

# Characteristics of Nitrile–Butadiene Rubber Layered Silicate Nanocomposites with Silane Coupling Agent

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**ABSTRACT:** Nanocomposites of organophilic montmorillonite (C18-MMT), nitrile–butadiene rubber (NBR), and a coupling agent were produced during a melt compounding process at room temperature. During the process, it was clearly observed that organo-MMT particles were exfoliated into nanoscale layers of approximately 1–30 nm thickness, in addition to their original 40  $\mu\text{m}$  thickness. These MMT layers were uniformly dispersed in the NBR matrix. The effects of a coupling agent such as 3-(mercaptopropyl)trimethoxy silane in C18-MMT/NBR nanocomposites were studied. The C18-MMT/NBR nanocomposites in the presence of the coupling agent were identified and characterized by X-ray diffraction, transmission electron microscopy, a universal test-

ing machine, thermogravimetric analysis, and IR spectroscopy. It was observed that an additional silane coupling agent, 3-(mercaptopropyl)trimethoxy silane, enhanced the chemical interaction and was accompanied by the formation of Si–O–Si coupling bonds between C18-MMT and the coupling agent and Si–C coupling bonds between NBR and the coupling agent. This work resulted in improved properties of organo-MMT/NBR nanocomposites because of the nanoscale effects and strong interaction of the coupling bonds between NBR and organo-MMT. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2633–2640, 2003

**Key words:** clay; crosslinking; rubber; melt; nanocomposites

## INTRODUCTION

A polymer–clay hybrid is defined as a molecular composite of polymer and organophilic silicate layers of clay minerals. These polymer–clay nanocomposites have recently aroused a significant amount of interest because the mutual interactions between the polymer and clay are considered to have an affect on their properties. Nanocomposites, whose components are based on a thermoplastic and rubber matrix containing a nanoscale dispersion of layered silicates as a reinforcing filler, are being improved through efforts to enhance their physical and mechanical characteristics. Because the properties of the nanocomposite hybrids are directly related to the morphology of these systems, the state of dispersion of an inorganic phase is critical.

These nanostructured hybrids exhibit properties that are dramatically different from those of their virgin polymer or conventional composites. This result offers the potential of discovering high performance materials.<sup>1–9</sup>

Recent studies have demonstrated that the condition of a melting compounding process plays a key role in achieving a high level of exfoliation.<sup>10–12</sup> The results from these studies indicate that an optimum balance between the residence time and the level of

shear is required to facilitate the exfoliation and dispersion of layered silicates. In addition, the proper choice of organoclay chemistry is critical.

Clay is the most natural and abundant mineral available as an inexpensive and inorganic material with a high degree of physical and mechanical strength and chemical resistance. It can afford an appreciable surface area for the adsorption of molecules because of its small particles and intercalation. Clay has been used extensively in the polymer industry either as a reinforcing agent to improve the mechanical properties of polymers or as a filler to reduce the amount of the polymer used in shaped structures. Montmorillonite (MMT) is hydrated alumina–silicate clay composed of the units of two silicate tetrahedral sheets with a central alumina octahedral sheet. The silicate layers of MMT are planar, stiff, about 10 Å in thickness, and 1000–2000 Å in length and width. They do not occur as isolated individual units but aggregate to form crystalline structures.<sup>3,13–16</sup> The efficiency of MMT in improving the properties of polymer materials is primarily determined by the degree of its dispersion in the polymer matrix, which in turn depends on its particle size. However, the hydrophilic nature of the MMT surface impedes its homogeneous dispersion in the organic polymer phase. To overcome this problem, it is often necessary to make the surface organophilic prior to use.<sup>4,5,17</sup>

Although in pristine layered MMT the interlayer cations are usually hydrated  $\text{Na}^+$  or  $\text{K}^+$ , ion exchange reactions with organic cations normally render the

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hydrophilic MMT surface organophilic. The role of organic cations in organo-MMT is to reduce the surface energy of the MMT surface by improving the wetting characteristics of the polymer or monomer. In addition, the alkyl ammonium cations can provide functional groups that react with the polymer or initiate polymerization of monomers to improve the strength of the interface between the inorganics and the polymer.<sup>6,7</sup>

It has also been reported that the reinforcing ability of clay increases with surface modification by silane coupling agents.<sup>18–21</sup> Coupling agents contain chemical functional groups that can react with hydroxyl groups on the clay's surface. Attachment to the clay surface can thus be made by covalent bonds. Moreover, coupling agents contain at least one other different functional group, which can coreact with the polymer matrix. Assuming that all these occur, the coupling agent may act as a bridge to bond the clay surface to the polymer matrix with the chain of primary bonds. This could be expected to lead to the strongest interfacial bond interaction.<sup>18</sup>

The present article reports the results of studies on the effect of the silane coupling agent 3-(mercaptopropyl)trimethoxy silane on the interaction between nitrile-butadiene rubber (NBR) and organo-MMT in a NBR/organo-MMT nanocomposite.

