Morphology, Thermal, and Mechanical Properties of Flame-Retardant Silicone Rubber/Montmorillonite Nanocomposites

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ABSTRACT: Flame-retardant methyl vinyl silicone rubber (MVMQ)/montmorillonite nanocomposites were prepared by solution intercalation method, using magnesium hydroxide (MH) and red phosphorus (RP) as synergistic flame-retardant additives, and aero silica (SiO_2) as synergistic reinforcement filler. The morphologies of the flame-retardant MVMQ/montmorillonite nanocomposites were characterized by environmental scanning electron microscopy (ESEM), and the interlayer spacings were determined by small-angle X-ray scattering (SAXS). In addition to mechanical measurements and limited oxygen index (LOI) test, thermal properties were tested by thermogravimetric analysis (TGA). The decomposition temperature of the nanocomposite that contained 1 wt % montmorillonite can be higher (129°C) than that of MVMQ as basal polymer matrix when 5% weight loss was selected as measuring point. This kind of silicone rubber nanocomposite is a promising flame-retardant polymeric material. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3275–3280, 2006

Key words: polysiloxanes; nanocomposites; flame retardance; mechanical properties; thermogravimetric analysis (TGA)

INTRODUCTION

Polymer/layered silicate nanocomposites have been recognized as one of the most promising research fields in materials chemistry because of their unique properties, such as enhanced mechanical property, increased thermal stability, improved gas barrier property, and reduced flammability.[1–5] In recent years, rubber/layered silicate nanocomposites have received great attention because these materials often exhibit unexpected properties, especially in mechanical properties as reinforcing fillers. As far as we are concerned, however, these kinds of nanocomposites have mainly been focused on natural rubber/layered silicate systems,[6–8] polydimethylsiloxane/layered silicate nanocomposites,[9,10] and styrene butadiene rubber (SBR)/montmorillonite nanocomposites,[11,12] while methyl vinyl silicone rubber (MVMQ)/montmorillonite systems have been much less reported in the literature.

MVMQ is one of the most important high-temperature-resistant synthetic rubbers with excellent thermal stability, low temperature toughness, and electrical-insulating properties. It has been extensively used in electrical-insulating products, sealing products, etc. Currently, it is reinforced by aero silica as other kind silicone rubber, which is more expensive than other fillers. Aero silica, with a very small particle size (5–20 nm), is easy to aggregate and is very difficult to disperse in the rubber matrix. Aero silica particles are liable to be inhaled into the human body and do harm to the worker's health; for example, it causes "silicosis."[13] So, it is significant to find a substitute for aero silica. While polymer-layered silicate nanocomposites have so many mechanical and chemical properties, we tried to use organically modified layered silicates to reinforce MVMQ and get low-cost but high-powered materials. In this study, we prepared MVMQ/OMMT nanocomposites by solution intercalation with magnesium hydroxide (MH) and red phosphorus (RP) as flame retardant additives to achieve nonhalogen flame retardant for MVMQ. The morphologies of the organosilicate montmorillonites were characterized by scanning electron microscopy (SEM) and the interlayer spacings were determined by small-angle X-ray

TABLE I
Summary of Fire-Retardant Silicone Rubber Compounds

Compound	MVMQ	OMMT	SiO$_2$	MH	RP	DCBP
MVMQ0	100	0	0	0	0	2.8
MVMQ1	100	0	20	20	5	2.8
FSNC0	100	1	0	0	0	2.8
FSNC1	100	1	20	20	5	2.8
FSNC2	100	3	20	20	5	2.8
FSNC3	100	5	20	20	5	2.8
FSNC4	100	7	20	20	5	2.8

scattering (SAXS). In addition to mechanical measurements, thermal properties were tested by thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

MVMQ (M_w: 620,000, vinyl content is 0.17%, no additives) and fumed silica (SiO$_2$, A-150) used in this work were produced by Dongjue Fine Chemicals Co. Ltd. (Nanjing, China). MH (industrial product, 2M-C01) was provided by HuaXing Chemical Engineering Factory (Hefei, China), and RP (industrial product, KY-1) and montmorillonite modified by hexadecyl trimethyl ammonium bromide (OMMT, average size 5 μm) were provided by Keyan Chemical Flame Retardant Materials Co. Ltd. (Hefei, China). Vulcanizing agent, bis (2,4-dichlorobenzoyl) peroxide (DCBP), was provided by QiangSheng Chemical Engineering Company (JiangSu, China).

