

Clay Modification and Its Effect on the Physical Properties of Silicone Rubber/Clay Composites

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ABSTRACT: Sodium montmorillonite (MMT) was modified with benzyldimethyltetradecylammonium* chloride (B13) to prepare M-MMT. Treatment of MMT and M-MMT with bis(3-triethoxy silylpropyl) tetra sulfide (TEPTS) introduced tetra sulfide groups (TS) on the surface of the clays and yielded MMT-TS and M-MMT-TS, respectively. A high temperature vulcanization silicone rubber (HTV) was compounded with MMT, MMT-TS, M-MMT, and M-MMT-TS, and the morphology of the resulting HTV/clay composites was analyzed by using the corresponding TEM images. The degree of swelling of the HTV composites in the toluene

solution was measured to gauge their crosslinking density and thus to exclude the possibility that the enhanced mechanical properties came from increase in the crosslinking density. The greatly improved mechanical properties, as a result of the incorporation of the TEPTS-modified clay into HTV, were attributed to the enhanced interaction owing to the plausible chemical reaction between the TEPTS-modified clay and the HTV matrix. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E298–E304, 2012

Key words: rubber; clay; composites

INTRODUCTION

Since silicone rubber was first commercialized in 1942 by Dow Corning, it has become one of the most important synthetic rubbers, used for various applications due to its excellent properties, such as flexibility, chemical resistance, and thermal stability.^{1–4} In most cases, the silicone rubber should be reinforced by particulate fillers to make up for the weak mechanical properties, and, thus, the reinforcement of rubber is considered to be a very important process in the elastomer technology.^{4,5} Silica and carbon black have been the most widely used traditional fillers for the reinforcement. However, these fillers should usually be added in large quantities (>20~50 wt %) to obtain polymer composites with good mechanical properties.⁶

Over the past few decades, the layered-silicate clays have attracted considerable attention in the polymer reinforcing research area.⁷ Because of the very high aspect ratio of clay, the advanced material properties can be achieved by the incorporation of a much smaller amount of clay compared to the conventional micron-sized fillers.^{8,9}

Because of the hydrophilic nature of pristine clays, compatibility between hydrophobic polymers and

the clays is seldom acceptable. Therefore, the clays are modified through the introduction of organic ammonium salts into the clay interlayer by way of cationic exchange.¹⁰ However, even after this modification, the clay layers still have the silanol groups on their edges, which can react with silane compounds possessing silanol groups to further raise the hydrophobicity of the clay and, thus, improve the compatibility between the components.¹¹

The mechanical properties of polymer/clay composites largely depend on the degree of exfoliation of the clay layers as well as on the interaction between the clay layers and the polymer matrix. LeBaron and Pinnavaia, Burnside and Giannelis, Osman et al., and Takeuchi and Cohen had reported that the polymer composites with exfoliated clay layers exhibited more advanced physical properties.^{12–16}

It has been shown that the difunctional silane compound, bis(3-triethoxysilylpropyl)tetra sulfide (TEPTS) could be grafted to the clay surface.^{17,18} In turn, the introduced tetra sulfide (TS) groups on the clay surface may react with the backbone chains of the silicone rubber. As a result, the enhanced the interaction between the modified clay and the silicone rubber may contribute to the reinforcement of the rubber.

In this research, montmorillonite (MMT) was modified with B13 to prepare M-MMT. MMT and M-MMT were treated with TEPST to yield MMT-TS and M-MMT-TS, respectively. The resulting clays were mixed and cured with HTV. The dispersion of

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the clay layers and the material properties of the HTV composites were explored as a function of the clay type.

