

Preparation and Characterization of Rubber–Clay Nanocomposites

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ABSTRACT: Rubber–clay nanocomposites were prepared by two different methods and characterized with TEM and XRD. The TEM showed clay had been dispersed to one or several layers. The XRD showed that the basal spacing in the clay was increased. It was evident that some macromolecules intercalated to the clay layer galleries. The clay layer could be uniformly dispersed in the rubber matrix on the nanometer level. The mechanical tests showed that the nanocomposites had good mechanical properties. Some properties exceeded those of rubber reinforced with carbon black, so the clay layers could be used as an important reinforcing agent as the carbon black was. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1879–1883, 2000

Key words: rubber–clay nanocomposites; TEM; XRD

INTRODUCTION

Clay is an inexpensive natural mineral so it has been used as a filler for rubber and plastic for many years, but its reinforcing ability is poor so it can only be used for conventional microcomposites. Clay has a layer structure; among the layers there are some ions that can be exchanged with other organic ions.¹ In recent years the interest in nanoscale materials was inspired by the fact that nanoscale materials often exhibited physical and chemical properties that were dramatically different from their bulk counterparts. A novel ideal was put forth that polymer could be intercalated to the clay layer galleries to form nanocomposites through a special method,^{2–5} and many kinds of materials sprung up that had an ultrafine phase dimension.^{6,7} Nanocomposites possess unique

properties such as stiffness, strength and gas barrier action for their dispersion structure.^{8–10} The methods for nanocomposites included *in situ* polymerization, solution intercalation, and melting intercalation. *In situ* polymerization needs special monomers and clay treatment; this limits its application in other polymers. The solution method needs a compatible polymer–solution system and organically modified clay; its disadvantage is that the solvent must be deabsorbed. Melting intercalation can be applied to most polymers, especially plastic, but it needs a polymer that has good process properties in the melting state.

Clay can be modified with organic quaternary ammonium salts; thus, some modified clay can be swollen in nonpolar solvents such as toluene. The clay layer can be steadily dispersed in water for the hydration of the ion among the layers; the layers are separated from each other. Some polar compounds can intercalate to the clay layer galleries. These characteristics provided a way to prepare the rubber–clay nanocomposites. The molecular weight of the rubber was higher than plastic; it had very high viscosity in the process state, and most of the rubbers had latex forms

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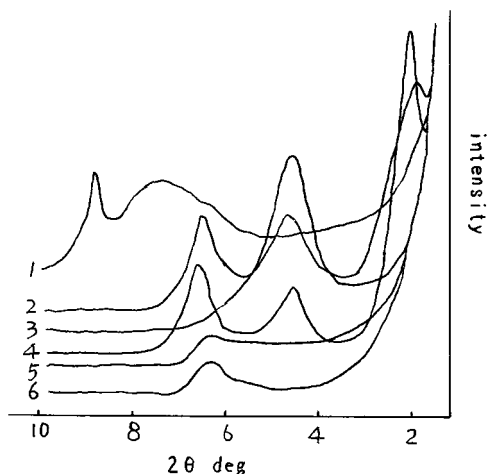


Figure 1 The XRD patterns of different materials. Curves 1–6 are the clay, modified clay, SBR–clay nanocomposites (solution method), BR–clay nanocomposites, SVBR–clay nanocomposites, and SBR–clay nanocomposites (latex method), respectively.

and could blend with a clay–water dispersion without coagulation. We developed a new method to prepare rubber–clay nanocomposites through mixing and coagulating of rubber latex, which we named the latex method. The rubber–clay nanocomposites had a fine dispersed phase structure and good mechanical properties.