Sample preparation

Synthesis of MVMQ/OMMT composite

A given weight of OMMT was dispersed in 100 g of MVMQ swelled in 180 mL toluene; OMMT was scattered into a small amount of toluene before dispersing in MVMQ. The mixture was heated for 8 h at 90°C. After that the MVMQ/OMMT products were ready for shear mixing with additives after drying at 75°C for 16 h.

Preparation of flame-retardant MVMQ/OMMT materials

The aforementioned master batches were mixed with flame-retardant additives at 25°C, using a twin-roll mill. The resulting mixtures were then compression molded into sheets (3 mm and 1 mm thickness). At the same time, the sample was vulcanized at 95°C for 8 min. Table I shows the mixing mass ratio of MVMQ/OMMT to flame-retardant additives (MH, RP) and reinforcement additive (SiO$_2$).

Characterization

XRD was performed on a Japan Rigaku K/max-γA X-ray diffractometer with Cu Kα radiation (λ = 1.54,178 Å, 2θ = 1.5–10°) at the scanning rate of 0.02°/s.

For environmental scanning electron microscopy (ESEM) examination, MVMQ nanocomposites were immersed into liquid nitrogen, fractured, and then coated with gold–palladium film. The center of the fractured surface for each sample was examined on Philips XL 30 ESEM-TMP.

TGA was conducted with a Netzsch STA 409C thermoanalyzer instrument. The 15-mg specimens were heated from 40 to 750°C with a linear heating rate of 10°C min^{-1}. All runs were performed in a nitrogen atmosphere at a flow rate of 50 mL min^{-1}.

Limiting oxygen index (LOI) determination was performed according to ASTM D2863. Test specimens of dimensions 100 × 6.5 × 3 mm^3 were cut from pressed plates. UL-94 vertical burning tests were performed with a plastic sample of dimensions 130 × 13 × 3 mm^3, suspended vertically above a cotton patch. The classifications are defined according to the American National Standard UL-94. The test methods are generally reproducible to an accuracy of ±0.5%, giving useful comparison of the relative flammability of different materials. Higher LOI values represent better flame retardancy.[14]

The tensile tests were carried out with a Universal Testing Machine DCS-5000 (Shimadzu, Japan) at a head speed of 200 mm min^{-1}. All measurements were repeated five times and the values averaged.

RESULTS AND DISCUSSIONS

Mechanical properties and flammability properties

Table II shows the mechanical properties and flammability properties of MVMQ/OMMT nanocomposites. As expected, the silicate-reinforced systems by mixing MVMQ/OMMT nanocomposites containing various amounts OMMT with the same content of SiO$_2$ and

TABLE II
Mechanical Properties of MVMQ Formulations and Their Corresponding Flammability Performances

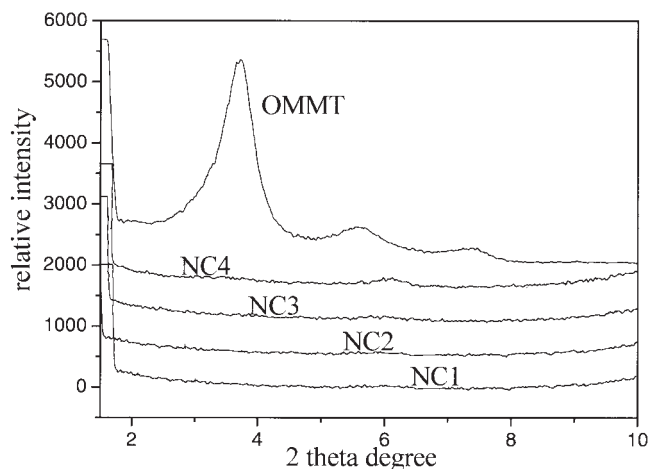| Compound	LOI	UL-94 test	Strength at break (MPa)	Elongation at break (%)
MVMQ0	27.1	V1	0.41	98
MVMQ1	29.0	V0	2.98	310.42
FSNC0	29.4	V0	2.07	298.65
FSNC1	31.1	V0	4.21	513.94
FSNC2	29.5	V0	3.22	438.59
FSNC3	29.8	V0	3.11	404.95
FSNC4	30.2	V0	2.96	380.34

Figure 1 XRD patterns of OMMT clay modified by C16 (OMMT), MVMQ/OMMT nanocomposites with 1 phr OMMT before vulcanization (NC1), MVMQ/OMMT nanocomposites with 3 phr OMMT before vulcanization (NC2), MVMQ/OMMT nanocomposites with 5 phr OMMT before vulcanization (NC3), MVMQ/OMMT nanocomposites with 7 phr OMMT before vulcanization (NC4).