## EXPERIMENTAL

### Materials

Kunipia F (Na<sup>+</sup>-MMT) with a cation-exchange capacity of 115 meq/100 g and a nominal particle size of 40 μm, was supplied by Kunimine Co. The NBR, which has a 29.3 mol % acrylonitrile content, was supplied by Hyundai Petrochemical Co. Ltd. The surface modifier of MMT, *n*-octadecylamine [CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>NH<sub>2</sub>], was purchased from Aldrich Chemical Co. The coupling agent, 3-(mercaptopropyl)trimethoxy silane, was supplied by Aldrich. The rubber additives (zinc oxide, stearic acid, and sulfur) were commercial grade.

### Preparation of organophilic MMT

During the process of preparing organophilic MMT, we tried to obtain MMT with a highly hydrophobic surface while simultaneously increasing the chemical affinity to NBR. Na<sup>+</sup>-MMT (20 g) was dispersed in 500 mL of water (60°C) by a mechanical stirrer. To obtain an alkylammonium salt, an alkyl amine such as *n*-octadecyl amine (12.4 g) and concentrated hydrochloric acid (4.6 mL) were dissolved in 100 mL of water. Then the dissolved solution was poured into the MMT-water dispersion that was vigorously stirred for 1 h. The mixed solution was stirred for 24 h at 60°C. The reaction products were filtered at room temperature and then repeatedly washed with distilled water

**TABLE I**  
Compositions of Prepared Nanocomposites Based on Organo-MMT, NBR, and Silane Coupling Agent

Materials	Mix Composition				
NBR (phr)	100	100	100	100	100
Organo-MMT (phr)	5	5	5	5	5
Silane coupling agent (phr)	0	1	2	5	10
Stearic acid (phr)	1	1	1	1	1
Zinc oxide (phr)	3	3	3	3	3
Sulfur (phr)	1.5	1.5	1.5	1.5	1.5

Organo-MMT, MMT intercalated with octadecyl amine; silane coupling agent, 3-(mercaptopropyl)trimethoxy silane; phr, parts per hundred filler.

until no Cl<sup>-1</sup> was detected from the filtrate. The product was dried in an oven under a vacuum at 60°C, and the resulting product was labeled C18-MMT.

### Preparation of C18-MMT/NBR hybrids

The C18-MMT/NBR hybrids were mixed at room temperature in an internal mixer (Brabender Plastimeter, model PL 2000) for 30 min at 50 rpm. Different combinations of C18-MMT, NBR, and coupling agent were prepared as listed below. The compositions of the prepared nanocomposites are listed in Table I.

The NBR was first melted for 5 min and then mixed with C18-MMT. The mixing was continued for another 10 min. When the mixing torque reached a constant value, the coupling agent, zinc oxide, stearic acid, and sulfur were added individually in the order noted.

### Dispersability of MMT in NBR matrix

To measure the change of a gallery distance of C18-MMT before and after the intercalation, X-ray diffraction (XRD) was performed at room temperature with an X-ray diffractometer (Rigaku D-Max 1400). The X-ray beam was nickel-filtered CuKα<sub>1</sub> (λ = 0.154 nm) radiation operating at 50 kV and 150 mA. The XRD data were obtained from 2° to 20° (2θ) at a scan rate of 2°/min. The samples were sheets with a smooth surface and dimensions of 10 × 10 × 1 mm. Transmission electron microscopy (TEM) was used to obtain a micrograph with a Philips CM-200 at an acceleration voltage of 200 kV. The TEM samples were embedded in a capsule with an embedding agent polymerized at 60°C for 24 h. The embedded sample was ultrathin sectioned using a microtome equipped with a diamond knife in a liquid nitrogen trap. The thin sections were 60–80 nm thick.

### Curing characteristics and molding specimens

The rheometric analysis of the C18-MMT/NBR/coupling agent nanocomposites was carried out at 180°C in an oscillating disk rheometer (Myung-Ji) per ASTM

**TABLE II**  
**Vulcanization Characteristics of Rubber Compounds**

Materials	Silane Content (PHF)	$T_{\min}$ (lb, in)	$T_{\max}$ (lb, in)	$t_{90}$ (min)
C18-MMT/NBR/coupling agent	0	4.1	20.8	21.00
	1	4.9	20.1	20.45
	2	5.3	20.6	20.53
	5	5.8	20.6	21.07
	10	6.4	20.6	20.39

$T_{\min}$ , minimum torque;  $T_{\max}$ , maximum torque;  $t_{90}$ , 90% of maximum torque.

D2084-01. The disk is oscillated through a small rotational amplitude ( $1^\circ$ ). The molding of test specimens was carried out at  $180^\circ\text{C}$  with 3-MPa pressure and at an optimum cure time ( $t_{90}$ ) using a laboratory hydraulic press. The vulcanization characteristics are summarized in Table II.

#### Measurement of thermogravimetric analysis (TGA)

The TGA was carried out in a TG analyzer (Perkin-Elmer TGA-7) over a range of temperatures from  $50$  to  $850^\circ\text{C}$  in  $\text{N}_2$  at a heating rate of  $20^\circ\text{C}/\text{min}$ .

#### Mechanical properties

Tensile tests were carried out with an Instron model 4204 at room temperature and the crosshead speed was  $500$  mm/min. Samples were standard dumbbell shapes, and all measurements were performed 8 times to obtain average values.