EXPERIMENTAL

Materials

Polydimethylsiloxane end-blocked with vinyl groups containing a vinyl-methyl-siloxane unit in the main chains named as GP-30[®] was purchased from Dow Corning (dimethyl, methylvinylsiloxane dimethylvinyl terminated (>60%), dimethylsiloxane, dimethylvinyl terminated (30 ~ 60%), amorphous silica (10~ 30%), molecular weight of ca. 200,000). The silicone rubber (GP-30[®]) was cured with a curing agent (LS-5; DMBPH peroxide; Dow Corning). Cloisite[®] Na⁺ (MMT) having 92.6 meq/100 g of cation exchange capacity was supplied by Southern Clay Products. (Gonzales, TX). The silane coupling agent, bis(3-triethoxysilylpropyl)tetra sulfide (TEPTS), was obtained from Shin-Etsu Chemicals. Benzyltrimethyltetradecylammonium*chloride (B13) was purchased from Aldrich (St. Louis, MO).

Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a VERTEX 80V (Bruker, Germany) infrared spectrometer. FT-IR spectra were recorded at a wave number range of 4000~400 cm⁻¹. X-ray diffraction (XRD) was measured by using Rigaku DMAX 2500 (Rigaku, Japan) with a CuK α radiation generator operating at 40 kV and 100 mA. Patterns were obtained within a scattering angle range of 2~10°. Transmission electron microscopy (TEM) images were obtained by a TEM 2000 EX-II instrument (JEOL, Tokyo, Japan) operating at an accelerating voltage of 100 kV to observe the nano-scale structure of the various composites. The ultrathin sections (<100 nm) were obtained by microtoming instrument (Super NOVA 655001 Leica, Swiss) with a glass knife and then were subjected to TEM observation without staining. Thermal stability was evaluated by thermal gravimetric analysis (TA Instruments, Q50, USA). The samples were heated at a heating rate of 20°C/min from room temperature to 800°C under a dry nitrogen purge flow of 90 mL/min. Mechanical properties of the silicone rubber composites were measured by using a universal testing machine (UTM, LLOYD Instruments, Model No. LR10K). The dumbbell-shaped specimens were prepared according to KS M 6518, and the tensile tests were performed at 50 mm/min. An average of at least five samples was taken. Tear strength of the specimens was also measured by using the same UTM with a cross-head speed of 100 mm/min.

Specimens were prepared in trouser shape according to KS M 6783, and the results of at least five specimens were averaged. Tear strength was calculated from eq. (1).

$$TR = \frac{F}{t}, \quad (1)$$

where TR, F , and t were tear strength (N/mm), tearing force (N), and specimen thickness (mm), respectively.

Clay modification

MMT mixed with 1 L of distilled water was stirred overnight to swell the clay. When the stirred MMT mixture was cooled down to 3°C, a premixed organic-ammonium salt in 100 mL distilled water was added drop wise and stirred for another 3 h at the same temperature. The modified clay (M-MMT) was washed several times with distilled water until white precipitated organic-ammonium salt particles were not observed in the sludge. The resulting M-MMT was dried in a vacuum oven at room temperature. The dried clay was dispersed in petroleum ether and was stirred for 1 h. The mixture was then filtered and washed with petroleum ether several times, followed by drying in a vacuum oven at room temperature.

The modification of MMT and M-MMT with TEPTS proceeded as follows: TEPTS was hydrolyzed in pH 4.0 for 2 h with hydrochloric acid in an ethanol (90 wt %)/deionized water (10 wt %) mixture. Then, MMT and M-MMT were added and the suspension was heated with reflux at 70°C for 14 h. The product was filtered and washed with ethanol several times to remove the unreacted TEPTS at room temperature and then was dried in a vacuum oven at 60°C for at least 48 h. The modified clays (MMT-TS and M-MMT-TS) were ground into powder 50 μ in size.

Preparation of the composites

HTV/clay and HTV/modified clay composites were prepared by the solution cast method. HTV was completely dissolved in toluene with 1 wt % of LS-5. An appropriate amount of clay was added to the solution, and the suspension was stirred under sonication for 3 h followed by drying in a vacuum oven at 60°C for 48 h. The dried hybrid was then molded into cured sheet with a thickness of about 2 mm by pressing under a pressure of 14 MPa at 175°C for 10 min. The molded sheet was post-cured in a convection oven at 200°C for 4 h. Table I summarizes the recipe for the preparation of the HTV composites.