flame-retardant additives have superior mechanical and flammability properties. Even at a low loading of OMMT 1, 3, 5, and 7 phr of MVMQ the mechanical properties and flammability properties increase considerably. The strength at break increases to 404.88%, 926.83%, 685.37%, 658.54%, and 621.95%, respectively, than that of unfilled pure MVMQ (MVMQ0); 30.54%, 41.27%, 8.05%, 4.36%, and 0.07% higher than that of pure MVMQ filled with 20 wt % SiO_2 (MVMQ1). Sample FSNC1 has the highest LOI values, 4 units and 2.1 units higher, respectively, than that of sample MVMQ0 and sample MVMQ1. LOI values of the other nanocomposite compounds are all increased to different extents.

The mechanical properties and flammability properties also testify that MH and RP have a synergistic flame-retardant effect to OMMT for MVMQ matrix; SiO_2 mainly has a reinforcement synergistic effect to OMMT for MVMQ matrix.

X-ray diffraction measurements

Small-angle X-ray diffraction technique was used to measure the interlayer distance of the silicate layers of the montmorillonite and modified montmorillonite with alkyl ammonium cations. It was also used to measure the silicate layers distribution of organo-modified montmorillonites in the polymer matrix.[15] Figure 1 shows the interlayer distances of OMMT and MVMQ/OMMT nanocomposites with no additives before vulcanization. Figure 2 shows the interlayer distance of OMMT and MVMQ/OMMT nanocomposites with all kinds of additives after vulcanization.

The characteristic peak corresponding to the (001) plane reflection of OMMT appears at around 2θ = 3.3°(corresponding to a d-spacing of 2.4–2.5 nm) as shown in Figure 1(OMMT), whereas no distinct peaks appeared in XRD patterns of NC1, NC2, and NC3. But only one diffraction peak appeared at around 2θ = 6.1° of NC4 (Fig. 1). The absence of the characteristic peak of OMMT in the range of 1.5–10° suggests that the layered OMMT has been exfoliated in the MVMQ/ OMMT nanocomposites. The use of inorganic additives in the MVMQ/OMMT/nanocomposite does not destroy the exfoliated structure. However, there is no peak at the same 2θ in the XRD pattern of sample FSNC4. It suggests that MVMO rubber matrix formed netlike structure and destroyed intercalated montmorillonite layers' regular forms and turned into exfoliated forms, which is schematically illustrated in Figure 3.

ESEM micrographs

Figure 4 shows that sample FSNC1 has the strongest interaction between inorganic fillers and rubber matrix while the interaction between pure MVMQ and fillers are weak [Figs. 4(A1) and 4(A2)]; some big fillers are tumbledown in the rubber matrix. When 1% OMMT is added, the interaction between rubber matrix and filler is the strongest. In rubber vulcanizing crosslinking process, OMMT can act as active sites to increase crosslinking degree and lead to denser netlike
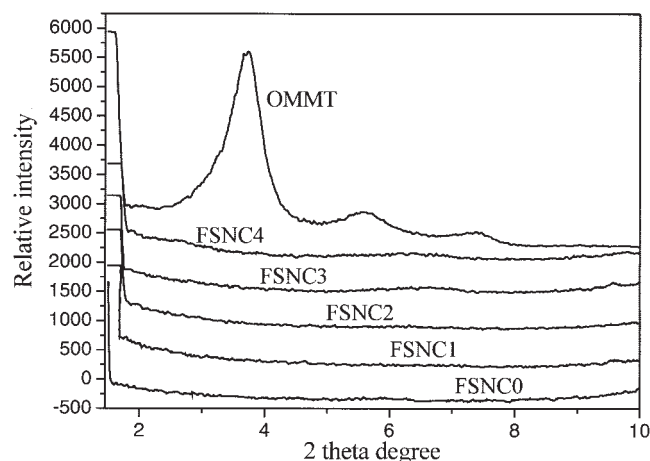

