Melt-Compounded Natural Rubber Nanocomposites with Pristine and Organophilic Layered Silicates of Natural and Synthetic Origin

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ABSTRACT: Composites based on natural rubber (NR) and containing organophilic and pristine layered silicates of natural and synthetic origin were produced by melt compounding and sulfur curing. The curing, thermomechanical, and mechanical properties of the mixes, which contained 10 phr (parts per hundred parts of rubber) silicates, were determined. The dispersion of the silicates was studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Organophilic clays accelerated the sulfur curing of NR, which was believed to occur because of a complexation reaction in which the amine groups of the clay intercalants participated. The property improvements caused by the fillers were ranked as follows: organophilic clays > pristine synthetic layered silicate (sodium fluorohec-torite) > pristine natural clay (purified sodium bentonite) > precipitated nonlayered silica (used as a reference). This was attributed to partial intercalation of the organophilic clay by NR on the basis of XRD and TEM results and to the high aspect ratio of the fluorohectorite. Apart from intercalation, severe confinement (i.e., the collapse of the interlayer distance) of the organoclays was observed. This peculiar feature was traced to the formation of a zinc coordination complex, which extracted the amine intercalant of the organoclays, thus causing the collapse of the layers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 813–819, 2004

Key words: clay; nanocomposites; organoclay; rubber; vulcanization

INTRODUCTION

Nowadays, there is a great interest in the development of polymeric nanocomposites with layered silicates as reinforcements. As long as the layered silicate layers fully delaminate (i.e., exfoliate), dispersing less than 10% of them may replace a three to four times greater amount of traditional fillers without the mechanical properties being sacrificed. Exfoliation, however, can hardly be achieved with pristine clays, as the distance between their layers (<1 nm) does not allow the penetration of the polymer molecules therein. The layer distance can be enlarged by cation exchange with suitable intercalants because the silicate layers are negatively charged. The present rule of thumb is that to support intercalation and exfoliation (i.e., further and complete layer expansion, respectively), the layer distance should be greater than 1.5 nm. This is usually achieved with ammonium salts, which render the surfaces of the silicates organophilic. This concept, originally developed by researchers at Toyota Central Research Laboratories, has been followed for both thermoplastic and thermoset resins, as reviewed recently.[1–5] In addition, it has been adopted for rubbers, although mostly for compounds in solution.[6–9] The latex route is also promising for some rubbers available in aqueous dispersions [e.g., natural rubber (NR)] because in this case pristine (nonorganophilic and nonintercalated by cation exchange) layered silicates can be used.[10–12] The melt-compounding route is less favored according to the open literature.[13–15] However, this may be of great practical relevance. In addition, the finding that the acting shear forces strongly favor the exfoliation of layered silicates is a strong argument for melt compounding with rubbers. To obtain a deeper understanding of melt intercalation with rubbers, we need to study several aspects, such as the effects of the organophilic intercalants and the purity of the layered silicates. It is also of paramount importance to determine whether or not the exfoliation of pristine layered silicates can be achieved *in situ*. In this work, we aimed to contribute to these open questions by using natural organophilic clays (organoclays) with various intercalants, natural clay (sodium bentonite), and synthetic layered silicates (sodium fluorohectorite) in sulfur-curing NR formulations. Note that NR was less used as a matrix material for melt-mixed nanocomposites.[16]

EXPERIMENTAL

Materials, recipes, and curing

NR (light-color-grade smoked Malaysian rubber) with a Mooney viscosity of ML (1+4) at 100°C = 78 was

