid, 10%), washed by water for several times until its pH was about 7, and then dried. After mastication, mixing and vulcanization (150 °C, 15–20 MPa, 15 min), the NR/palygorskite composites

Table 1. Chemical compositions of palygorskite raw material/wt.%.

Material	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O
Palygorskite	53.60	21.53	7.64	6.04	2.01	3.52	1.07

were gained. The chemical compositions of the composites are listed in Table 2.

Characterization

The average particle diameter was examined by the Laser Particle Size Analyzer (JL-1155). The infrared ray absorption spectra of the palygorskite and the modified palygorskite were performed on an Avatar370 spectrometer. Both the tensile strength, tear strength and 300% modulus of the nature rubber and NR/palygorskite composites were tested by a WE-50 fluid universal tester, respectively. The morphology of the fracture surface of the composite was observed by a Quanta 200 environment scanning electron microscope (ESEM).

Results and discussion

Factors influencing average diameter of palygorskite

Four factors influencing the average diameter of palygorskite are discussed, which are palygorskite concentration, kinds and concentration of dispersant, ultrasonic time and ultrasonic power.

The effect of palygorskite concentration

The effect of palygorskite concentration on the average diameter of palygorskite is shown in Figure 1. With increasing the concentration of palygorskite, the average diameter firstly reduces and then increases. Another extremum at 20% (wt.) may be the deviation of the Laser Particle Size Analyzer. So when the concentration is 10%, the average diameter is minimum.

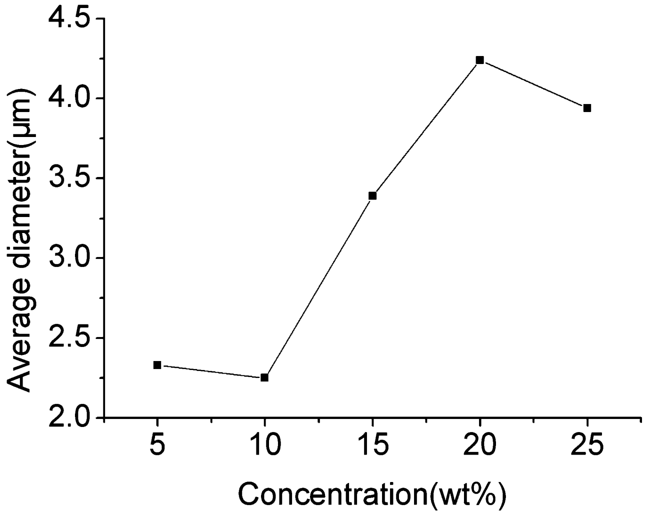

Figure 1. The relationship between concentration and average diameter.

The effect of kinds and content of dispersant

Sodium polyacrylate and sodium hexametaphosphate was used as dispersant in this study. Dispersant was introduced after palygorskite was stirring in aqueous solution for a few minutes. After dispersant has mixed uniformly with palygorskite aqueous solution, ultrasonic dispersal was carried out. The effect of concentration of sodium polyacrylate and sodium hexametaphosphate on the average diameter of palygorskite is shown in Figure 2. It can be seen that using sodium polyacrylate exhibits better dispersal effect, especially when the concentration is 0.3%, the best dispersal effect is obtained.

The effect of ultrasonic time

The effect of ultrasonic time on the average diameter of palygorskite is shown in Figure 3. It can be seen that by increasing the ultrasonic time, the average diameter of palygorskite decreases obviously, which suggests better dispersal effect. When ultrasonic time is 11 min, the best dispersal effect is obtained.

The effect of ultrasonic power on the average diameter of palygorskite

The effect of ultrasonic power on the average diameter of palygorskite is shown in Figure 4. It can be seen that the average diameter reduces with the increase of ultrasonic

Table 2. Chemical compositions of NR/palygorskite/wt.%.

Natural rubber	Stearic acid	Zinc oxide	Accelerator DM	Accelerator M	Sulfur	Filler
100	2.0	21.53	1.2	0.8	2.5	5

Accelerator DM: dibenzothiazole disulfide, Accelerator M: 2-mercaptobenzothiazole.