TABLE I
Recipe for the Preparation of the HTV Composites (phr)

Sample	LS-5	MMT	MMT-TS	M-MMT	M-MMT-TS
HTV	1	–	–	–	–
HTV/MMT	1	5	–	–	–
HTV/MMT-TS	1	–	5	–	–
HTV/M-MMT	1	–	–	5	–
HTV/M-MMT-TS	1	–	–	–	5

The degree of swelling

Square-shaped specimens (2 mm thickness, about 1.5~2 g) were immersed in toluene over 72 h at ambient temperature. The swelled specimens were wiped gently with a kitchen tissue to remove unabsorbed solvent and then their weight was determined. The degree of swelling was determined using eq. (2).

$$Q(\%) = \frac{W_s - W_i}{W_i} \times 100 \quad (2)$$

where W_i is the initial weight of the specimen, and W_s is the weight of the specimen at the maximum solvent uptake.

RESULTS AND DISCUSSION

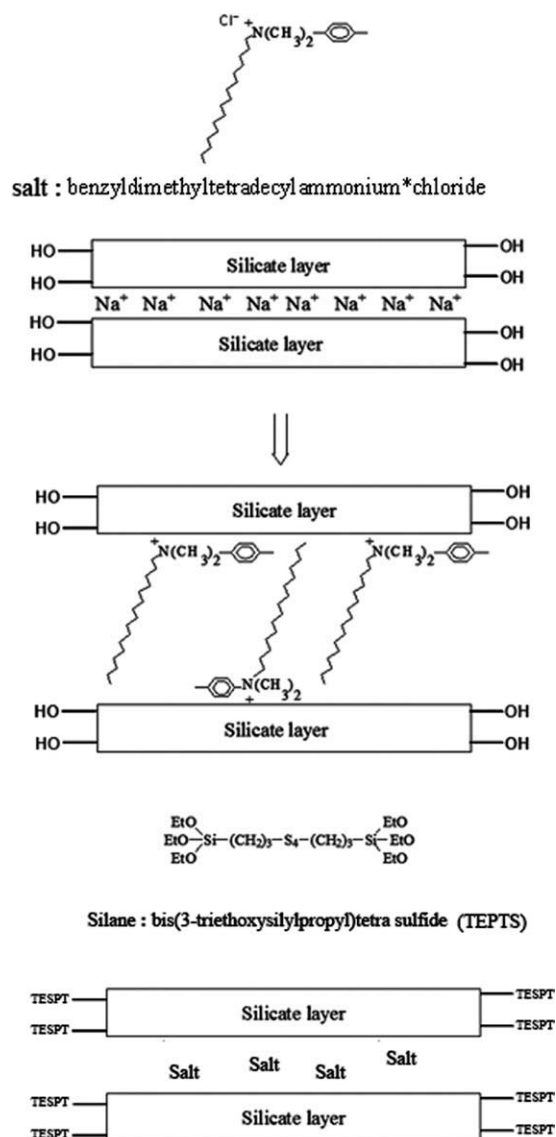
Clay modification

MMT was modified with B13 to prepare M-MMT. B13 was presumed to be infiltrated into the clay layers, as schematized in Scheme 1. MMT and M-MMT were further modified with bis(3-triethoxysilylpropyl)tetra sulfide silane (TEPTS) to synthesize MMT-TS and M-MMT-TS, respectively. Through the condensation reaction between the hydrolyzed TEPTS and the silanol groups of the clay, TS groups may be introduced on the clay surface. The mechanism of chemical reaction between the silicone rubber and TEPTS can be schematized as described in Scheme 2. A radical can be produced at the vinyl group of HTV due to the peroxide of LS-5, and the radical formed can react with the sulfide groups of TEPTS so that some of the HTV molecules can be chemically bound to the clay layers.