TABLE I
Properties of the Silicates Used

Silicate	Grade/supplier	Characteristics
Sodium fluorohectorite	Somasif ME-100, Co-op Chemical, Tokyo, Japan	Synthetic layered clay CEC = 100 mequiv/100 g, interlayer distance 0.94 nm
Sodium bentonite	EXM 757, Süd Chemie, München, Germany	Purified natural layered clay, CEC = 80 mequiv/100 g, interlayer distance = 1.24 nm
MMT–ODA	Nanomer I.30P, Nanocor Inc., Arlington Heights, IL	ODA, modified MMT, specific gravity = 1.9 g/cm^3, particle size = 16–20 μm, interlayer distance = 2.10 nm
MMT–TMDA	Cloisite 30B, Southern Clay Products, Inc., Gonzales, TX	TMDA, modified MMT, specific gravity = 1.5–1.7 g/cm^3, interlayer distance = 1.85 nm
Silica	Ultrasil VN2 GR, Degussa, Frankfurt, Germany	Synthetic amorphous precipitated silica

CEC = cation exchange capacity.

obtained from Malaysia. The basic properties of the silicates used are listed in Table I. The formulation used is given in Table II. Except for NR and the fillers, all the ingredients were delivered by Bayer AG (Leverkusen, Germany). Mixes were prepared in a laboratory two-roll mixing mill (LRM-150/3E, Labtech, Bangkok, Thailand). Compounding was performed at room temperature without the cooling of the roll mill, which was operated at a friction ratio of 1:1.25. NR was first masticated for 3 min before the ingredients were added in the same order given in Table II. During mixing (10-min overall time), 3/4 cuttings were made from the compound from both sides. The samples were then cured at 150°C in an electrically heated hydraulic press to their respective cure times (t_{90}). These values were derived from a Monsanto MDR 2000 moving die rheometer (Alpha Technologies, Swindon, UK) (cf. Table III).

Testing

Dynamic mechanical thermal analysis (DMTA) spectra were recorded on rectangular specimens (length $\times$ width $\times$ thickness = 6 cm $\times$ 1 cm $\times$ 0.25 cm) in the tensile mode at a frequency of 10 Hz with a Eplexor 150 N device (Gabo Qualimeter, Ahlden, Germany). DMTA spectra [i.e., the storage modulus and mechanical loss factor (tan δ)] were measured from -120 to 80°C at a heating rate of 2°C/min. The tensile tests were performed on dumbbell-shaped specimens according to ASTM Standard D 412 on a Zwick 1485

universal testing machine (Zwick GmbH, Ulm, Germany) at a crosshead speed of 50 cm/min. Five specimens were tested, and the average of the values was taken. The hardness and resilience were tested according to the respective ASTM standards.

Transmission electron microscopy (TEM) studies were carried out with a LEO 912 Omega transmission electron microscope (Carl Zeiss, Oberkochen, Germany) with an acceleration voltage of 120 keV. The specimens were prepared with an Ultracut E ultramicrotome (Leica Microsystems, Wetzlar, Germany) equipped with a cryochamber. Thin sections of about 100 nm were cut with a diamond knife at $-120°C$. X-ray diffraction (XRD) diffractograms were obtained with a D500 diffractometer (Siemens, Munich, Germany) with Ni-filtered Cu Kα radiation (λ = 0.1542 nm). The samples were scanned in the step mode at a 1.5°/min scanning rate in the range of 2Θ < 12°.

RESULTS AND DISCUSSION

Curing characteristics

The curing characteristics are summarized in Table III. The minimum torque of the organoclay [monotmorillonite–octadecylamine (MMT–ODA) and monotmorillonite–methyltallow bis-2-hydroxyethyl quaternary ammonium (MMT–TMDA)] containing recipes is higher than those containing silica and nonmodified silicates. This suggests that the organoclays are intercalated by the NR. The maximum torque follows the same pattern as a function of the type of silicate. The rather high maximum torque for the fluorohectorite indicates its very high aspect ratio (the length-to-diameter ratio of the individual platelets is greater than 1000). In the presence of organoclays, both the cure time (t_{90}) and scorch time (t_2), as well as their difference ($t_{90} - t_2$, i.e., the cure rate), are considerably reduced. Such an accelerating effect has already been reported[13,17,18] and traced to a transition complex formation with amines and sulfur-containing compounds,[17] which facilitates the development of ele-