Figure 2 XRD patterns of OMMT, MVMQ/OMMT nanocomposites with 1 phr OMMT only after vulcanization (FSNCO), MVMQ/OMMT nanocomposites with 1 phr OMMT and filled with all other additives after vulcanization (FSNC1), MVMQ/OMMT nanocomposites with 3 phr OMMT and filled with all other additives after vulcanization (FSNC2), MVMQ/OMMT nanocomposites with 5 phr OMMT and filled with all other additives after vulcanization (FSNC3), MVMQ/OMMT nanocomposites with 7 phr OMMT and filled with all other additives after vulcanization (FSNC4).
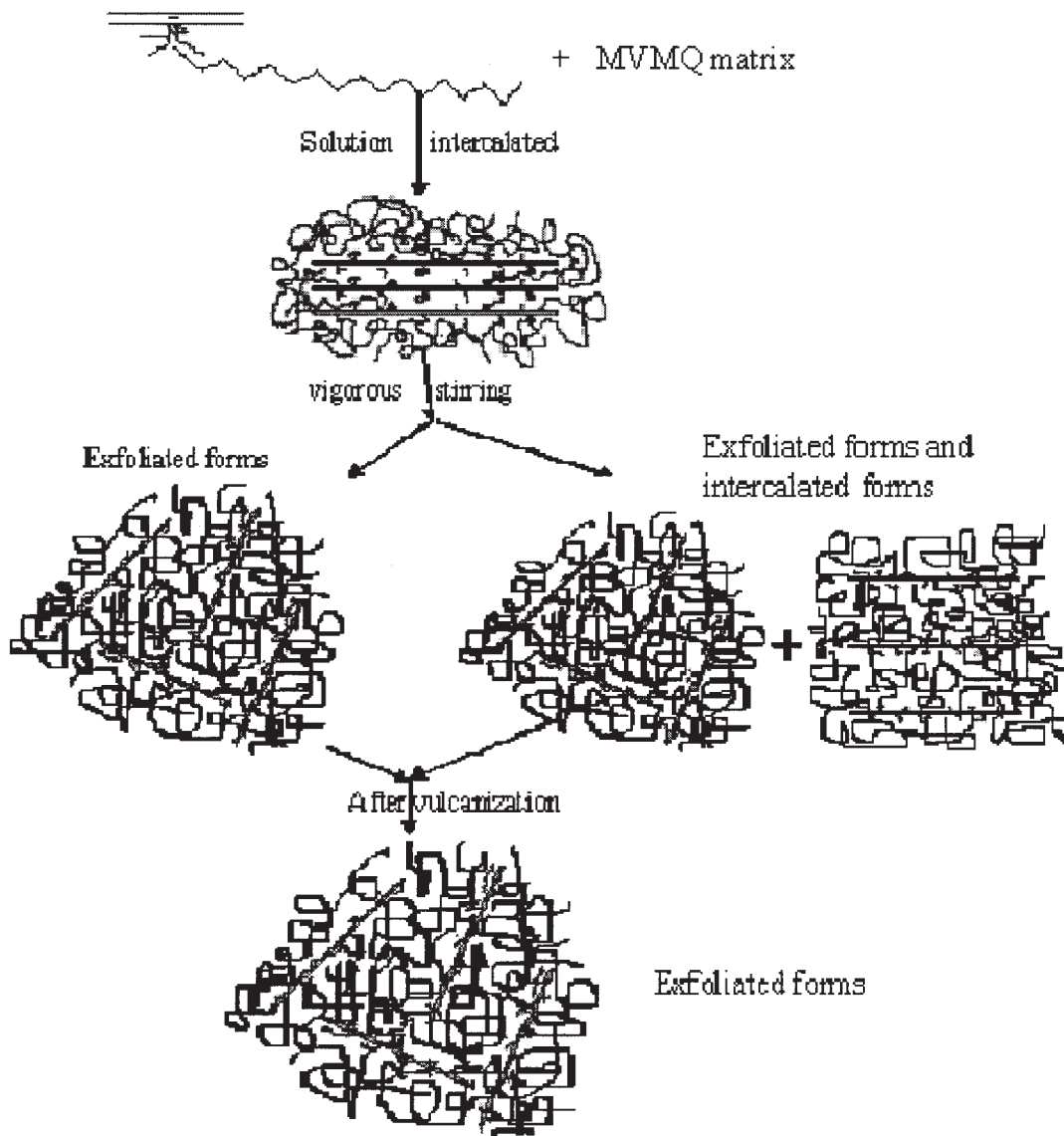
Figure 3 Scheme of the processing for solution intercalated preparation of MVMQ/OMMT nanocomposites before and after vulcanization.

structure. The filler particles are enswathed in the rubber matrix netlike structure, and so the interaction between rubber matrix and filler increases. But along with the increase in content of OMMT, the inorganic particles aggregate seriously (Fig. 4). This is owing to the huge surface area and high activity of OMMT particles themselves. According to the principles of similitude and compatibility of molecular, OMMT particles aggregate themselves, and cumber OMMT's dispersion in rubber matrix to lead to MVMQ/OMMT nanocomposites structure's conversion from exfoliated forms to intercalated forms (Fig. 1). On the other hand, the aggregated OMMT particles absorb MH or RP or SiO_2 particles to form serious aggregation among filler particles. Abundant aggregations lead to structure disfigurement, and consequently, mechanical properties of nanocomposites present downtrend.

