

Morphology and Mechanical Properties of Clay/Styrene-Butadiene Rubber Nanocomposites

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Received 11 December 1997; accepted 10 January 2000

ABSTRACT: Based on the character of a clay that could be separated into many 1-nm thickness monolayers, clay styrene-butadiene rubber (SBR) nanocomposites were acquired by mixing the SBR latex with a clay/water dispersion and coagulating the mixture. The structure of the dispersion of clay in the SBR was studied through TEM. The mechanical properties of clay/SBR nanocomposites with different filling amounts of clay were studied. The results showed that the main structure of the dispersion of clay in the SBR was a layer bundle whose thickness was 4–10 nm and its aggregation formed by several or many layer bundles. Compared with the other filler, some mechanical properties of clay/SBR nanocomposites exceeded those of carbon black/SBR composites and they were higher than those of clay/SBR composites produced by directly mixing clay with SBR through regular rubber processing means. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1873–1878, 2000

Key words: clay; styrene-butadiene rubber; nanocomposites

INTRODUCTION

Carbon black used to be the most important reinforcing agent in the rubber materials industry. But its polluting nature, the monotonous black color of the rubber material, and its dependence on petroleum caused researchers to develop other satisfying reinforcing agents instead. It was well known that the particle size, structure, and surface characteristics of reinforcing agents were three main factors that effect or decide its reinforcing ability, especially the particle size. Experiments showed that the tensile strength of ultrafine CaCO_3 /styrene-butadiene rubber (SBR) composites was improved and 3 times higher than

that of a regular size CaCO_3 /SBR blend. The reason why silica had this excellent reinforcing ability was that it possesses an ultrafine particle size of 10–20 nm.

Clay has been used as a rubber filler for many years. There are abundant natural clay resources in China. The reinforcing ability of clay is poor because of its big particle size and low surface activity. A new way to improve the reinforcing ability of clay was recently found. Clay is composed of many monolayers that are 1 nm thick and 200–300 nm long. The layers cannot be separated from each other through general rubber processing means. Because ions absorbed by clay can be exchanged by other ions, research succeeded in intercalating many kinds of polymers in layers to prepare clay/polymer nanocomposites.^{1–3} These nanocomposites exhibited outstanding mechanical properties such as high stiffness and strength.^{4–6} However, there were few studies on the clay/rubber nanocomposites.

Correspondence to: Y. Wang.

Contract grant sponsor: NSF; contract grant number: 59773008.

Contract grant sponsor: SINOPEC; contract grant number: X598016.

Journal of Applied Polymer Science, Vol. 78, 1873–1878 (2000)
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A clay layer can be steadily dispersed in water for the hydration of the ions between them. Most rubbers have latex forms. So, mixing a rubber latex and clay/water dispersion and then coagulating the mixture produces a clay/rubber nanocomposite. In this study we used an SBR latex to prepare the clay/SBR nanocomposite. The dispersed structure of the clay in the SBR matrix and the mechanical properties of the clay/SBR nanocomposites were studied.

EXPERIMENTAL

Materials

Styrene-butadiene latex was available from Qilu Petrochemical Corp.; the solid content was 25%. SBR 1500 was available from Jilin Chemical Industry Corp. Natural clay fractionated from bentonite was produced in Hebei Province; its particle size was 4 μm . Carbon black (SRF and HAF), silica (Hi-Sil-233), and another clay (TC) in common use in rubber industry components were provided by Beijing Second Rubber Factory; the other components were provided by Beijing Tenth Rubber Factory. Other composites were prepared by blending SBR with other reinforcing agents. They were named the HAF/SBR composites, silica/SBR composites, SRF/SBR composites, clay/SBR composites, and TC/SBR composites.

Preparation

Clay was dispersed in water with strong stirring (4% dispersion in water), then the latex was added and mixed for a period of time. It was coagulated in dilute hydrochloric acid solution, washed with water until its pH was about 7, and dried at 80°C for 24 h.

Compounds

The compounds used were SBR 100, ZnO 5, stearic acid (SA) 2, diphenyl guanidine (accelerator D) 0.5, dibenzothiazole disulfide (accelerator DM) 0.5, tetramethyl thiuram disulfide (accelerator TT) 0.2, sulfur 1.5, *N*-isopropyl-*N'*-methylphenyl-*p*-phenylene diamine (antiaging agent 4010NA) 1.0, and various reinforcing agents.