TABLE II
Formulation of the Mixes

Material	Parts
NR	100
Filler (various)	10
ZnO	5
Stearic acid	2
Sulfur	2.5
N-Cyclohexylbenzothiazole-2-sulfenamide	0.6

TABLE III
Rheometric Properties of the NR Mixes

Parameter	Silica	Fluorohectorite	Bentonite	MMT–ODA	MMT–TMDA
Minimum torque (dNm)	0.61	0.67	0.58	1.04	1.23
Maximum torque (dNm)	7.87	8.30	7.99	8.34	8.69
Maximum − minimum torque (dNm)	7.27	7.63	7.41	7.30	7.46
Scorch time t_2 (min)	8.37	7.42	5.48	5.17	3.17
Cure time t_{90} (min)	14.71	12.99	11.77	10.12	8.54
Cure rate $t_{90} - t_2$ (min)	6.34	5.57	6.29	4.95	5.37

mental sulfur.[19,20] The reduction in the cure and scorch times for fluorohectorite and bentonite may be due to some catalytic effect of the silicates on the crosslinking reaction. The fillers also affect the reversion rate of the NR stocks. The lowest reversion rate was found for the organoclays, and the highest was found for the silica containing versions. Reduced reversion is a further beneficial effect of organoclays in NR recipes.

DMTA

The storage modulus of the different silicate-filled vulcanizates as a function of temperature is displayed in Figure 1(a). The MMT–ODA-filled composite registers the highest storage modulus. After the glass-transition temperature (T_g), the mixes show a similar change with the temperature. The intercalated and exfoliated silicate layers of MMT–ODA reinforce the matrix to a great extent, as reflected in the storage moduli. Interestingly, a very high reinforcing effect has been observed for the pristine fluorohectorite. This is due to the high aspect ratio of the fluorohectorite, which is markedly lower in the nonexfoliated stage than in the exfoliated stage (>1000), but it is still enough for a good reinforcement. Tan δ as a function of temperature is depicted in Figure 1(b). Clearly, all silicate versions except MMT–ODA have a pronounced T_g peak, which reflects the high mobility of the polymer chains when their contacts to the filler are low. However, in the MMT–ODA-filled composite, the T_g peak is strongly reduced, indicating a strong interaction between NR and silicate. Moreover, there is a secondary relaxation peak for this composite in the tan δ/temperature curve. This may be assigned to the rubber between the clay layers in an intercalated (partially exfoliated) and/or confined (reaggregated) system. Here the rubber behaves differently than that of the bulk, being under high constraints. Therefore, this rubber portion has a higher T_g than that of the bulk. TEM pictures shown later support this suggestion. It should be noted that DMTA is a proper tool for obtaining some preliminary information about the dispersion of the silicates.[12,17,21,22]

Technological properties

The changes in the modulus for the NR composites with different fillers are given in Figure 2. The refer-