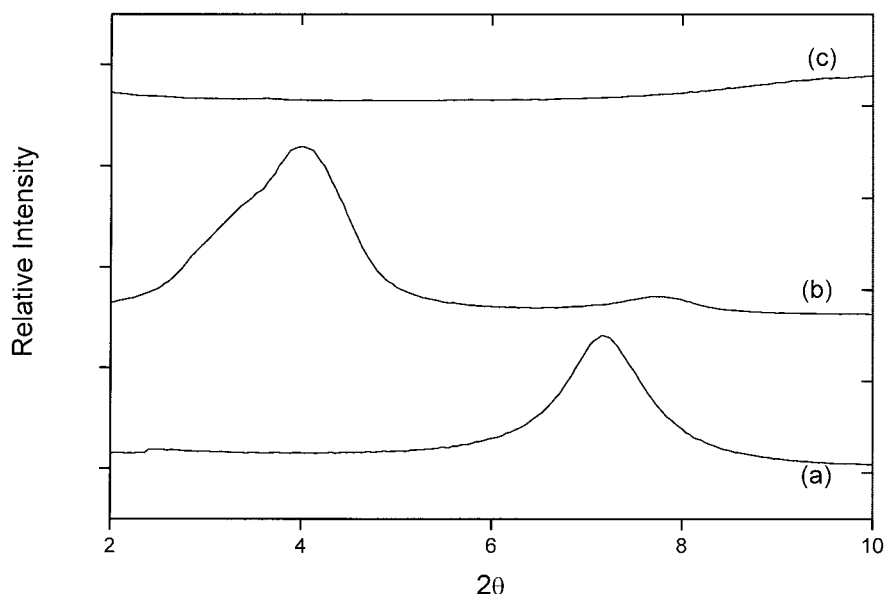
#### IR spectroscopy

The chemical structure characteristics of C18-MMT/NBR/coupling agent nanocomposites were identified by an IR measurement. While preparing the IR sample, C18-MMT in a KBr dispersion was pressed into pellets and NBR compounding materials were molded into sheets at  $180^\circ\text{C}$ . The prepared IR samples were run on a Jasco Fourier transform IR spectrometer (model FTIR-620) at a resolution of  $4\text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

#### XRD study

Figure 1 shows the XRD patterns of pure  $\text{Na}^+$ -MMT, C18-MMT, and the C18-MMT/NBR hybrid. The XRD pattern of  $\text{Na}^+$ -MMT shows a characteristic peak ( $d_{001} = 1.23$  nm) at a  $2\theta$  of  $7.16^\circ$ . The peak of C18-MMT is shifted to a lower angle compared to that of  $\text{Na}^+$ -MMT.



**Figure 1** X-ray diffraction patterns of pure  $\text{Na}^+$ -MMT (spectrum a), C18-MMT (spectrum b), and the C18-MMT/NBR hybrid (spectrum c).

The d-spacing (nm) of C18-MMT is 2.18 at a  $2\theta$  of  $4.04^\circ$ . This clearly indicates the intercalation of alkyl ammonium cations between the silicate layers. After the melting intercalation process, the characteristic diffraction peak disappeared above  $2^\circ$ . It is thought that the characteristic diffraction peak does not appear because the space between the silicate layers is 4.4 nm or more at a  $2\theta$  of  $2^\circ$ . In other words, these results imply that the intercalated silicate layers are exfoliated during the melting and compounding process and are randomly dispersed in the NBR matrix.