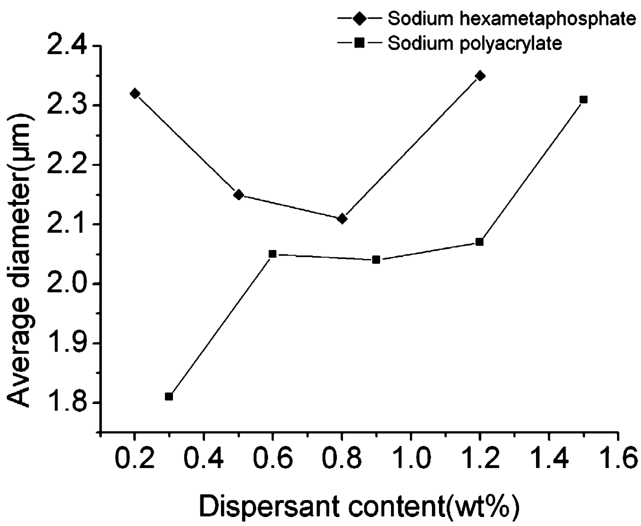

Figure 2. The effect of content of different dispersal on the average diameter of palygorskite.

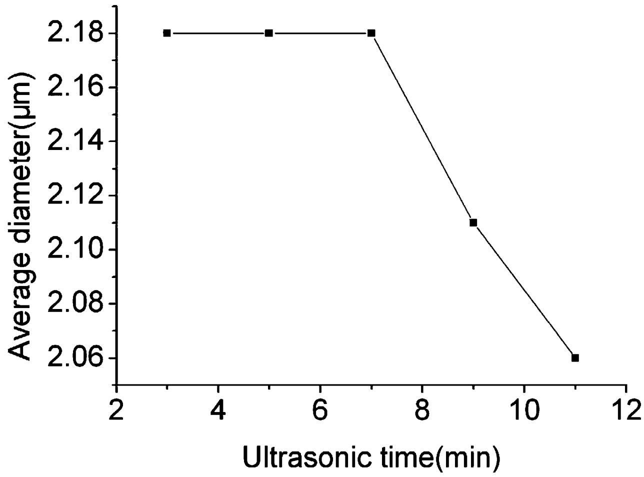

Figure 3. The relationship between ultrasonic time and average diameter.

power, and when ultrasonic power is 200 W, the average diameter is minimum.

From the above results, the optimal conditions suitable for this study is as follows: The concentration of palygorskite is 10%, the concentration of sodium polyacrylate is 0.3%, ultrasonic time is 11 min and ultrasonic power is 200 W.

Analysis of IR patterns

Figure 5 shows the FTIR spectrum of palygorskite, modified palygorskite using CTAB and CTAB. The two intense adsorption bands of the symmetric CH_3 and CH_2 stretching modes at 2,910 and 2,820 cm^{-1} and the band of CH_2 scissoring a mode at 1,480 cm^{-1} mean that palygorskite has been modified successfully.

Properties of the composites

The properties of NR and the NR/palygorskite composites are listed in Table 3. The results show that the tensile strength, tear strength, 300% modulus and shall hardness of

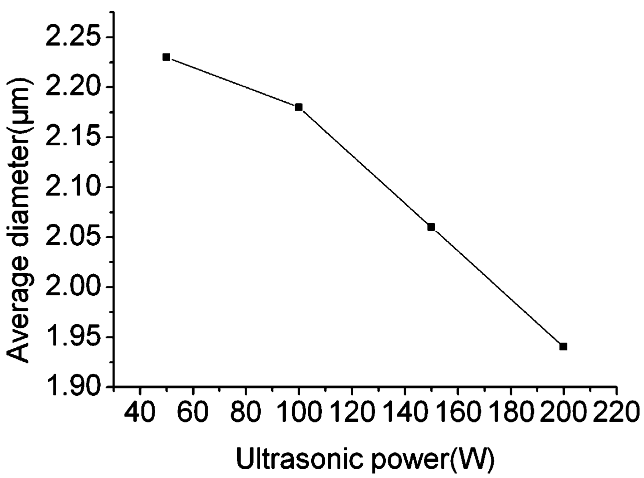

Figure 4. The relationship between ultrasonic power and average diameter.

