

Structure of Carboxylated Acrylonitrile-Butadiene Rubber (CNBR)–Clay Nanocomposites by Co-coagulating Rubber Latex and Clay Aqueous Suspension

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ABSTRACT: Carboxylated acrylonitrile-butadiene rubber (CNBR)–clay mixtures were prepared by co-coagulating rubber latex and clay aqueous suspension, then combining the mixtures with a rubber ingredient and vulcanizing by a traditional rubber mixing processing procedure. Transmission electron microscopy (TEM) showed that the silicate layers of clay were delaminated or intercalated with CNBR and dispersed in the CNBR matrix at a nanometer level during co-coagulating. X-ray diffraction indicated that the amount of CNBR intercalating between the layers increased with the increase of content of clay in CNBR, which is in contrast with the results of other studies. Some reasons were put forward for this discrepancy. The aspect ratio (width/thickness) of the platelet inclusions was reduced and the silicate layers were aligned more orderly during the compounding operation on an open mill. The intercalated CNBR, on co-coagulating, still remained within the interlayer space after curing. In these nanocomposites, the particles of silicate layers were dispersed at the nanometer level and the structure was a combination of delaminated and intercalated silicate layers dispersed in the continuous CNBR matrix. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2842–2848, 2001

Key words: clay; carboxylated acrylonitrile-butadiene rubber; nanocomposite; TEM; XRD

INTRODUCTION

Clay minerals, such as montmorillonite and vermiculite, have been widely used to prepare polymer–clay nanocomposites. Synthesis, characterization, and properties of polymer–clay nanocomposites have been discussed in the reviews by Akelah et al.¹ and Giannelis.² Synthesis of polymer–clay nanocomposites has typically involved *in situ* polymerization, polymer intercalation from solution, and direct polymer

melt intercalation. The structures of polymer–clay nanocomposites are usually characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM), etc. In addition, the matrices frequently used are plastic resins, such as nylon 6,³ polyimide,^{4–7} epoxy resin,⁸ polystyrene,⁹ polypropylene,^{10,11} polycaprolactone,¹² and poly(ethylene terephthalate),¹³ and the elastomeric matrices, such as a lightly brominated isobutylene bromomethylstyrene copolymer,¹⁴ hydroxyl-terminated polydimethylsiloxane,¹⁵ amine-terminated poly(butadiene-co-acrylonitrile),¹⁶ and polyurethane.¹⁷ Recently, a versatile and environmentally benign approach has been developed by us for the preparation of nanocomposites

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of elastomeric matrix based on rubber latex. The process involves mixing the rubber latex and the clay aqueous suspension and co-coagulating by adding electrolyte.^{18–21} In our previous work, several rubber-clay nanocomposites, such as butadiene styrene vinyl-pyridine rubber, styrene butadiene rubber (SBR), natural rubber (NR), chloroprene rubber (CR), nitrile rubber (NBR), and carboxylated acrylonitrile butadiene (CNBR) were prepared successfully. Because the nanocomposite based on elastomer will be processed and vulcanized in the future, an investigation on the effect of processing and vulcanization on the structure of nanocomposite should be interesting. Here we report the effect of the shearing force, vulcanization, and clay amount on the dispersion of clay in the CNBR matrix. The research in this field is rare. The properties of clay-CNBR nanocomposite can be seen in our previous publication.²¹

EXPERIMENTAL

Materials

The clay (Na-montmorillonite), with a cationic exchange capacity (CEC) of 93 mequiv/100 g, is from Liufangzi Clay Factory, Jilin, China. CNBR latex (AN 31–35%) is from Taiwan Nancar Corp.

Preparation of CNBR-Clay Nanocomposites

First, the CNBR latex, the clay aqueous suspension, and compatibilizer were mixed and vigorously stirred for 1 h, and then the electrolyte was added to co-coagulate the CNBR and clay. The coagulum was washed several times with water and dried in oven for 18 h at 80°C, and then the CNBR-clay nanocompound was obtained.

The vulcanizing ingredients and other additives were mixed into the nanocompound with a two-roll mill by a standard procedure; then, the compound was cured in a compression mold (150°C × 30 min). The compositions of vulcanizable nanocompound are shown in Table I. The vulcanizates are referred to as CNBR-clay nanocomposites.