ence materials (silica- and bentonite-filled composites) exhibit almost the same changes in their moduli. Fluorohectorite and MMT–TMDA make the NR more stiff than the reference filler. The highest modulus at all elongations is registered for NR modified by
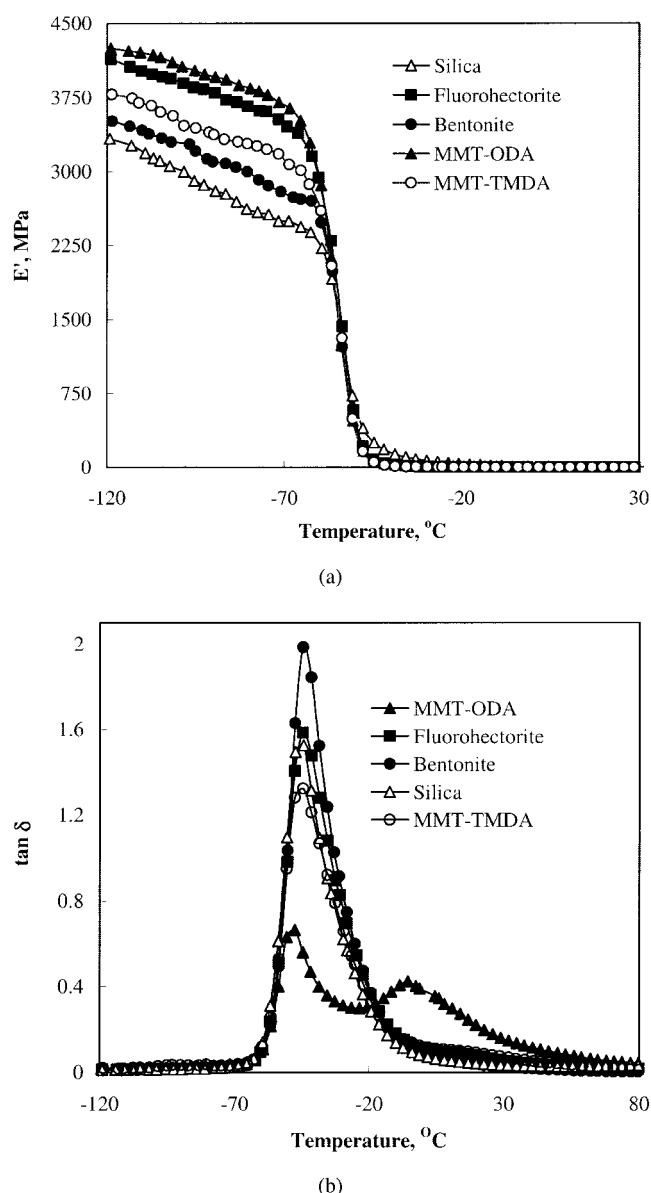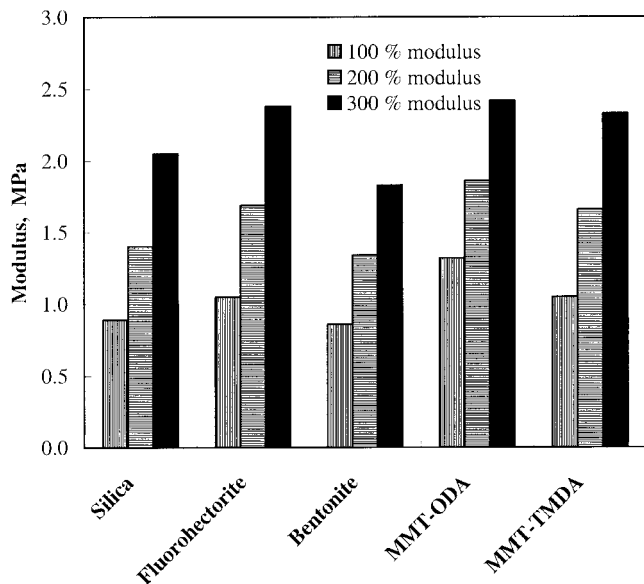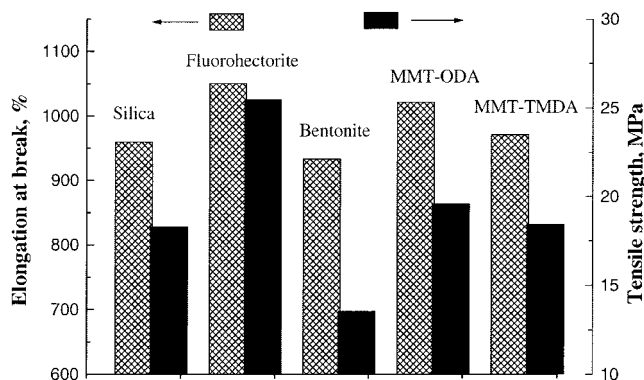

(a)

(b)