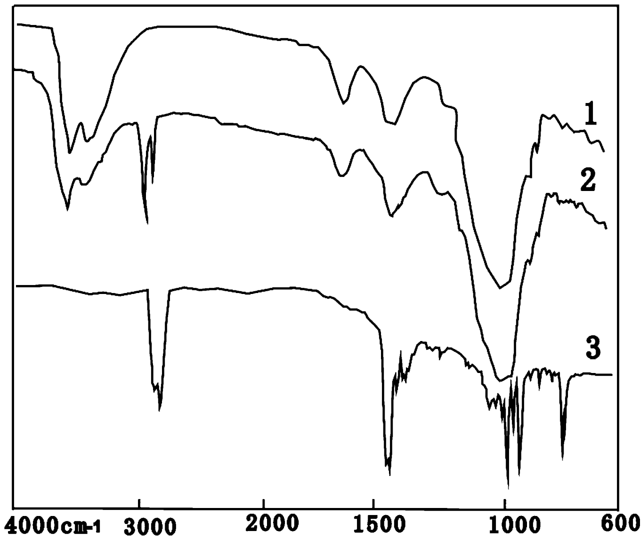

Figure 5. IR patterns of palygorskite, modified palygorskite using CTAB and CTAB. 1 Palygorskite 2 Modified palygorskite using CTAB 3 CTAB.

the composites are higher than that of NR and the properties of composites using modified palygorskite which are dispersed by ultrasonic wave are the best, the tensile strength, tear strength, 300% modulus and shall hardness increase by 77.14%, 118.18%, 242.86%, and 65.2%, respectively. It can therefore be concluded that the properties of NR can be modified dramatically by using palygorskite as an additive. CTAB can react with the active functional groups on the surface of palygorskite and facilitate the separation of palygorskite in the natural rubber blending process, and improve the interaction between natural rubber and palygorskite.

Analysis of ESEM images

The microstructure of the composites is observed and analyzed by SEM. It can be seen that the palygorskite which is undispersed by ultrasonic wave has bad dispersibility and fibrous structure in the NR, easy agglomeration in Figures 6, 7, 8 and 9, but palygorskite which is dispersed by ultrasonic wave has better dispersibility, slice and stick shape is observed. Modified palygorskite which is dispersed by ultrasonic wave are dispersed into the rubble uniformly,

Table 3. Properties of NR and the NR/palygorskite composites.

	Tensile strength	Elongation	Tear strength	300% modulus	Shall hardness
NR	10.5	920	20.9	7	24
1# composites	8.05	820	25.2	8	29
2# composites	13.2	860	27.6	10	30
3# composites	18.6	700	45.6	24	43

1# composites using unmodified palygorskite which are not dispersed by ultrasonic wave.
2# composites using unmodified palygorskite which are dispersed by ultrasonic wave.
3# composites using modified palygorskite which are dispersed by ultrasonic wave.

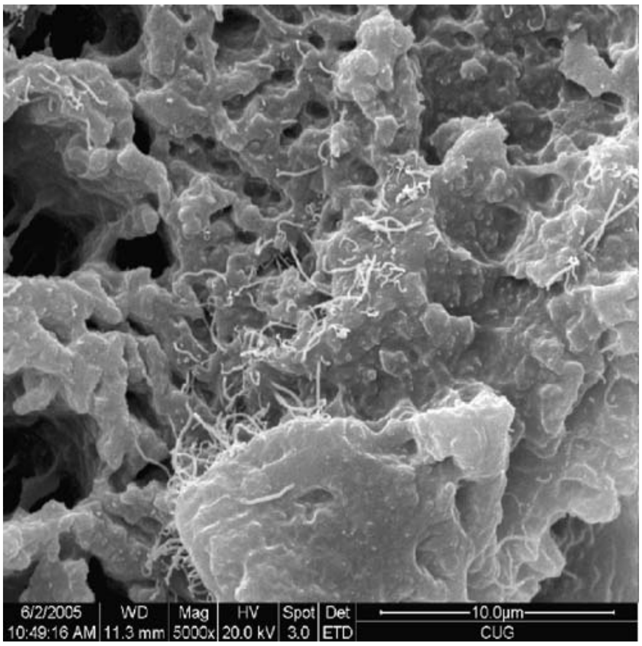

Figure 6. SEM micrograph of the 1# composites.

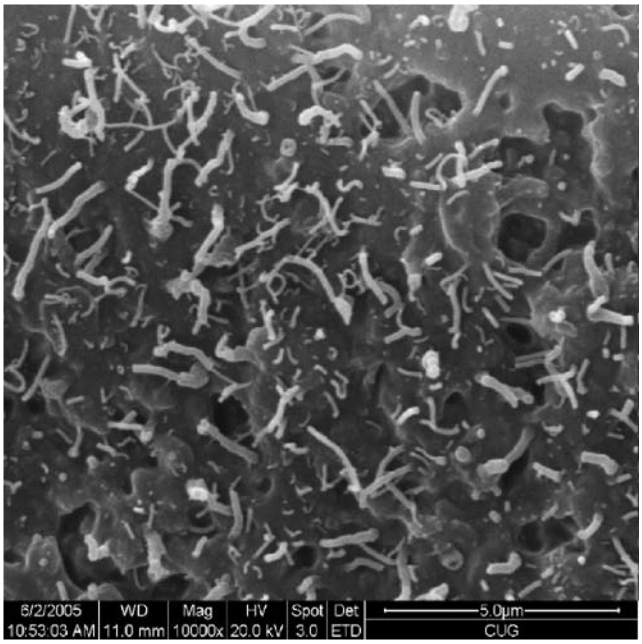

Figure 8. SEM micrograph of the 2# composites.