### TEM analysis

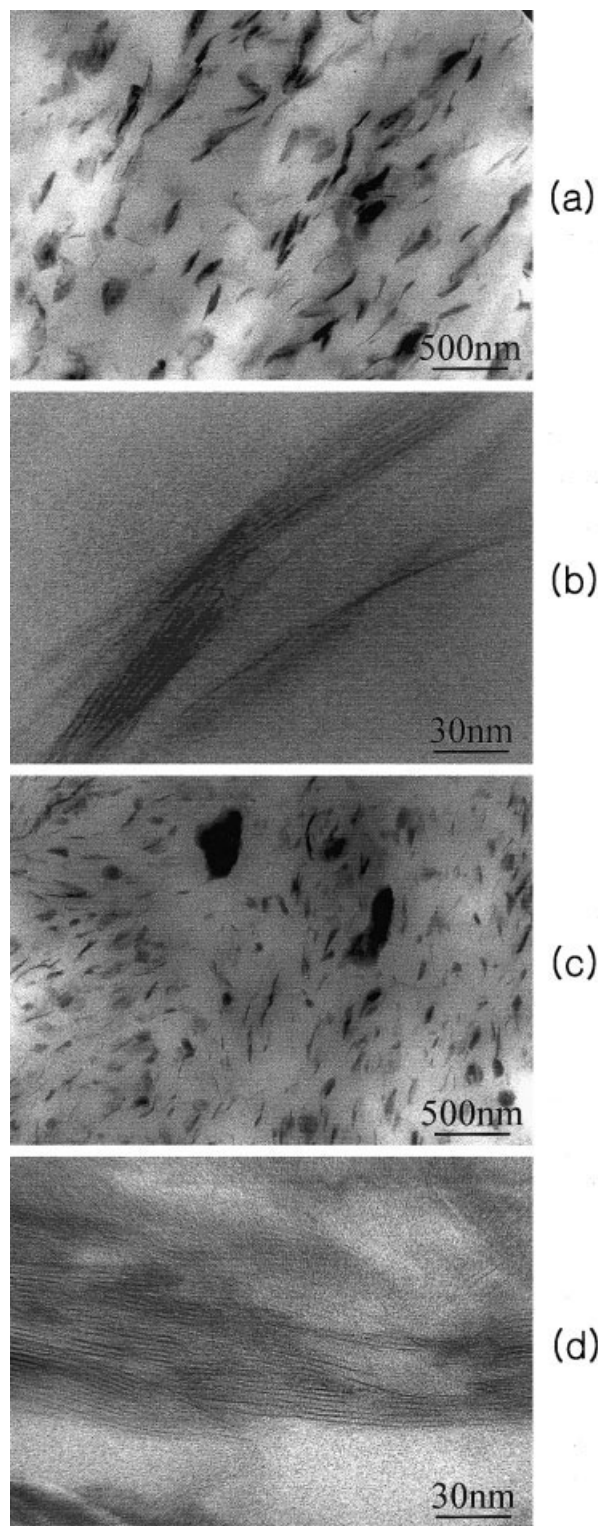
The nanostructure was studied by TEM, which provides clear evidence for the delamination of clay in the NBR matrix. As shown in Figure 2, the TEM micrographs for C18-MMT/NBR/coupling agent nanocomposites reveal that the particle size ranges from 1 to 30 nm. Here the intercalated structure of C18-MMT and the exfoliated layers can be observed. The micrographs reveal that each dark line (multiplet of C18-MMT) often corresponds to several clay layers. This means that the NBR matrix does not completely diffuse into all clay (C18-MMT) galleries during the melting and compounding process. However, each layer of clay (C18-MMT) is nearly dispersed homogeneously in the NBR matrix, although a small amount of unexfoliated layers (dark line or multiplet of C18-MMT) still exist. In the presence of the coupling agent, an arrangement of the layers similar to the image in Figure 2(a) is observed. However, it can be seen that the image in Figure 2(b), where the coupling agent is added, is more uniformly dispersed within the NBR matrix than the former image. As a consequence, it is deemed that the coupling agent is effective in enhancing the dispersion of clay.

### Curing characteristic

Figure 3 shows the rheographs of C18-MMT/NBR nanocomposites filled with different loadings of 3-(mercaptopropyl)trimethoxy silane content at  $180^\circ\text{C}$ .

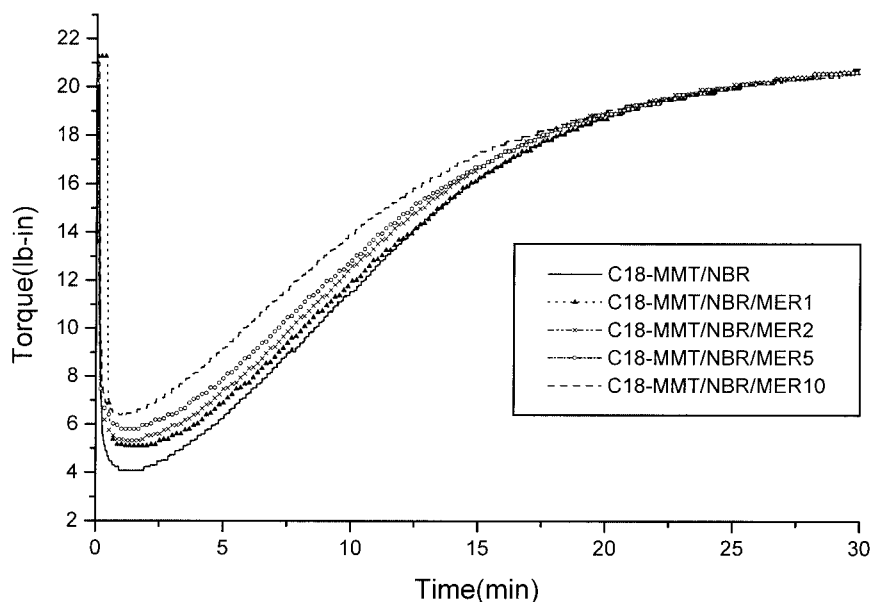
The addition of 3-(mercaptopropyl)trimethoxy silane causes an increase in the rheometric torque in the early stages because of a greater interaction between C18-MMT and the NBR matrix. This means that a higher torque indicates that 3-(mercaptopropyl)trimethoxy silane promotes linking of  $-\text{OH}$  groups on C18-MMT and nonactivated double bonds in the NBR matrix.

The results show that the addition of 3-(mercaptopropyl)trimethoxy silane has changed the values of the minimum torque, indicating that the presence of the coupling agent does affect the plasticity of the unvulcanized elastomeric compositions.



**Figure 2** TEM images of C18-MMT/NBR/silane coupling agent nanocomposites (a,b) without coupling agent and (c,d) with 2 phf coupling agent.

In addition, there is no change of maximum torque values with the addition of the coupling agent. This indicates that the 3-(mercaptopropyl)trimethoxy silane coupling agent takes no part in crosslinking at  $180^\circ\text{C}$  in a sulfur curing system.