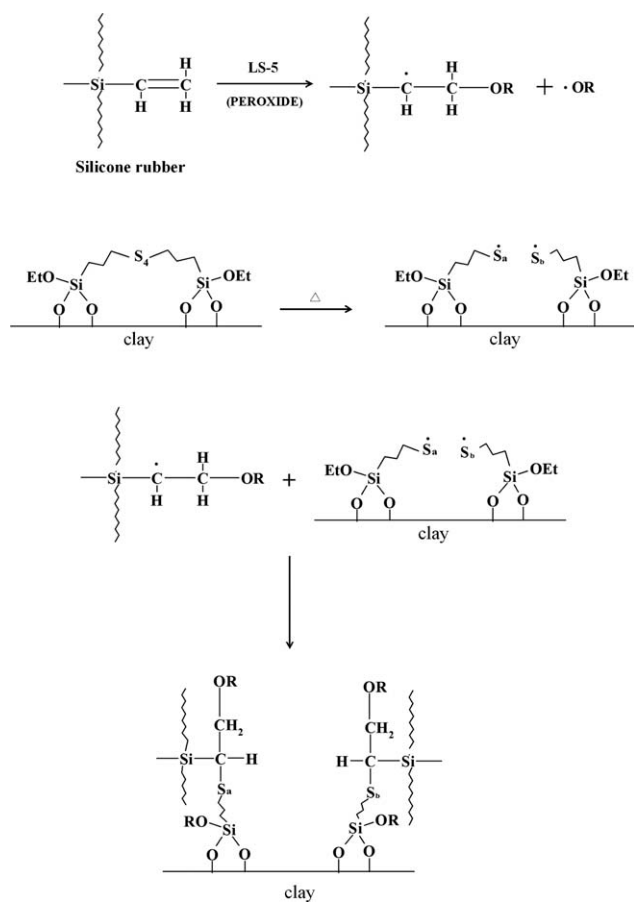
The grafting of TEPTS on the clay surface can be confirmed by the FT-IR spectra, as exhibited in Figure 1. The aliphatic hydrocarbons of the B13-modified clays, M-MMT, and M-MMT-TS display the absorption peaks at 2925 and 2852 cm^{-1} corresponding to the C-H stretching vibrations. The peaks at 1485–1445 cm^{-1} came from the deformation vibration of the acyclic aliphatic chain $[-(\text{CH}_2)_n-]$ of the infiltrated B13 molecules. The TEPTS-modified clays, MMT-TS, and M-MMT-TS show the S-S-C stretching peaks at 590 cm^{-1} , while the same peaks were

absent in the spectra of MMT and M-MMT. The small peaks at 2925 and 2852 cm^{-1} appearing also in the FTIR spectrum of MMT-TS come from the C-H stretching vibrations of the trimethylene residues of the grafted TEPTS.

The XRD diffraction patterns of the clays and silicone rubber/clay composites are presented in Figure 2. The modification of MMT with B13 enlarged the clay layer as evidenced by the XRD



Scheme 1 Scheme of the clay modification process.



Scheme 2 Scheme of the chemical reaction mechanism between the modified clay and silicone rubber.

peak position which was shifted from 7.2 to 4.5° . The interlayer distance of MMT was 11.7 \AA ($2\theta = 7.2^\circ$). The d_{001} peak of MMT-TS also appeared at $2\theta = 7.2^\circ$, indicating that the interlayer distance of MMT was not changed, even after the modifi-

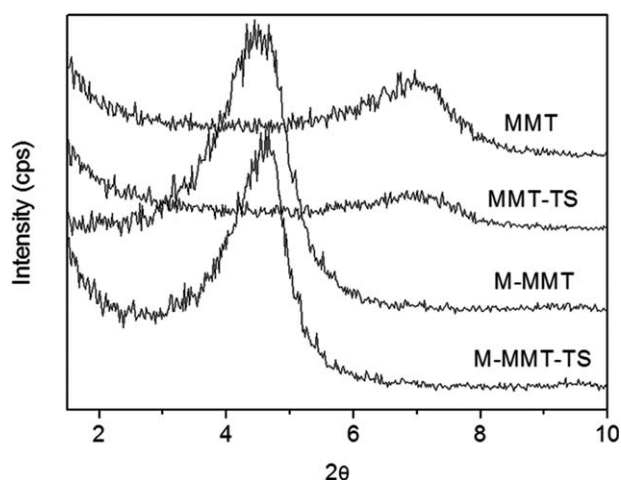


Figure 2 XRD patterns of MMT and the modified clays.