some stick particles insert into the rubber and it is difficult to find stick shape. The ratio of the number of micrometer particles to that of nanometer was statistical value according to the ESEM images. There are 20% particles belonging to nanomaterials and 80% micromaterials.

Conclusions

1. The optimal conditions of preparing minimum average diameter includes: The concentration of palygorskite is 10%, the concentration of sodium polyacrylate is 0.3%, ultrasonic time is 11 min and ultrasonic power is 200 W.
2. The properties of composites using modified palygorskite which are dispersed by ultrasonic wave are the best, the tensile strength, tear strength, 300% modulus and shall hardness increase by 77.14%, 118.18%, 242.86%, and 65.2%, respectively.
3. Modified palygorskite which is dispersed by ultrasonic wave is dispersed into the rubble uniformly, some stick particles insert into the rubber and it is difficult to find stick shape. There are 20% particles belonging to nanomaterials and 80% micromaterials.

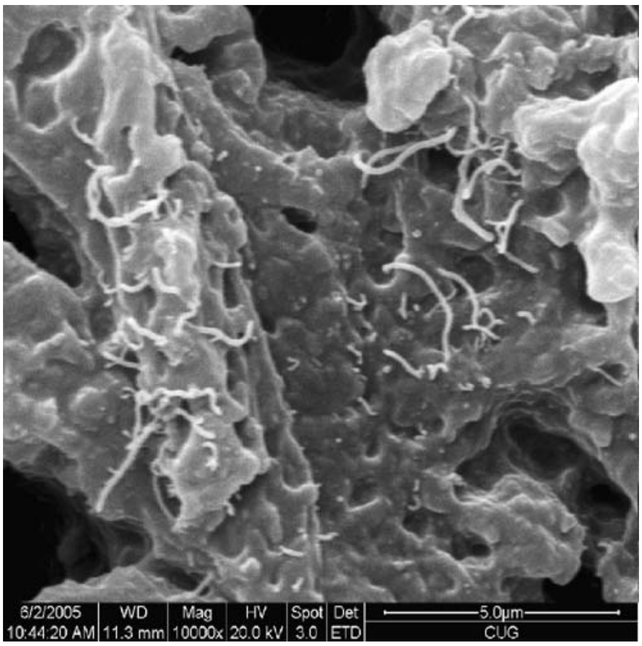

Figure 7. SEM micrograph of the 1# composites.

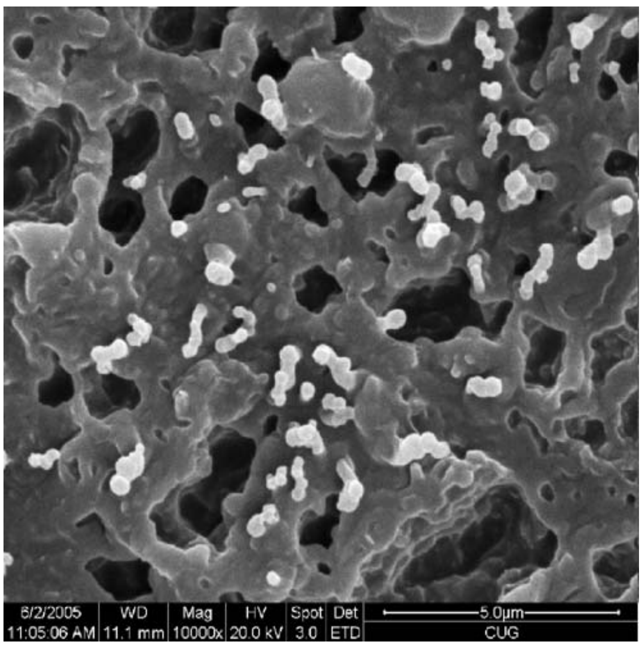

Figure 9. SEM micrograph of the 3# composites.

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