Figure 1 Complex storage modulus (E') and tan δ as a function of the temperature for different silicate-filled nanocomposites.
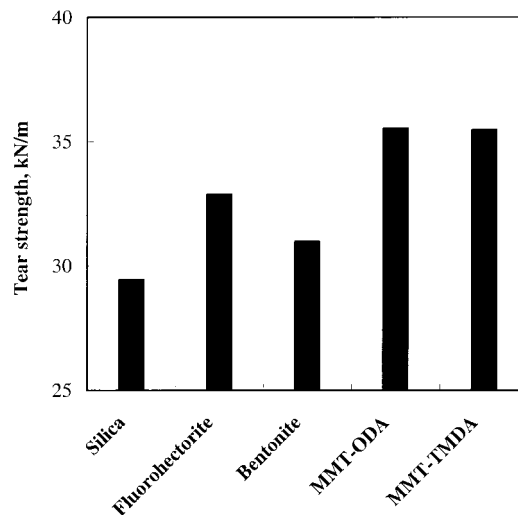
Figure 2 Modulus at different elongations for the nano-composites filled with various silicates.

Figure 4 Tear strength of the NR nanocomposites filled with various silicates.

MMT–ODA. The difference in the moduli for the different silicate-filled composites is prominent at low elongations (100 and 200%). This is because the filler–polymer interactions play a critical role at low elongations, just as at high elongations the strain-induced crystallization of NR dominates. The tensile strength (Fig. 3) shows a maximum for the fluorohectorite-filled NR vulcanizate, which is followed by that one containing MMT–ODA. Bentonite–NR shows the lowest tensile strength, and that of MMT–TMDA is almost equal to the reference material with silica. The unexpectedly low tensile strength of the MMT–ODA-filled vulcanizate may be due to the hindrance of the strain-induced crystallization by finely dispersed silicate layers. The ranking of the fillers with respect to the elongation at break is the same. The tear strength (Fig. 4) is highest for the organoclay-filled vulcanizates, which are followed by fluorohectorite and bentonite. The high tear strength of the organophilic modified clay-

filled vulcanizates may be explained by the intercalation–exfoliation phenomenon. In Figure 5, the variations of the resilience and hardness with the type of the filler are depicted. Both the resilience and hardness are relatively high in the presence of organoclays. The resilience is maximum for the NR containing MMT–ODA, whereas its hardness is lower than that of the composite with MMT–TMDA. Accordingly, the proportion of filler–rubber links is greater for MMT–ODA than for MMT–TMDA. This is because MMT–ODA offers a large amount of surface area through intercalation and exfoliation of silicate layers. This is supported by TEM data discussed later.

Dispersion of the silicates

Figure 6 shows XRD spectra of NR composites containing 10 phr (parts per hundred parts of rubber) silicate fillers. As expected, the precipitated silica shows no reflections as being amorphous. The interlayer distance of the pristine layered silicates does not

Figure 3 Tensile strength and elongation at break of the NR nanocomposites.
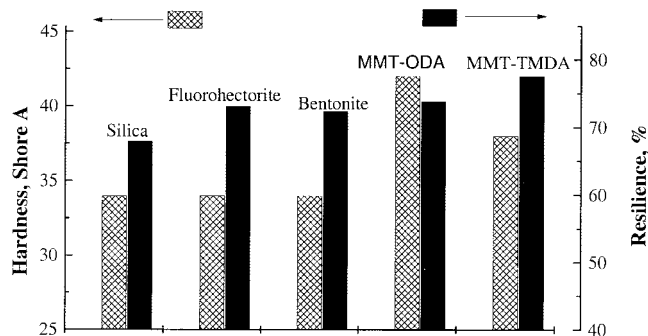
**Figure 5** Resilience and hardness of the nanocomposites filled with various silicates.
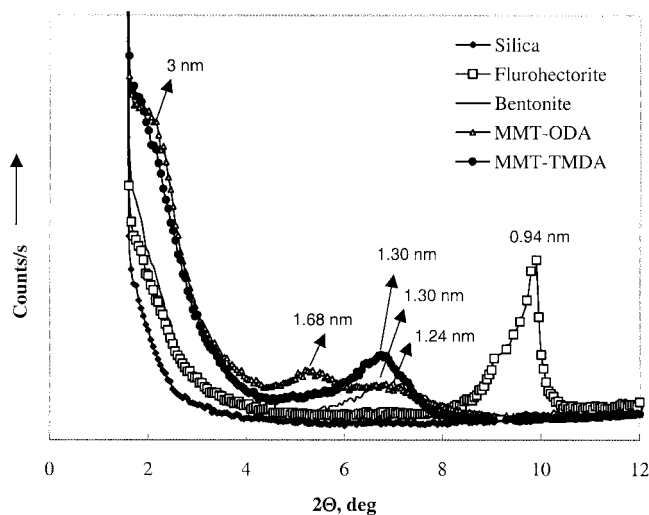
Figure 6 XRD spectra of the NR composites filled with various silicates (10 phr).