But along with increase in content of montmorillonite there are many holes in the fractured surface. This indicates that some fillers fall off just in the only fracture [Figs. 4(C1) and 4(C2), 4(D1) and 4(D2), 4(E1) and 4(E2)]. The micrographs at high amplifier testify the conclusion clearly. At first, there are more and bigger holes in the fractured surface along with the increasing content of montmorillonite; especially in Figure 4(E2) (sample FSNC4), there is a very bulky hole. The other very important result is that the rubber nanocomposites matrix formed netlike structure after vulcanization. This netlike structure is propitious to enhance the interaction between fillers and matrix, Figure 4(B2) is a good example, the region marked "a" and "b" testified that there is very strong interaction between rubber matrix and fillers. Fillers embed in rubber matrix closely.
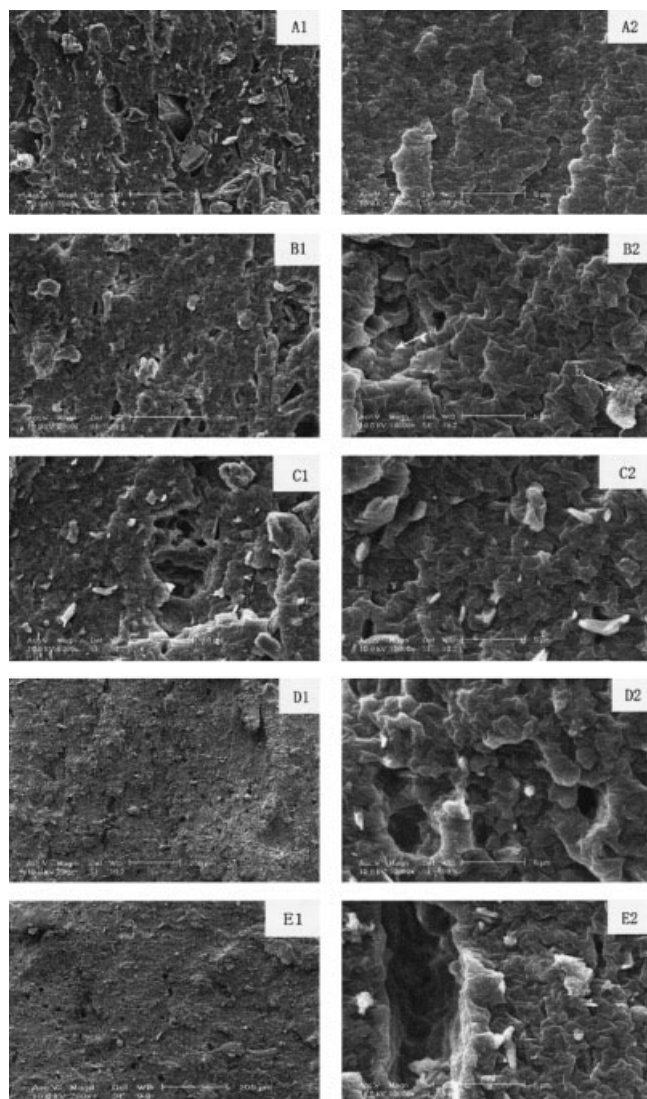
Figure 4 Fig. 4 ESEM micrographs at different amplifiers: (A1 and A2) sample MVMQ1, (B1 and B2) sample FSNC1, (C1 and C2) sample FSNC2, (D1 and D2) sample FSNC3, (E1 and E2) sample FSNC4.

Figure 5 TG (A) and DTG (B) curves of MVMQ composites under nitrogen atmosphere.