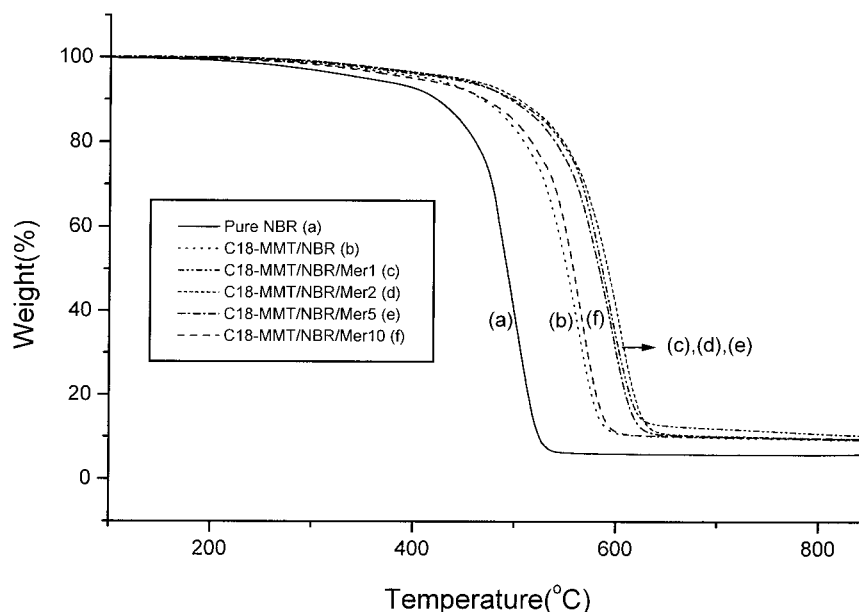
**Figure 3** Rheographs of C18-MMT/NBR/coupling agent nanocomposites. MER1, -2, -5, and -10 indicate the contents (phf) of 3-(mercaptopropyl)trimethoxy silane.

#### TGA study

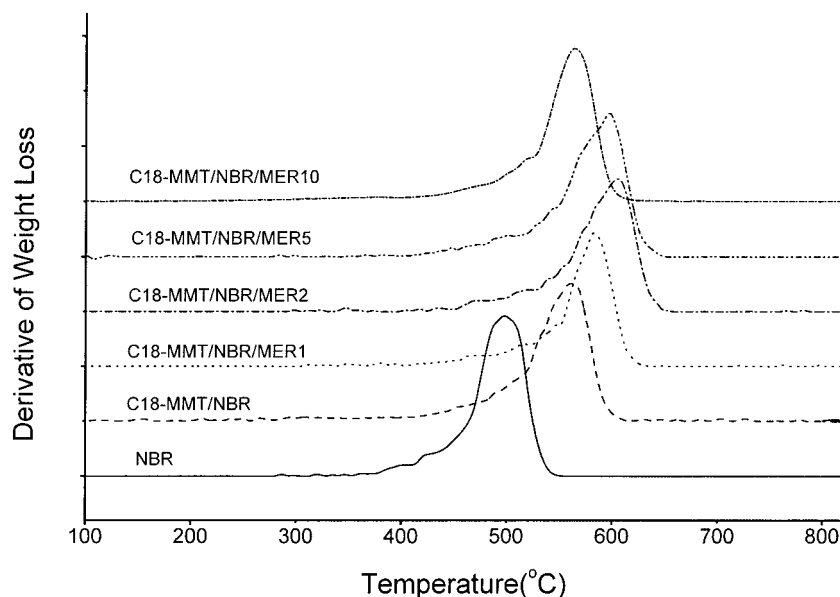
Figures 4 and 5 show TG and derivative curves of C18-MMT/NBR/coupling agent (3-mercaptopropyl trimethoxy silane) nanocomposites, respectively. The decomposition onset temperature (DOT) is defined as the temperature at which 5% of the weight loss appears, and the maximum decomposition temperature (MDT) is defined as the temperature at which maximum weight loss appears.

It is evident that pure NBR and C18-MMT show DOTs of 351.8 and 400.1°C, respectively. In the presence of the coupling agent, DOT and MDT depend

on the concentration of the coupling agent. The details of the decomposition temperature are given in Table III. We observed that a large weight loss occurs in C18-MMT/NBR/coupling agent nanocomposites at a higher temperature, which ranges from 412.7 to above 600°C; in the case of pure NBR, the temperature range was between 351.8 and 496°C. For the C18-MMT/NBR nanocomposite without a coupling agent, the temperature ranged from 400.1 to 558.1°C. As a result, we concluded that a coupling agent affects the thermal stability of the C18-MMT/NBR nanocomposite.



**Figure 4** Thermogravimetric analysis of C18-MMT/NBR/coupling agent nanocomposites. MER1, -2, -5, and -10 indicate the contents (phf) of 3-(mercaptopropyl)trimethoxy silane.



**Figure 5** Derivatives of the weight loss with respect to the temperature. MER1, -2, -5, and -10 indicate the contents (phf) of 3-(mercaptopropyl)trimethoxy silane.