change in the NR mixes. Fluorohectorite and bentonite show the same initial values, that is, 0.94 and 1.24 nm, respectively (cf. Table I). MMT–ODA shows two peaks and a shoulder corresponding to 1.30, 1.68, and approximately 3 nm intergallery distances. An intergallery distance of 3 nm supports the idea that NR molecules penetrate between the silicate layers. The other two distances (i.e., 1.68 and 1.30 nm) indicate that a considerable portion of this organoclay is confined because its initial layer distance is 2.10 nm. *Confined* means that in a part of MMT–ODA, the interlayer distance is strongly reduced. Furthermore, two populations of lower clay gallery distances, 1.68 and 1.30 nm, appear according to the related XRD spectrum in Figure 6. The scenario is somewhat similar for the mix with MMT–TMDA. For the related composite, a peak (1.30 nm) and a shoulder (ca. 3 nm) have been resolved. Note that the former value is lower than the initial intergallery distance (1.85 nm; cf. Table I). Therefore, a part of this organoclay is intercalated, and another one is confined.

Confinement is usually noticed for three cases:[23] (1) the amount of the bulk polymer is not sufficient for intercalation and exfoliation (this may happen because too much organoclay is added to the recipe), (b) the initial intercalant is thermally degraded because of a high processing temperature, and (c) a thermodynamically unstable, reactively exfoliated nanocomposite is melt-processed.

In our case, all these possibilities can be ruled out. Partial intercalation along with partial confinement may be due to coordination complexing, which occurs in accelerated sulfur curing in the presence of zinc. Note that zinc is prone to coordination complexing in which amine groups of the intercalant and sulfur of the sulfuric curatives may participate (see refs. 19, 20, 24, and 25 and references therein). If