cation with TEPTS. This is because the silicate layers of MMT, has silanol groups mainly on their edges rather than on their flat surface.^{19,20} Therefore, the silane compound such as TEPTS reacted at the edges of clays and could not contribute to increase in the interlayer distance of the clay. In the same context, M-MMT-TS also exhibited the XRD peak at the same 2θ position as that of M-MMT.

Morphology of the HTV/clay composites

The compounding of MMT with HTV did not enlarge the interlayer spacing in that both HTV/MMT composite and neat MMT showed their XRD peaks at $2\theta = 7.2^\circ$. This indicates that the crystalline stacked structure of MMT was preserved during the compounding without discernible intercalation of HTV molecules. In contrast, the intensity of the XRD

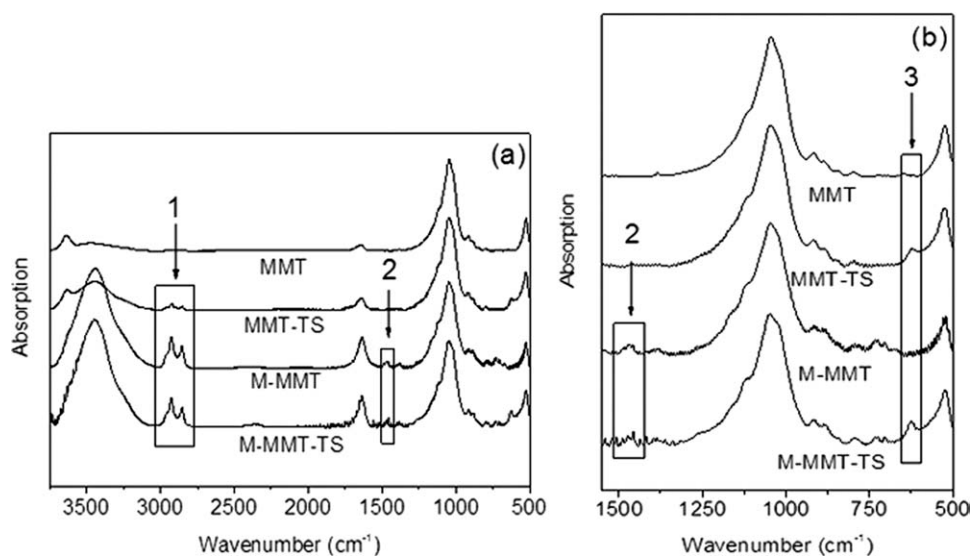


Figure 1 FT-IR spectra of MMT and the modified clays.

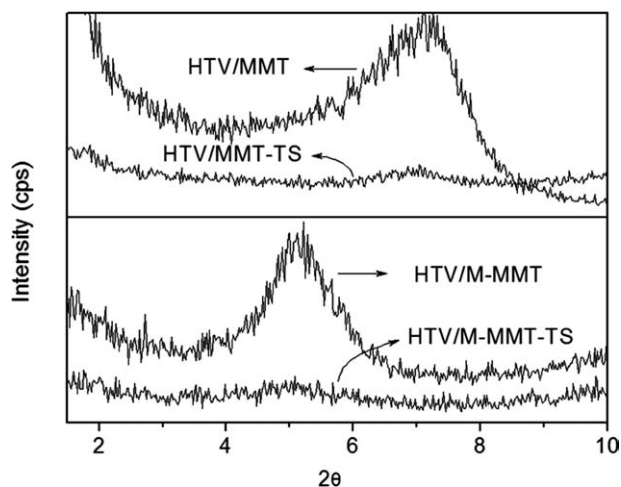


Figure 3 XRD patterns of the HTV/clay composites.