Characterization

XRD analyses were carried out on Rigaku RINT using CuK_α radiation, a 0.02° step size, and 6.00°, 2 θ /min. The thin films of the nanocompounds and

Table I Compositions of Nanocomposites (w/w)

Na-Montmorillonite (clay)-CNBR	10/100	20/100	30/100	40/100
Zinc oxide	5.0	5.0	5.0	5.0
Steric acid	1.0	1.0	1.0	1.0
Accelerator TT	0.75	0.75	0.75	0.75
Accelerator DM	1.5	1.5	1.5	1.5
Sulfer	1.5	1.5	1.5	1.5
Dibutylphthalate	10.0	10.0	10.0	10.0
Antioxidant 4010NA	2.0	2.0	2.0	2.0

nanocomposite vulcanizates were cut with a microtome, and TEM observations were performed with an H-800 TEM, using an acceleration voltage of 200 kv.

RESULTS AND DISCUSSION

To investigate the effect of shear force on the structure of nanocomposite, different times of passing the nip region of the two-roll mill were used for the mixture of CNBR and clay.

The TEM photographs of the mixture of CNBR and clay (CNBR-Clay = 100/30) with different times through a two-roll mill are shown in Figure 1, where the dark lines are the intersections of the silicate layers. Silicate layers were exfoliated, intercalated, and dispersed in the CNBR matrix at the nano level, although there was a slight amount of ~ 20–40-nm thick silicate layers that are believed to be the intercalated silicates by CNBR and nonintercalated silicates coming from delamination of clay by CNBR. However, the exfoliated single silicate layer was not easy to see because of its slight reflection of electrons compared with that of intersections of silicates. Therefore, the CNBR-clay mixture is considered to be a nanocompound.

Silicate layers were first entangled and folded three times. After five times, the orientation of silicate layers improved considerably. However, passing the nip of a two-roll mill more than five times is of no use in improving the orientation of silicate layer. When the times through a two-roll mill increased, the aspect ratio (width/thickness) of platelet inclusions decreased. These results indicated that the high shearing forces in the nip region of open-mill