this is so, then a part of the initial amine intercalant (i.e., ODA and TMDA) may be removed (extracted) from the intergallery region. Thus, the distance between the layers is reduced; this is called *confinement*. There is one further, but still indirect, support for this model explanation. Recall that in the tan δ/temperature traces in Figure 1(b), two T_g peaks are resolved, at least for NR with MMT–ODA. The high-temperature relaxation is likely due to that part of the polymer that is located in the confined gallery regions. Similar results (i.e., XRD and DMTA) have been also found for pristine and organophilic layered silicate reinforced epoxidized NR recipes.[17] To check the dispersion of the layered
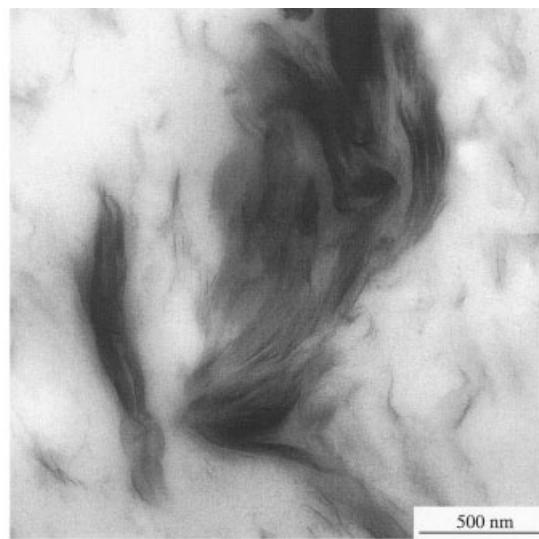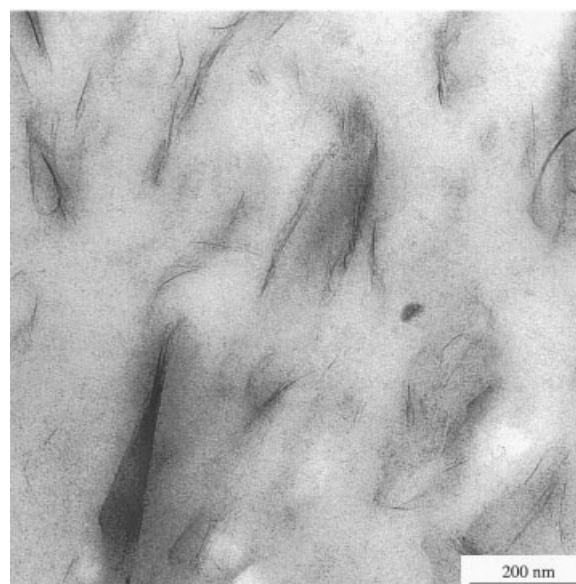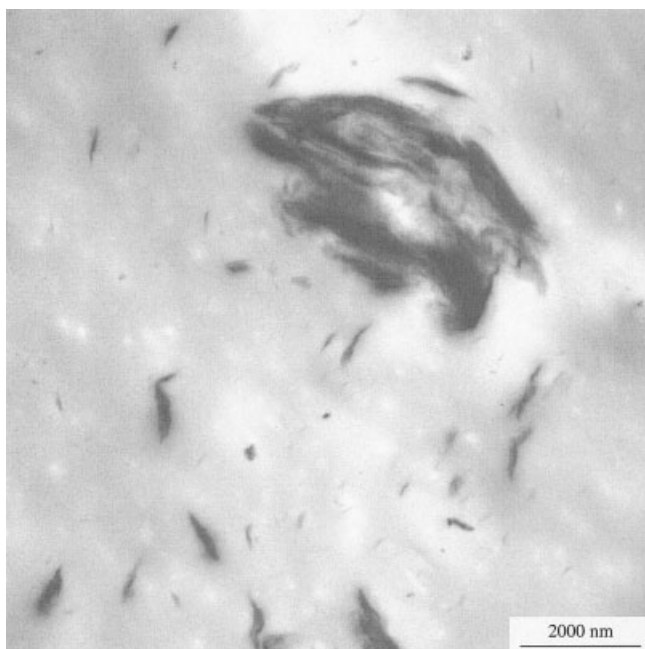

Figure 7 TEM pictures of an NR composite containing 10 phr MMT–ODA at various magnifications.
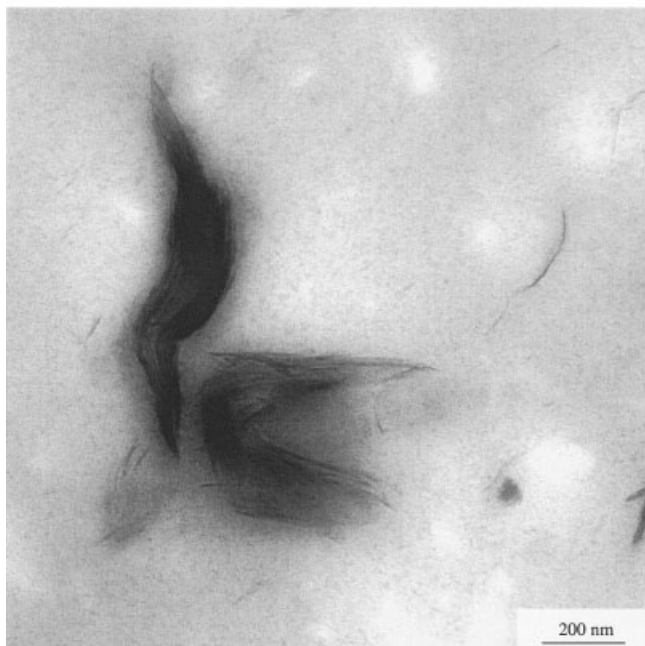
silicates TEM pictures were also taken of the related NR mixes.