Processing

The nanocomposites or SBR and other components were mixed by a 6-in. external mixer ac-

ording to the regular sequence; then the blends were vulcanized in a standard mold at 150°C. The curing time was tested and decided upon with a rheometer 750 made from Beijing Huan Feng Mechanical Factory.

Characterization

The dispersed structure of the clay in the composites was studied by TEM. Samples were produced using an ultramicrotome and glass knives, and they were examined with a Hitachi H-800 TE microscope using an acceleration voltage of 200 kV.

Mechanical Tests

Mechanical tests were carried out according to GB (Chinese standard) and ASTM.

RESULTS AND DISCUSSION

Morphology of Nanocomposites

Figure 1(a) shows the dispersed structure of clay in the nanocomposites where the filled amount of clay is 20 per hundred parts rubber (phr). It is apparent that many clay layer bundles exist whose thickness is about 4–10 nm and length is about 200–300 nm, which is equal to the length of the clay layer.

Figure 1(b) shows that some layer bundles are further divided into several thinner bundles, and the other layer bundles are still bonded together. Figure 1(a) also shows that there are many aggregations composed of several or many layer bundles where most of the layer bundles are parallel some layer bundles are tightly closed [Fig. 1(a, c)], and the spacing among some of the layer bundles is large [Fig. 1(a, b)].

It is well known that there are many monolayers of clay in composites, but it is very difficult to find these monolayers because of high clay content aggregations formed by the layer bundles.

Figure 2 shows the dispersed structure of clay in the composites where the filled amount of clay is 40 phr. We found that in these composites the layer bundles of clay were finer than those in Figure 1 and the spacing between layers or layer bundles was bigger, so the amount of aggregation of the tightly closed layer bundles was reduced.

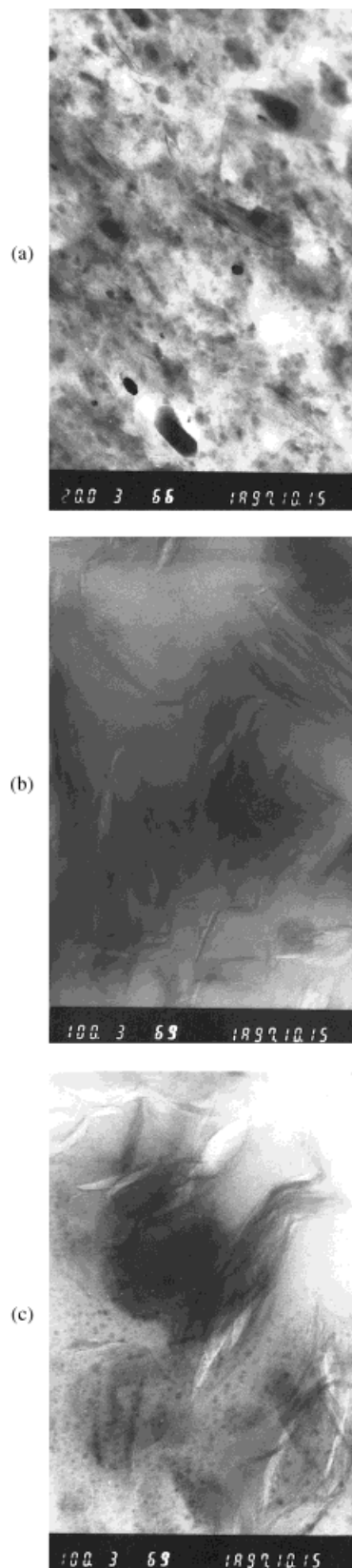


Figure 1 A TEM photo of the clay/SBR nanocomposites with 20 phr of clay.