peak at $2\theta = 7.2^\circ$ decreased significantly when MMT-TS was compounded with HTV, as can be seen in Figure 3 which was drawn at the same scale. This was attributed to the fact that some of the crystalline stacked layers of MMT-TS were delaminated,

leading to some exfoliation during the compounding of M-MMT-TS with HTV.²¹ The enhancement of the interfacial interaction between the MMT-TS layers and HTV due to the plausible chemical reaction between the grafted TEPTS and the HTV matrix, as shown Scheme 2, should be responsible for the partial disruption of the MMT-TS layers. In the same context, the XRD peak of HTV/M-MMT-TS composite was much less intense than that of HTV/M-MMT composite.

According to the TEM images displayed in Figure 4, aggregated stacks of the clay layers are seen in HTV/MMT composite. HTV/M-MMT composite also exhibits some aggregated stacks of the clay layers together with some intercalated and exfoliated clay layers. In case of HTV/M-MMT-TS composite, both exfoliated and intercalated clay layers can be observed, while neither exfoliated nor intercalated morphology can be found in the HTV/MMT composite. The degree of exfoliation of HTV/MMT-TS and HTV/M-MMT-TS composites is expected to be much higher than that obtained in the present study if the compounding was carried out through melt-

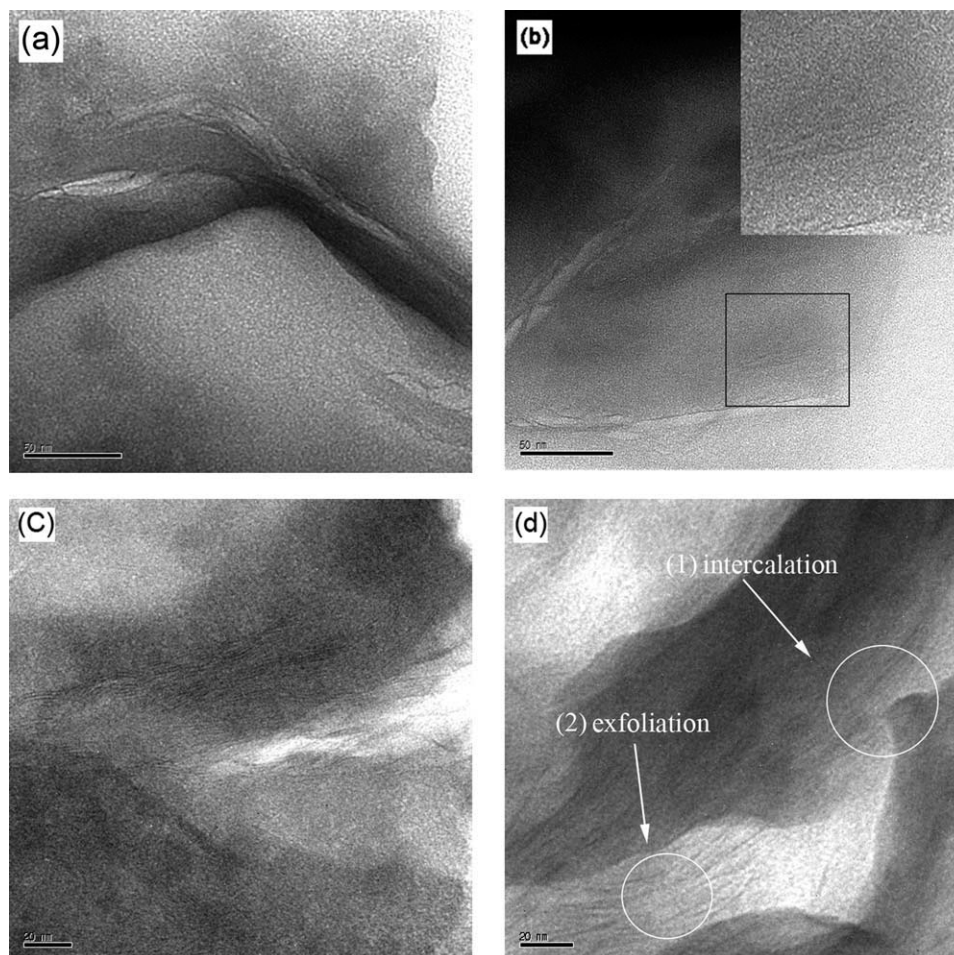


Figure 4 TEM images of the HTV/clay composites: (a) HTV/MMT, (b) HTV/MMT-TS, (c) HTV/M-MMT, and (d) HTV/M-MMT-TS.