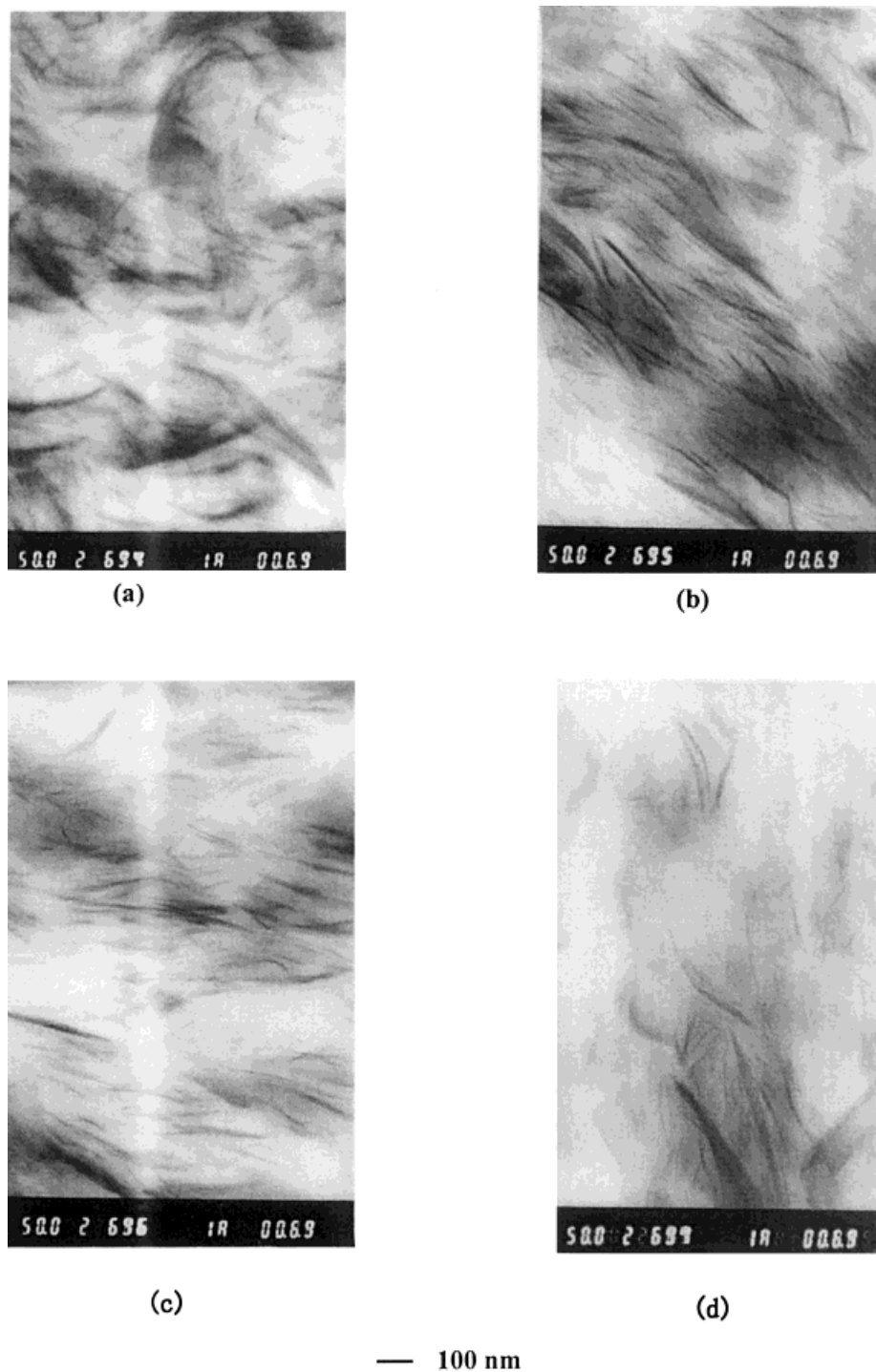


Figure 1 TEM photographs of the CNBR–clay nanocompound (CNBR–clay = 100/30) with different passing times through the two-roll mill: (a) 3 times; (b) 5 times; (c) 10 times; (d) 20 times.

rolls reduced the aspect ratio and made silicate layers align in a more orderly fashion. These phenomena usually take place during mixing of

vulcanizing agents into the mixture of CNBR and clay, similar to mixing of the fiber into the rubber formulation. In addition, the nanocom-

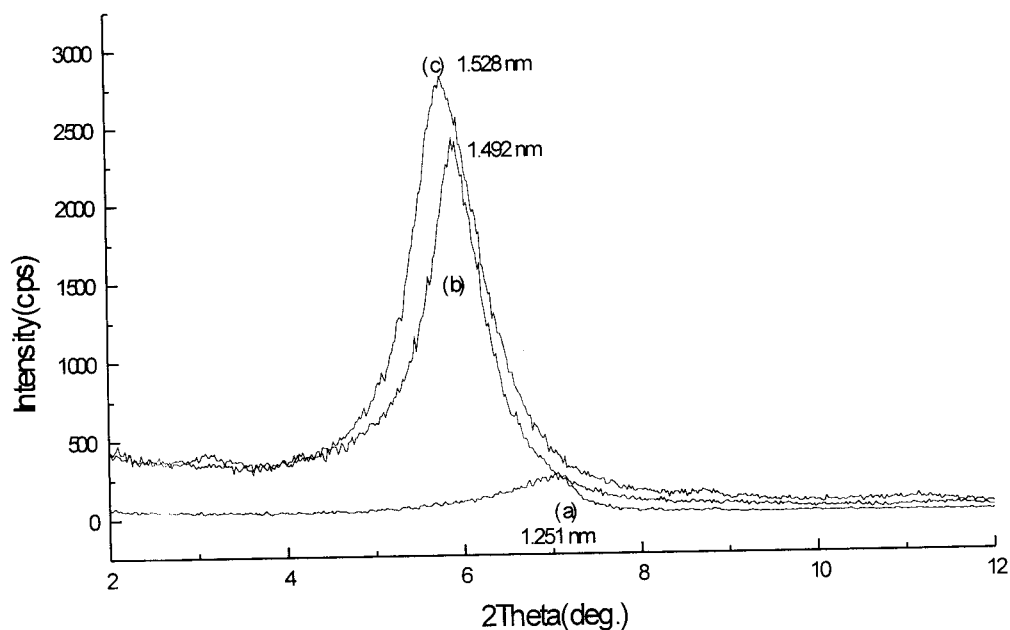


Figure 2 XRD patterns of (a) clay, (b) CNBR-clay mixture (CNBR-clay = 100/30), and (c) CNBR-clay vulcanizate (CNBR/clay = 100/30).

posites passing the nip for more times exhibited finer dispersion of clay, which is attributed to the high shear force, which helps to further exfoliate the swelled clay by CNBR.