TEM analysis

On the basis of these results, TEM investigations were focused on the NR composites containing MMT–ODA, MMT–TMDA, and fluorohectorite. TEM pictures in Figure 7(a,b) show that a portion of MMT–
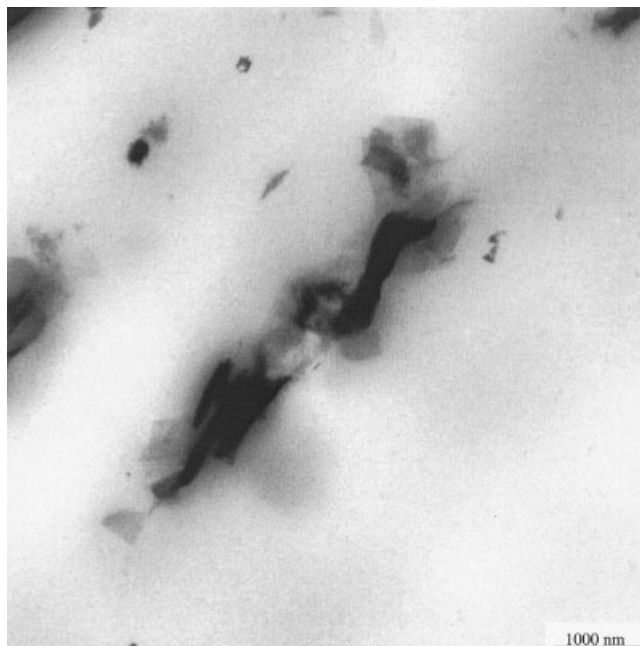
(a)

(b)

Figure 8   TEM pictures of an NR composite containing 10 phr MMT–TMDA at various magnifications.

Figure 9   TEM picture of an NR composite containing 10 phr sodium fluorohectorite.

ODA is well exfoliated, and the other part is not at all. Similar findings also hold for MMT–TMDA [Fig. 8(a,b)]. One can, however, recognize that the exfoliation degree of MMT–TMDA is markedly lower than that of MMT–ODA. This agrees with the XRD results and is well reflected in the mechanical performance. Figure 9 sheds light on the reason for the unexpectedly good mechanical performance achieved by fluorohectorite filling. This figure shows that the fluorohectorite layers are not disintegrated; however, the aspect ratio of the particles composed of stacked and distorted layers is high enough to produce a reinforcing effect.

CONCLUSIONS

Based on this work, devoted to the study of the effects of layered silicates of natural and synthetic origin with and without organophilic treatments in NR formulations, the following conclusions can be drawn:

- Through the addition of organophilic clays, better mechanical performance and faster curing can be achieved than with pristine layered silicates and amorphous silica.
- XRD and TEM results show that organoclays are partly exfoliated, partly intercalated, and partly confined (reaggregated). The latter phenomenon (close-up of the galleries) depends on the type of organophilic intercalant used. Onium intercalants with long alkyl chains likely produce the best results in NR recipes.
- A close-up of the interlayer distance of the silicates, termed *confinement*, has been speculated to

be an effect of zinc–sulfur–amine complexation: a part of the amine compound is removed from the intergallery region of the organoclay, and so the intergallery distance is reduced.

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