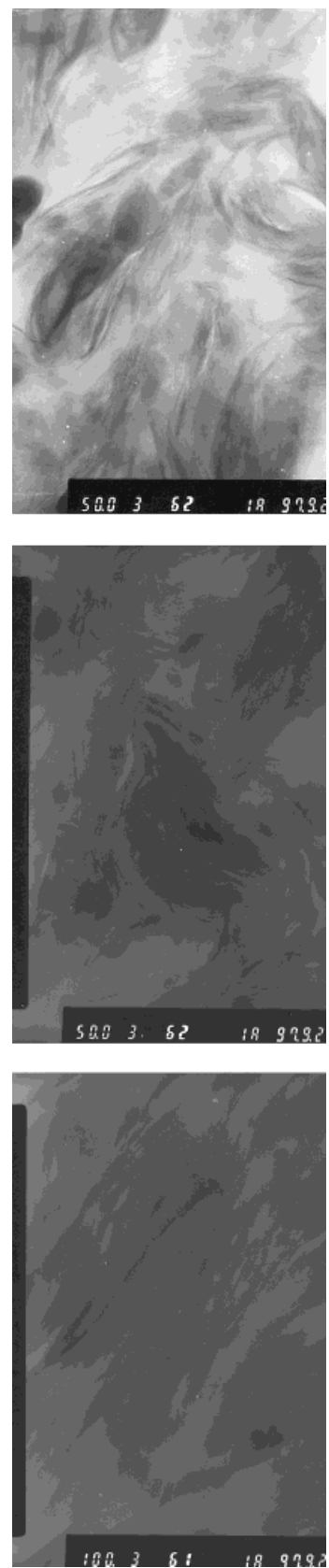


Figure 2 A TEM photo of the clay/SBR nanocomposites with 40 phr of clay.

Mechanical Properties of Clay/SBR Nanocomposites

Figure 3 shows the mechanical properties of clay/SBR nanocomposites and those of other reinforcing agent filled SBR composites.

Hardness and 300% Tensile Stress

The hardness of clay/SBR nanocomposites with different filled amounts of clay was higher than that of other composites. It was attributed to the layer structure of the clay and the extremely high interfacial action between the layer or layer bundle and the rubber. The hardness of clay/SBR composites was far lower than that of clay/SBR nanocomposites because of the large particle size.

Tensile Strength

When the amount of clay was less than 20 phr, the tensile strength of the nanocomposites was the highest among all the composites; the tensile strength of nanocomposites filled with 10 phr clay was far higher than that of other composites. When the filled amount of clay was 40 phr, the tensile strength of the nanocomposites was higher than that of silica/SBR and lower than that of HAF/SBR.

Tear Strength

The tear strength of the nanocomposites was very excellent, no matter how much clay was filled. Credit was given to special layer structure of the clay in the nanocomposites, the extreme interfacial action, and the slide between the layer bundles, which could decrease the energy of the expansion of the crack.

Tensile Strain

The tensile strain of the nanocomposites showed a trend that went up at first and then went down with the increase of the filled amount of clay much like the developmental trend of other properties such as the 300% tensile stress, tensile strength, and tear strength. When the filled amount of clay reached 40 phr, the tensile strain of the nanocomposites was the same as that of HAF/SBR.

Rebound Resilience

Under the same filled amount of clay, the rebound resilience of the nanocomposites was almost the

same as that of silica/SBR and it was lower than that of other composites. This was related to the special structure of the dispersed phase in the nanocomposites.

Processing Properties

We found that the Mooney viscosity of the nanocomposites was far higher than that of the TC/SBR composite. It was thought that layers effectively restricted the movement of macromolecules by their high interfacial action. Because the strength of the nanocomposites was high, they quickly surrounded the rollers well. Because part of the reinforcing agent had existed in the nanocomposites and the other compound could be fed into them and quickly dispersed, the mixing time was greatly reduced, especially in the higher filled amount of clay.

Advantages and Disadvantages

Advantages. From the hardness, 300% tensile stress, tensile strength, tear strength, and tensile strain the conclusion could be drawn that the mechanical properties of the clay/SBR nanocomposite had reached the level of the HAF/SBR composites. The layer in the nanocomposites gave them good aging resistance due to its prevention of contact with air. The excellent mechanical properties, good processing properties, and low price could hasten the applications of the nanocomposite in industry.

Disadvantages. When the filled amount of clay in the composite was higher than 40 phr, some properties of the nanocomposites stopped rising and even went down. The rebound resilience of the nanocomposites was not satisfied.

The advantages and disadvantages of the nanocomposite originated from their special morphology. The layer and layer bundles strongly restricted the movement of the macromolecules, but on their edge and at their four corners extreme stress concentration was produced that was more serious with the increase of volume of the clay and the tensile strain. Although the interfacial area between the layer bundles or layers and elastomer was great, their interfacial adhesion was poor, except for the four sides of the layers and layer bundles where the hydroxyl group had high chemical activity. The stress concentration and poor interfacial adhesion resulted in the interfacial separation, especially in the