The XRD patterns of Na-Montmorillonite (clay), CNBR-clay mixture (nanocomposite; CNBR-clay = 100/30), and CNBR-clay vulcanizate (nanocomposite; CNBR-clay = 100/30) are presented in Figure 2, where peaks correspond to the (001) plane reflections of the clay. The diffraction peaks of nanocomposite ($2\theta = 5.92^\circ$) and nanocomposite ($2\theta = 5.78^\circ$) shifted to lower angles compared with the diffraction peak at $2\theta = 7.06^\circ$ (d spacing = 1.251 nm) for clay. This result indicates an intercalated layer structure as a result of swelling by CNBR, which should be evident in TEM photographs. However, those silicate layers exfoliated into the CNBR matrix could not be reflected by X-ray because of a random and single dispersed structure.^{1,2} In addition, in our opinion, the peak of the XRD pattern should be an average reflection of intercalated silicate layers with a series of spaces and delaminated silicate layers, so the space calculated should be an average value of different spaces within a series of intercalated silicates. After vulcanization, the diffraction peak shifted to lower angle and the $d(001)$ spacing increased slightly, showing that

the penetrated CNBR could not leave the inter-layer space on curing. The d spacing and the span between the internal lamellar surface were only expanded to ~ 1.5 and 0.5 nm, respectively, suggesting horizontal packing of the polymer molecules.¹⁶

TEM photographs of the CNBR-clay nanocomposites with different loading levels of clay are shown in Figure 3. At all loadings of clay, the particles of silicate layers were dispersed into CNBR matrix at the nanometer level, although there were some non-exfoliated layers (~ 20 – 40 nm). This result is direct evidence that the nanocomposites of silicate layers and CNBR have formed. However, according to TEM, as the content of clay increased, the amount of non-exfoliated (or intercalated) layers also increased.

The XRD patterns of the corresponding CNBR-clay nanocomposites (in Figure 3) are presented in Figure 4. All the samples showed diffraction peaks that shifted to lower angles compared with the diffraction peak for clay. The basal spacing increased with the growth of the content of clay in CNBR, indicating more CNBR intercalating between the layers. Of particular note was that the growth of basal spacing with the increase in the content of clay in CNBR was different from organoclay/poly(amic acid)⁷ and organoclay/polyole-