Higher thermal stability in the presence of the coupling agent is attributed to the formation of coupling bonds. In other words, the enhanced thermal stability of NBR-based nanocomposites in the presence of the coupling agent was not only due to the difference in chemical structure, but also due to the restricted thermal motion of the macromolecules in the silicate layer. Optimal thermal stabilization is obtained at a coupling agent content of about 1–5 parts per hundred filler (phf). At 10 phf the thermal stabilization is slightly decreased. When the coupling agent content is 1–5 phf, relatively more restricted structures and more exfoliated structures are formed. At a higher coupling agent content, we found that the decrease of the thermal stability causes the defect of nanocomposites because the excessively added coupling agent exists as a nonreactant after curing.

**TABLE III**  
Thermogravimetric Data of C18-MMT/NBR/Coupling Agent Nanocomposites

Materials	Silane Content (PHF)	DOT (°C)	MDT (°C)
3-(Mercaptopropyl) trimethoxysilane		80.2	298
NBR		351.8	496.0
C18-MMT/NBR/coupling agent	0	400.1	558.1
	1	433.5	586.6
	2	445.5	607
	5	440.5	597.3
	10	412.7	562

DOT, decomposition onset temperature (°C); MDT, maximum decomposition temperature (°C); coupling agent, 3-(mercaptopropyl)trimethoxy silane.

### Mechanical properties

The mechanical properties are summarized in Figure 6. The effect of the coupling agent in the C18-MMT/NBR nanocomposite is pronounced because the possibility of the formation of coupling bonds is confirmed indirectly by the improvement of the mechanical properties.

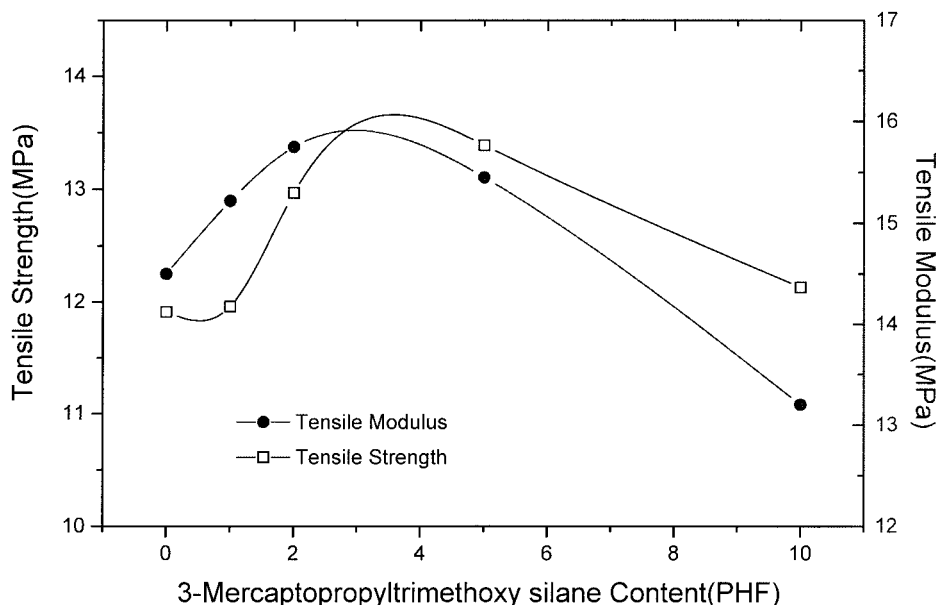
We observed that incorporation of below 5 phf coupling agent in the C18-MMT/NBR nanocomposites enhances the tensile strength and modulus, but above 5 phf content it decreases these properties.

The enhancement of the mechanical properties in C18-MMT/NBR nanocomposites containing below 5 phf coupling agent is caused by the better interaction between C18-MMT and NBR, which is promoted by the C18-MMT surface treatment with silane.

However, at a higher coupling agent content, the strength is decreased. We suppose that the excessively added silane compound exists as a nonreactant after curing or multimolecular layers form between the boundaries of C18-MMT and NBR, thus causing a defect in the nanocomposites.