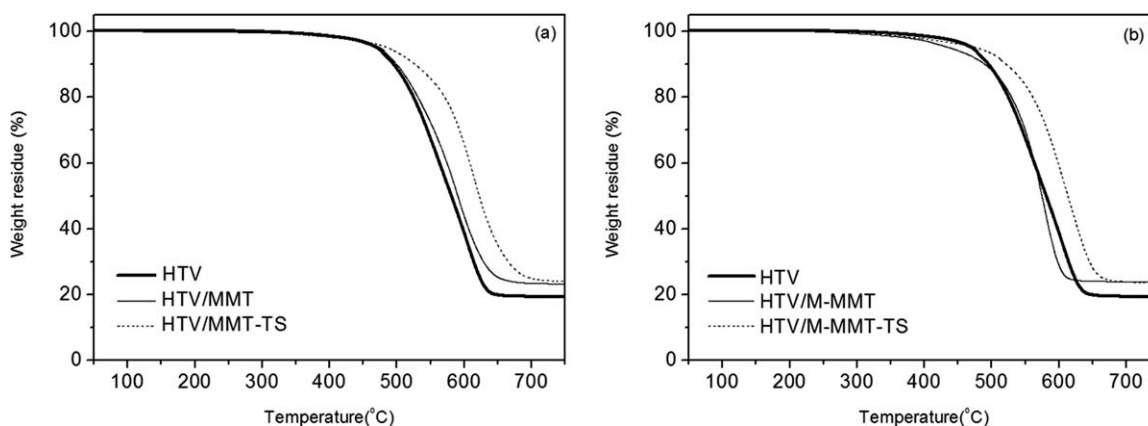


Figure 5 TGA profile of the HTV/clay composites.

mixing instead of the solution blending due to the fact that shear force can not be effectively transferred from the matrix to the clay surface, because the viscosity of the silicone rubber solution should be much lower than that of the clay.

Thermal properties of the composites

HTV, HTV/MMT, and HTV/modified clay composites were subjected to TGA under a nitrogen atmosphere to examine their thermal properties, and the results are exhibited in Figure 5 and Table II. T_{10} and T_{50} correspond to 10 and 50% of weight loss, respectively. The incorporation of MMT, whether modified or not, enhanced the thermal stability of the clay considerably, even though the clay was not well dispersed in the composite. Incorporation of the TEPTS-modified clays (MMT-TS or M-MMT-TS) in the silicone rubber composites raised the thermal stability of the silicone rubber much more effectively than MMT and MMT-TS. This was ascribed to the fact that the dispersion of the TEPTS-modified clays was better than MMT and M-MMT in the corresponding composites. Moreover, the degree of exfoliation of MMT-TS and M-MMT-TS was higher than that of MMT and M-MMT. The stronger S-C bond (bond dissociation energy 699 kJ/mol) in MMT-TS and M-MMT-TS compared to the C-C bond (bond dissociation energy 607 kJ/mol) may be partly responsible for the thermal stability enhancement.

TABLE II
Temperature Corresponding to 10 and 20% of Weight Loss and the HTV Composites

	T_{10} (°C)	T_{50} (°C)
HTV	495	581
HTV/MMT	500	590
HTV/MMT-TS	527	622
HTV/M-MMT	472	574
HTV/M-MMT-TS	522	613

HTV/M-MMT began to lose weight faster than either neat HTV or HTV/MMT as can be seen in Figure 5(a,b). This can be rationalized by the fact that B13 molecules in M-MMT are more vulnerable to thermal degradation than the other components. In the same context, both T_{10} and T_{50} of HTV/M-MMT-TS were lower than those of HTV/MMT-TS.