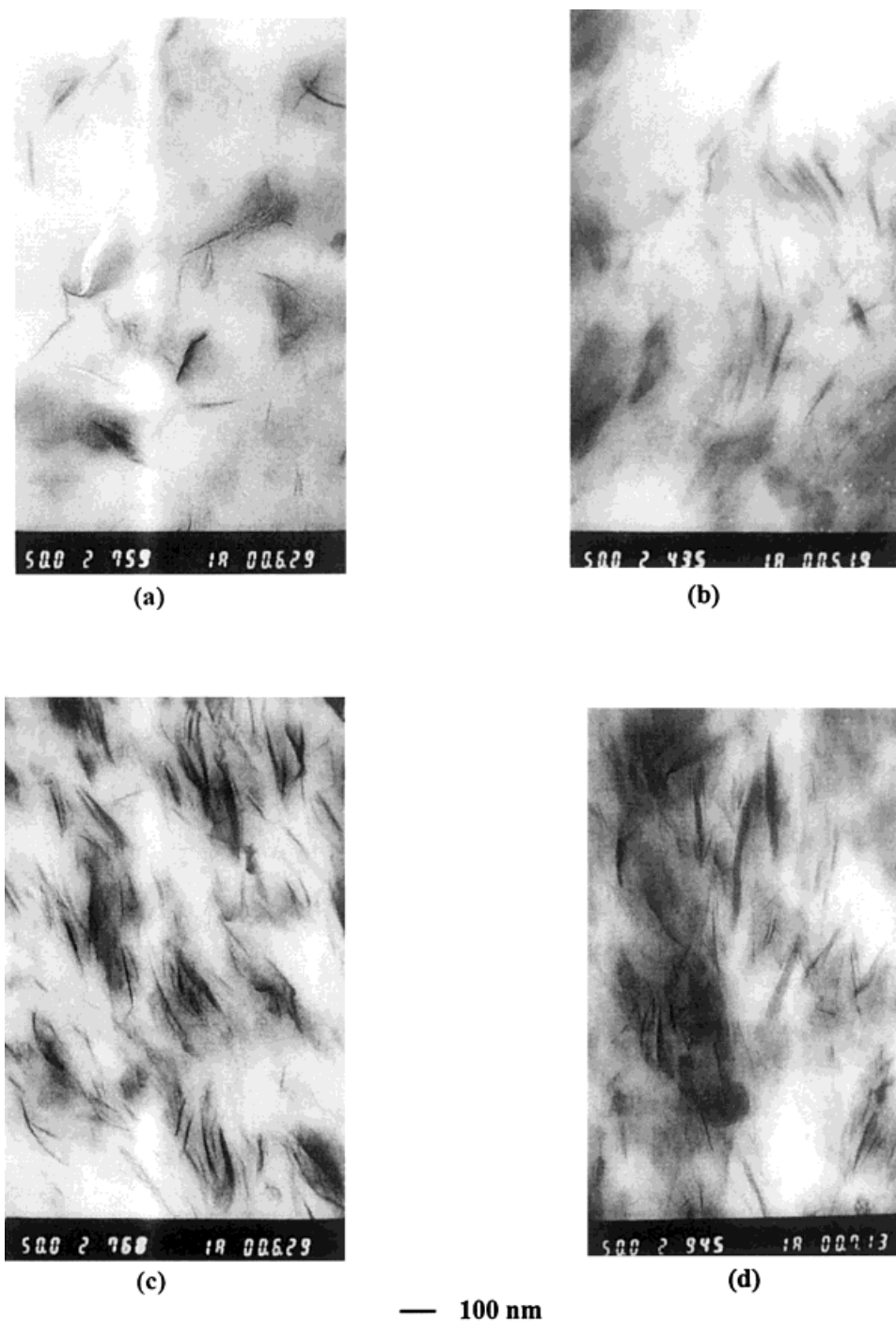


Figure 3 TEM photographs of the CNBR–clay nanocomposites with different weight content of clay. CNBR–clay (w/w): (a) 100/10; (b) 100/20; (c) 100/40.

fine diol²² systems, in which the d spacing for organoclay increased with the decrease in the ratio of organoclay/polymer, presumably because of the different preparation method. On co-coagulating, the rubber latex aggregating rate should

match that of silicate layers. In addition, the size of the rubber latex particle is the important effect factor in preparing rubber–clay nanocomposites based on the rubber latex. The mechanism of preparation of nanocomposites based on this tech-

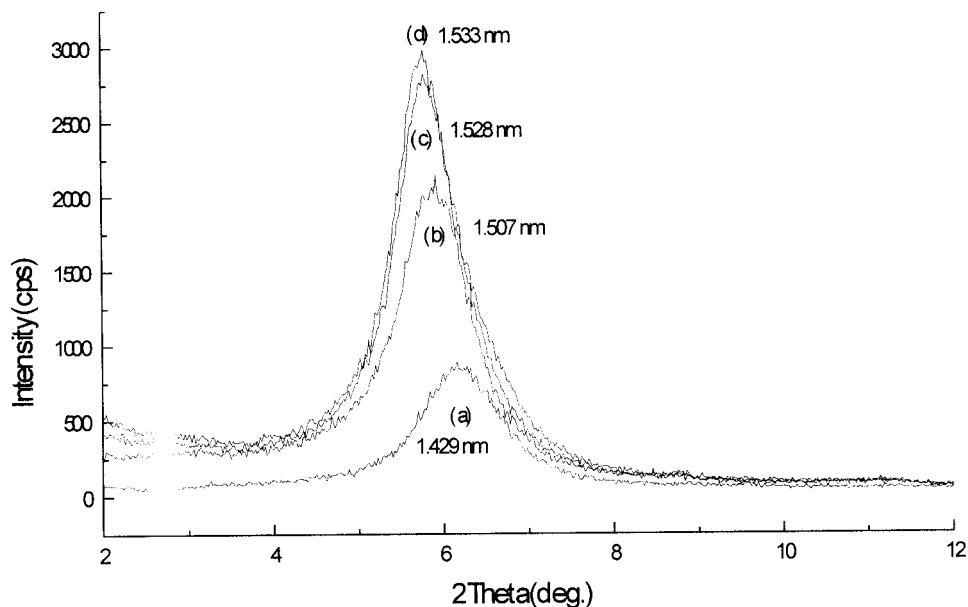


Figure 4 XRD patterns of the CNBR-clay nanocomposites. CNBR-clay (w/w): (a) 100/10; (b) 100/20; (c) 100/30; (d) 100/40.

nique²⁰ will be discussed in detail in a future paper.

The results just presented suggest that the structure of CNBR-clay nanocomposites was a combination of delaminated and intercalated layers dispersed in the continuous CNBR matrix.

CONCLUSIONS

CNBR-clay nanocomposites were successfully prepared by co-coagulating rubber latex and clay aqueous suspension. The aspect ratio of the platelet inclusions was reduced and silicate layers were aligned in a more orderly fashion during the compounding operation on an open mill. The intercalated CNBR that occurred during the co-coagulating process still remained within the interlayer after curing. As the content of clay increased, the basal spacing increased slightly. The structure of the CNBR-clay nanocomposites was a combination of exfoliated and intercalated silicate layers dispersed in the continuous CNBR matrix.

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