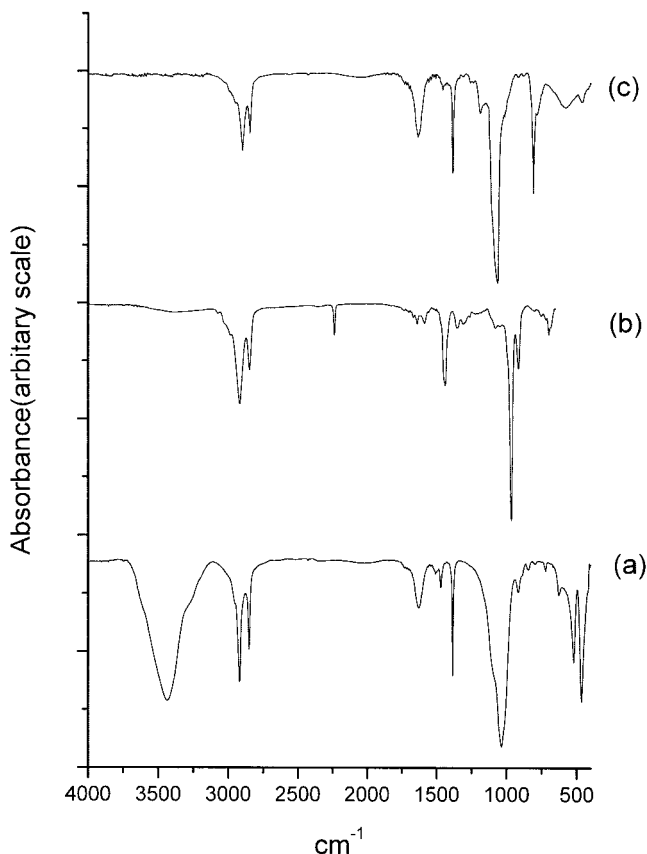
### IR spectroscopy

Figure 7 shows the IR spectra of C18-MMT, pure NBR, and the silane coupling agent 3-(mercaptopropyl)trimethoxy silane. The C18-MMT peaks are manifested by a strong Si—O stretch at  $1036\text{ cm}^{-1}$  and a structure —OH stretch at  $3426\text{ cm}^{-1}$ . The IR spectrum of C18-MMT shows characteristic bands corresponding to the ammonium salt, methyl group, and aliphatic groups. The C—H stretch of the aliphatic group appears at  $2919$  and  $2850\text{ cm}^{-1}$  for C18-MMT.



**Figure 6** The effect of the 3-(mercaptopropyl)trimethoxy silane coupling agent content on the tensile strength and modulus of C18-MMT/NBR/coupling agent nanocomposites.

The absorption band at  $1627\text{ cm}^{-1}$  is the  $\text{NH}_3^+$  in octadecyl ammonium. The characteristic peaks of the NBR matrix appear at  $2237\text{ cm}^{-1}$  for the C—N stretch

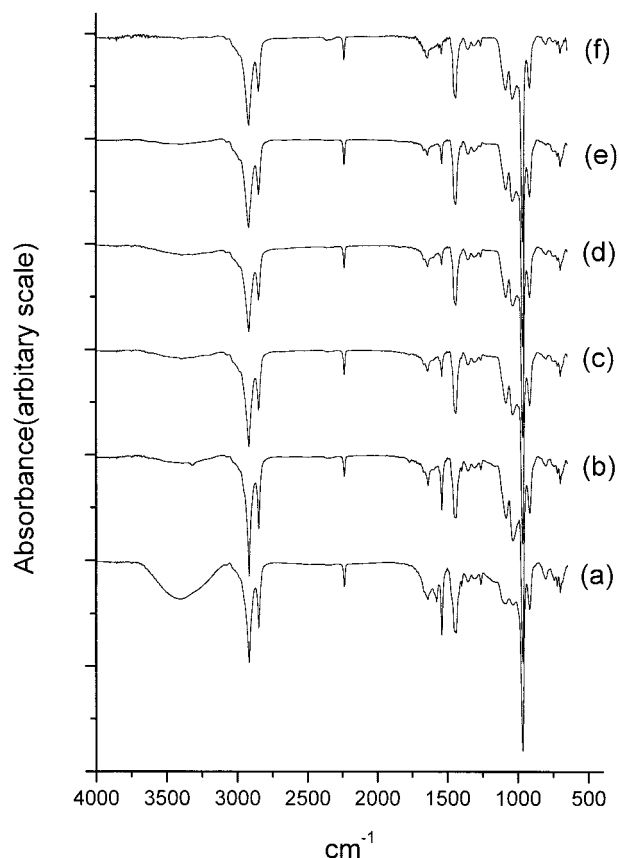


**Figure 7** Fourier transform IR spectra of C18-MMT (spectrum a), pure NBR (spectrum b), and 3-(mercaptopropyl)trimethoxy silane (spectrum c).

and at  $1639\text{ cm}^{-1}$  for the C=C stretch. The IR spectrum of the coupling agent shows a strong absorbance at  $1084\text{ cm}^{-1}$  for a Si—O—CH<sub>3</sub> stretching vibration, a CH<sub>3</sub> peak at  $1384\text{ cm}^{-1}$ , and a C—S stretch at  $581\text{ cm}^{-1}$ .

Figure 8 shows the IR spectra of the C18-MMT/NBR/coupling agent nanocomposite with various contents of the silane coupling agent. In general, the coupling agent can be attached to clay fines by chemical bonding or by adsorption or coating to form a monomolecular layer on the surface of the clay mineral. Molecules of the coupling agent coated or adsorbed on the clay surface give basically no effect to the IR vibration of various groups within the clay. This corresponds to a relatively weak combination between the clay fines and the coupling agent. The molecules of the coupling agent chemically bonded to the surface of the clay mineral will change the IR spectra.<sup>23</sup> Thus, the IR spectra can provide interesting information regarding the clay surface, the coupling agent, and the NBR matrix. The IR absorption spectrum of C18-MMT/NBR/coupling agent nanocomposites showed characteristic bonds due to aliphatic C—H stretching at  $2916$  and  $2848\text{ cm}^{-1}$ ; C—C skeletal in-plane vibrations at  $1638$ ,  $1539$ , and  $1439\text{ cm}^{-1}$ ; and a C—S stretch weak bond at  $700\text{ cm}^{-1}$ .