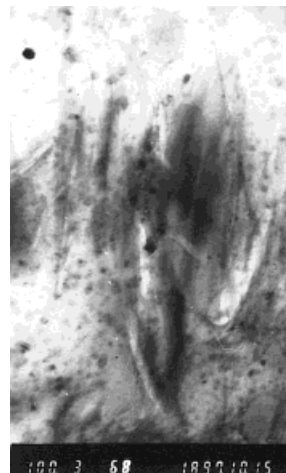
EXPERIMENTAL

Materials

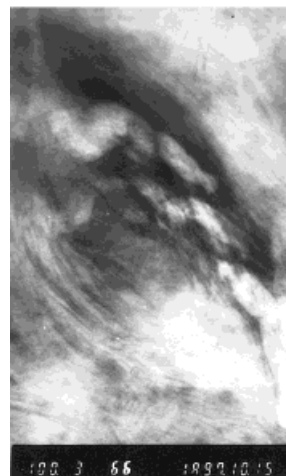
Styrene–butadiene latex (SBR) was available from Qilu Petrochemical Corp.; the solid content

Table I Basal Spacing (d_{001}) in Clay and Nanocomposites

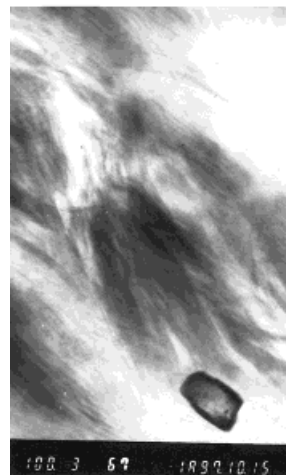
Sample	Clay Content (%)	d_{001}
Clay	—	1.24
Modified clay	—	1.90
SVBR–clay nanocomposites	40	1.46
SBR–clay nanocomposite		
Latex	40	1.46
Solution	20	4.16
BR–clay nanocomposites	40	4.41



(a)



(b)



(c)

Figure 2 A TEM photo of the (a) SBR–clay nanocomposites (solution), (b) SVBR–clay nanocomposites, and (c) SBR–clay nanocomposites (latex).

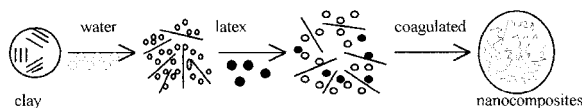


Figure 3 A schematic of the formation of the nanocomposites.

was 22%. Styrene-vinylpyridene-butadiene latex (SVBR) was available from Nippon Zeon Co. Ltd.; its solid content was 42%. SBR 1500 was available from Jilin Chemical Industry Corp.; BR 9000 was available from Beijing Yanshan Petrochemical Corp. Nature clay was fractionated from bentonite produced in Heibei Province. Modified clay was available from Li'an Coating Agents Factory, China. Carbon black (SRF and N330) was available commercially.

Preparation

Clay was dispersed in water with strong stirring (2% dispersed 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 50°C (the latex method). Organic modified clay was dispersed in toluene with stirring; then a rubber-toluene solution was added and stirred vigorously for about 12 h. Finally, the solvent was removed (the solvent method), and nanocomposites were obtained. The nanocomposites and other rubbers reinforced with carbon black were processed with conventional technology, vulcanized, and tested.

Characterization

The structure of the dispersed silicate layer in the composites was studied with XRD and TEM. The XRD intensity curves were recorded with a GDR

Table II Properties of SVBR-Clay Nanocomposites

Clay (phr)	Hardness (Shore A)	Tear Strength (kN/m)	Tensile Strength (MPa)	Elongation (%)
10	62	24.3	8.00	164
20	70	24.9	10.9	258
30	83	22.3	14.1	161
40	91	22.1	13.9	81

Vebscarl Zeiss Jena HZG4/B and Cu-K α radiation. 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 Property Tests

Mechanical tests were carried out according to GB (Chinese Standard).