Mechanical properties of the composites

The tensile properties and tear strength of the composites are summarized in Tables III and IV, respectively. Incorporation of the clays improved elongation at the break as well as maximum stress. The improvement of the tensile properties was more significant when the TEPTS-modified clays were compounded with HTV instead of MMT or M-MMT. It is noteworthy that, the modification of MMT with B13 was effective for the enhancement of the tear strength, and when the M-MMT was treated again with TEPTS, the tear strength went up further.

Since higher crosslinks usually lead to better mechanical properties, the improved tensile properties of HTV composites with the TEPTS-modified clays compared to those of HTV composites with MMT and M-MMT was initially believed to come from the increased degree of crosslinking due to the plausible sulfide linkages between silicone rubber backbone chains and the TEPTS-modified clays.

TABLE III
Tensile Properties of the HTV Composites

Sample	Max stress (MPa)	Elongation at break (%)
HTV	3.8	500
HTV/MMT	5.2	690
HTV/MMT-TS	6.4	980
HTV/M-MMT	6.2	1170
HTV/M-MMT-TS	6.3	1102

TABLE IV
Tear Strength of the HTV Composites

Sample	Tear strength (N/mm)
HTV	1.9
HTV/MMT	1.4
HTV/MMT-TS	7.8
HTV/M-MMT	3.1
HTV/M-MMT-TS	5.0

The polymer crosslinking density can be determined by using the method developed by Flory-Rehner. However, the crosslinking density of silicone rubber cannot be estimated by the Flory-Rehner equation, because the silicone rubber chains do not have the Gaussian distribution due to the significantly high bond angles. In this regard, we measured the degree of swelling of the HTV composites in toluene solution to gauge their crosslinking density as summarized in Table V.

Curiously enough, the degree of swelling in toluene solution became higher when the clay modified with TEPTS was added. The degree of swelling increased in the order of HTV < HTV/MMT < HTV/M-MMT < HTV/M-MMT-TS < HTV/MMT-TS.

Kaneko and Yoshida also observed that the degree of crosslinking of silicone rubber was reduced as a result of compounding with an organically modified MMT.²² The decrease in the crosslinking density as a result of the incorporation of the TEPTS modified clay was ascribed to the fact that some of the vinyl groups of HTV were consumed by the reaction with TS groups of the TEPTS-modified clay so that the number of the intermolecular crosslinking sites, which could otherwise be attacked by the peroxide curing agent, was reduced. Therefore, it can be concluded that the enhanced tensile properties came solely from the increased interfacial interaction between the TEPTS-modified clay and HTV and the better dispersion of the clay layers, which delocalized the stress effectively during the mechanical tests.

CONCLUSION

Sodium montmorillonite (MMT) was modified with B13 to prepare M-MMT. The treatment of MMT

TABLE V
The Degree of Swelling of the HTV/Clay Composites in Toluene Solution

	HTV	HTV/ MMT	HTV/ MMT-TS	HTV/M- MMT	HTV/M- MMT-TS
The degree of Swelling	3.16	4.49	4.65	4.51	4.59

and M-MMT with TESPT introduced TS groups into the clays to yield MMT-TS and M-MMT-TS, respectively. TS grafted to the clays played a vital role in controlling the morphology of the HTV/clay composites and, thus, the various material properties. The TESPT-modified clays were better dispersed in the HTV matrix than the corresponding neat clays. Both tensile strength and elongation at the break of the HTV/clay composites were superior to those of neat HTV whether or not the clay was modified with TEPTS. The improvement of the tensile properties was more significant when the TESPT-modified clays were incorporated. The degree of swelling of the HTV/clay was higher when the clay modified with TEPTS was incorporated, revealing that the improvement of the mechanical properties was not attributed to the plausible participation of TS in the curing of HTV chains, but to the enhanced interfacial interaction between the components.

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