Moreover, the decrease in the intensity of the peak at  $3398\text{ cm}^{-1}$  signifies that the OH of the C18-MMT (clay) surface and the —OCH<sub>3</sub> of the silane coupling agent react during the molding process at  $180^\circ\text{C}$ . In general, because the grafting of organic groups on the coupling agent molecules are bound at C18-MMT, the strength of the Si—O vibration and absorption should be increased. The Si—O vibration and absorption be-



**Figure 8** Fourier transform IR spectra of  $\text{Na}^+$ -MMT/NBR (spectrum a) and C18-MMT/NBR/coupling agent (spectra b–f) compounds. Coupling agent content: none (spectrum b), 1 phf (spectrum c), 2 phf (spectrum d), 5 phf (spectrum e), and 10 phf (spectrum f).

come very strong at 1089 and  $1038\text{ cm}^{-1}$ . It is rather difficult to obtain any information about the changes attributable to the interaction between the various contents of coupling agents.

### CONCLUSION

We confirmed the effect of a coupling agent by adding 3-(mercaptopropyl)trimethoxy silane to a C18-MMT/NBR nanocomposite.

Additional 3-(mercaptopropyl)trimethoxy silane causes an increase in the early stages of rheometric torque because of a strong interaction between C18-MMT and the NBR matrix. Higher torque indicates that 3-(mercaptopropyl)trimethoxy silane promotes linking of  $\text{—OH}$  groups on C18-MMT and nonactivated double bonds in the NBR matrix.

According to the TGA, the DOT and MDT depend on the concentration of the coupling agent. The cou-

pling agent content of 1–5 phf has more thermal stability, and relatively more restricted structures and exfoliated structures are formed.

In the investigation of the stress–strain properties we observed that incorporation of below 5 phf coupling agent causes an enhancement in the tensile strength and modulus, but above 5 phf these properties are decreased by the increased coupling agent content. The enhancement of the mechanical properties in C18-MMT/NBR nanocomposites containing the coupling agent may be attributable to better C18-MMT dispersion and coupling bond formation.

The formation of the coupling bond between NBR and C18-MMT occurs via the formation of  $\text{Si—O—Si}$  and  $\text{S—C}$  bonds in the IR spectroscopy analysis.

### References

1. Akelah, A. In *Polymer and Other Advanced Materials: Emerging Technologies and Business Opportunities*; Prasad, P. N., Mark, J. E., Fai, T. J., Eds.; Plenum: New York, 1995.
2. Akelah, A.; Moet, A. *J Appl Polym Sci Appl Polym Symp* 1994, 55, 153.
3. Giannelis, E. P. *Adv Mater* 1996, 8, 29.
4. Theng, B. K. G. *Formation and Properties of Clay–Polymer Complex*; Elsevier: Amsterdam, 1979.
5. Theng, B. K. G. *The Chemistry of Clay—Organic Reactions*; Adam Hilger: London, 1974.
6. Solc, J.; Nichols, K.; Galobaedes, M.; Giannelis, E. P. In *SPE ANTEC '97 Processing*; 1997; p 1931.
7. Novak, B. M. *Adv Mater* 1993, 5, 422.
8. Huang, J. C.; Zhu, Z. K.; Yin, J.; Qian, X. F.; Sun, Y. Y. *Polymer* 2001, 42, 873.
9. Zanetti, M.; Camino, G.; Thomann, R.; Mülhaupt, R. *Polymer* 2001, 42, 4501.
10. Cho, J. W.; Paul, D. R. *Polymer* 2001, 42, 3.
11. Dennis, H. R.; Hunter, D. L.; Chang, D.; Kim, S.; White, J. L.; Cho, J. W.; Paul, D. R. In *SPE ANTEC Thec Papers*; 2000; p 428.
12. Dennis, H. R.; Hunter, D. L.; Chang, D.; Kim, S.; White, J. L.; Cho, J. W.; Paul, D. R. *Polymer* 2001, 42, 9513.
13. Blumstein, A. *J Polym Sci Part A Polym Chem* 1965, 3, 2653.
14. Sikka, M.; Cerini, L. N.; Ghosh, S. S.; Winey, K. I. *J Polym Sci Part B Polym Phys* 1996, 34, 1443.
15. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okaada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A Polym Chem* 1993, 31, 1755.
16. Burnside, S. D.; Giannelis, E. P. *Chem Mater* 1995, 7, 1597.
17. Krishnamoorti, R.; Vaia, R. A.; Giannelis, E. P. *Chem Mater* 1996, 8, 1728.
18. Plueddemann, E. P. *Silane Coupling Agents*; Plenum: New York, 1982.
19. Naviroj, S.; Ishida, H.; Fitzgerald, J. J.; Koenig, J. L. *J Macromol Sci Phys* 1983, 22, 291.
20. Ishida, H.; Miller, J. D. *Macromolecules* 1984, 17, 1659.
21. Wolff, S.; Wang, M. J.; Tan, E. H. *Rubber Chem Technol* 1993, 66, 163. s
22. Speier, J. L.; Keil, J. W. U.S. Pat. 3,440,302, 1969.
23. Dai, J. C.; Huang, J. T. *Appl Clay Sci* 1999, 15, 51.