RESULTS AND DISCUSSION

Figure 1 shows the XRD intensity curve of the products. The basal spacing (d_{001}) in the clay and nanocomposites are shown in the Table I. The d_{001} data of the nanocomposites obtained by the latex method exhibited a clay galleries expansion from 1.24 to 1.46 nm. A single layer of the macromolecule intercalated to the interlayer space; the d_{001} data of the nanocomposites obtained by the solution method showed the organoammonium modified clay galleries were expanded from 1.90 to 4.1 nm, so some layer of molecules intercalated to the galleries. When the clay was mod-

Table III Properties of SBR-Clay Nanocomposites with Latex Method

Clay (phr)	Hardness (Shore A)	Tear Strength (kN/m)	Tensile Strength (MPa)	Elongation (%)	Permanent Set (%)
10	62	13.4	5.3	318	6
20	64	23.8	7.5	454	18
30	68	31.2	12.4	504	40
40	72	30.9	15.8	568	56
60	74	36.5	13.9	732	64

Table IV Properties of SBR–Clay Nanocomposites with Solution Method

Clay (phr)	Hardness (Shore A)	Tear Strength (kN/m)	Tensile Strength (MPa)	Elongation (%)	Permanent Set (%)
5	46	12	2.1	505	8
10	48	15	4.3	524	16
20	50	18	7.2	530	36
40	59	24	11.3	750	92

ified with an organic compound, it had some compatibility with rubbers, so the clay galleries could be easily intercalated with the polymer.

Figure 2 shows a TEM photo of the nanocomposites. The dark lines in the photo correspond to the intersections of the silicate layer with a thickness of about 1 nm. The clay is dispersed to one or several layers in the rubber matrix. These indicated that nanocomposites had been formed. The clay layer could be steadily dispersed in water and the layers could be separated from each other. When the latex was added with stirring, the latex particle could be mixed uniformly with the layers; they interpenetrated each other. As they were dropped into the dilute hydrochloric acid solution, the ions among the layers were exchanged; at the same time the latex and the clay layers were coagulated together and some layers might have coagulated themselves, so the dispersed structure in the water was kept. Most of the layer could be dispersed in the rubber matrix on a nanometer level. Figure 3 is an illumination of this process.

Tables II–VII summarize the mechanical properties of these nanocomposites and other reinforced rubber materials; their properties improved with the increase of the amount of clay. Materials had different properties with different reinforcing methods. The data exhibited that clay was a good reinforcing agent like the carbon black

in the studied range. Some properties exceeded those of the materials reinforced by carbon black, especially the hardness, tear strength, and tensile strength. The excellent mechanical properties of the nanocomposites could be considered from their origin in the uniformly dispersed silicate layer. The mechanical properties of the nanocomposites produced by the latex method were better than those produced by the solution method. The improved properties of the former could be interpreted to be its better dispersion of silicate layers and the interaction between the clay layers and the SVBR.

CONCLUSION

Three kinds of rubber–clay nanocomposites were prepared by latex and solution methods. Clay could be dispersed in the rubber matrix as one or several layers, while polymer molecules intercalated to the clay galleries. The nanocomposites had good mechanical properties. Compared with other methods, the latex method was more convenient and could be widely used to prepare polymer–clay nanocomposites. Clay could be used as a promising reinforcing agent in the rubber industry if it was dispersed on a nanometer level through some special method.

Table V Properties of BR–Clay Nanocomposites

Clay (phr)	Hardness (Shore A)	Tensile Strength (MPa)	Elongation (%)	Permanent Set (%)
5	44	1.6	225	4
10	45	3.1	360	8
20	48	6.4	724	28
40	50	8.9	670	48

Table VI Properties of SBR by Comparative Reinforcing Methods (20 phr Clay)

Method	Hardness (Shore A)	Tear Strength (kN/m)	Tensile Strength (MPa)	Elongation (%)	Permanent Set (%)
Latex	64	23.8	7.5	454	18
Solution	50	12.8	7.2	530	36
SRF	56	20	6.9	424	4
N330	58	25	14.0	488	4

Table VII Properties of BR by Comparative Reinforcing Method (20 phr Clay)

Method	Hardness (Shore A)	Tear Strength (kN/m)	Tensile Strength (MPa)	Elongation (%)	Permanent Set (%)
Solution	48	15.7	6.4	724	28
SRF	48	19.6	3.5	476	4
N330	50	19.6	5.9	500	4

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