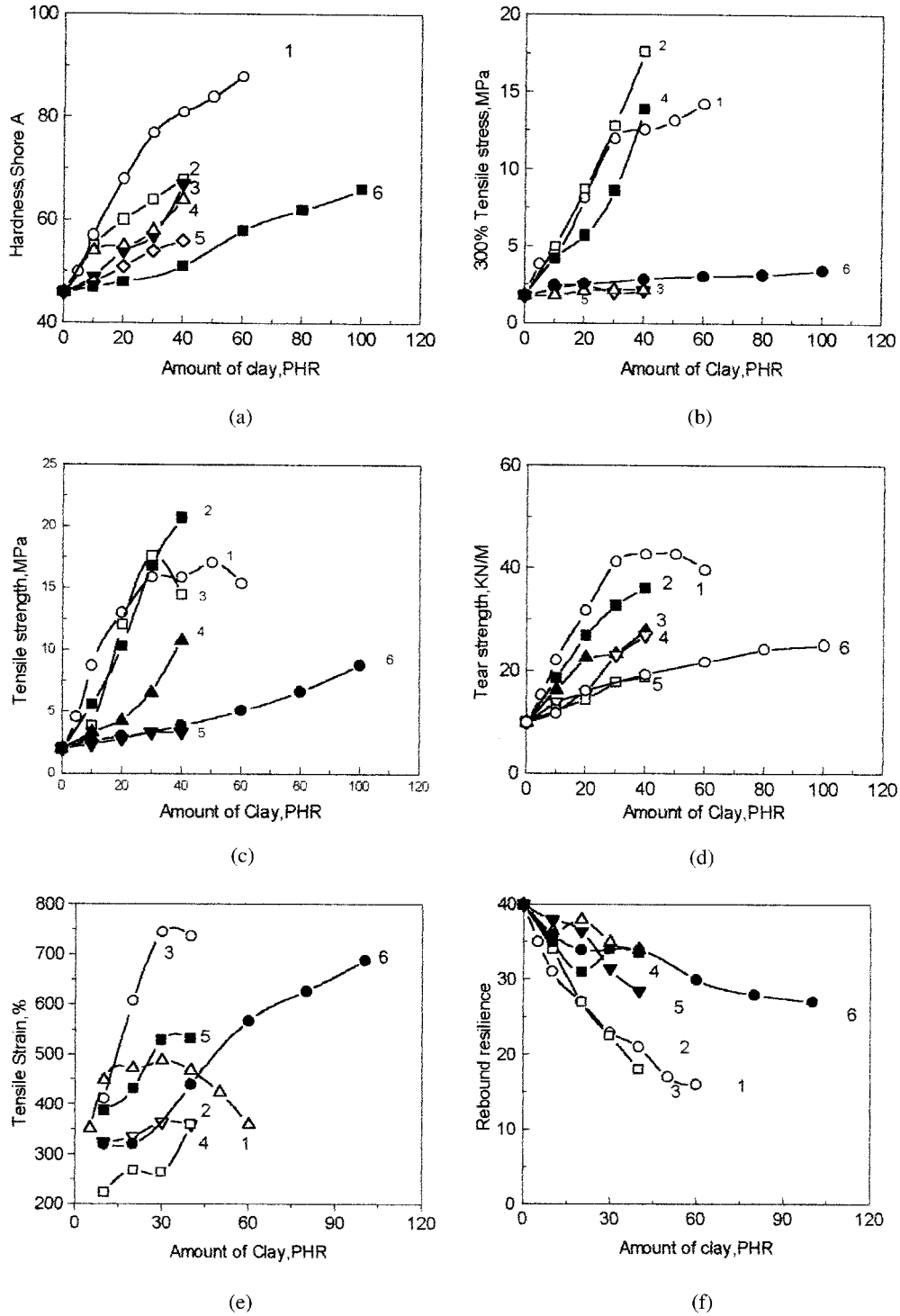


Figure 3 The mechanical properties of clay/SBR nanocomposites. Curves 1–6 are the clay/SBR nanocomposites, HAF/SBR composites, silica/SBR composites, SRF/SBR composites, clay/SBR composites, and TC/SBR composites, respectively.

higher tensile strain. In addition, when the volume of clay was higher than 40 phr, it was more difficult to separate the clay layers from each other.

CONCLUSION

Mixing SBR latex and a clay/water dispersion was the method used to acquire clay/SBR nanocomposites. Most of the mechanical properties of the nanocomposites were far higher than that of the clay/SBR composites. All the mechanical properties of the nanocomposites reached the level of the HAF/SBR composites. The processing properties of the nanocomposites was also very excellent. If the interfacial adhesion and dispersion of clay could be further improved, the me-

chanical properties of the nanocomposite would be more satisfactory.

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