Thermogravimetric analysis and derivative thermograms

Thermal stability is an important property in that the nanocomposite morphology plays an important role. Flame-retardant composites were analyzed by TGA. All these samples undergo two degradation steps, as shown in Figure 5. The 5% weight-loss temperature ($T_{-5\%}$) and the 50% weight-loss temperature ($T_{-50\%}$) and residue at 750°C are listed in Table III. This table reveals that MVMQ/OMMT nanocomposites show a distinct increase in $T_{-5\%}$. The major difference between the samples without and with nanocomposites is the weight loss after 350°C. The residues of the samples are increased. Among them, the sample FSNC1 with 1 wt % OMMT has the highest residue at 750°C. The analogous weight loss curves also reflect
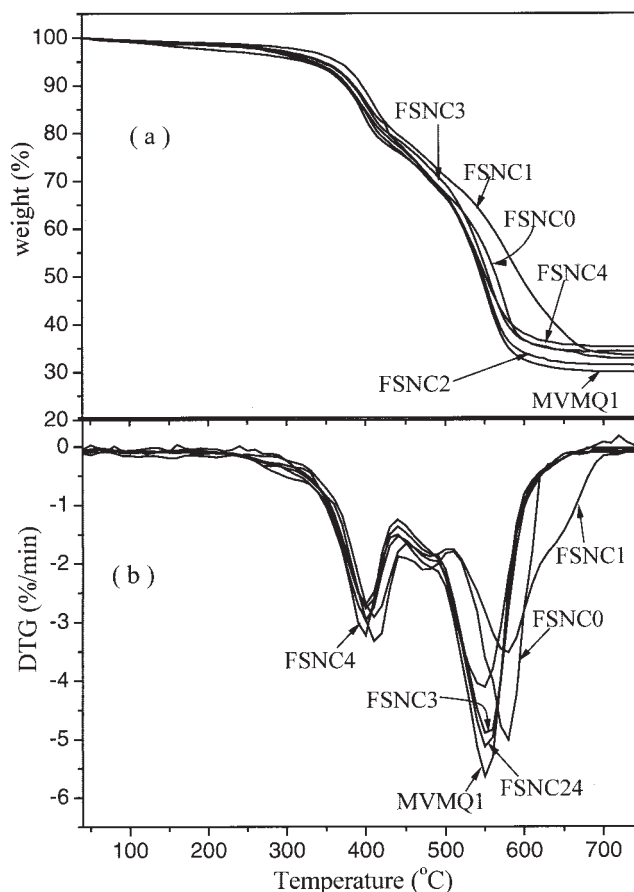
the flame retardant synergistic mechanism by using MVMQ/OMMT nanocomposites mainly due to the physical process in condensed phase.

Figure 5(B) shows the derivative thermograms (DTG), which gives the weight loss rates in the heating process. It can be seen that the weight loss rates obtained from the samples using MVMQ/OMMT nanocomposites as polymer matrix (samples FSNC1–FSNC4) are much smaller than that using pure MVMQ as polymer matrix (sample MVMQ1). Among them, the sample FSNC1 with 1 wt % OMMT has the

TABLE III
Thermal Properties of MVMQ and MVMD/OMMT Hybrids

Compound	$T_{-5\%}$ (°C)	$T_{-50\%}$ (°C)	Residue (%)
MVMQ1	229.4	545.5	29.90
FSNC0	336.8	556.8	32.53
FSNC1	358.7	594.7	33.50
FSNC2	327.8	548.3	31.37
FSNC3	311.2	553.2	34.21
FSNC4	299.6	549.8	35.28

smallest weight loss rate. These TGA results and values of LOI and UL-94 testify that nanodispersed lamellae of OMMT (exfoliation or intercalation) in MVMQ rubber matrix have the main flame-retardant effect. An ablative reassembling of the silicate layers may occur on the surface of a burning nanocomposite, creating a physical protective barrier on the surface of the material.[16,17] The physical process of layers reassembling acts as a protective barrier and can limit the oxygen diffusion to the substrate or give a less-disturbing low volatilization rate. Accordingly, the rate of thermal decomposition is decreased, and the temperature of degradation and residue are increased.

CONCLUSIONS

MVMQ/OMMT nanocomposites have a good flame-retardant synergistic effect with MH and RP in the MVMQ/OMMT/MH/RP/SiO$_2$ blends. The nanocomposites show higher thermal stabilities, flame-retardant properties (high LOI and measured up to UL-94 V0 level), and excellent mechanical properties. The $T_{-5\%}$ of the nanocomposite with 1 wt % OMMT (FSNC1) can be higher (129.3°C) than that of MVMQ as basal polymer matrix; the LOI is high to 31.1. On the other hand, SiO$_2$ has a good reinforcement synergistic effect with MVMQ/OMMT nanocomposite in the MVMQ/OMMT/MH/RP/SiO$_2$ hybrids. The nanocomposite with 1 wt % OMMT (FSNC1) has the best mechanical properties. Its strength at break is 4.2 MPa and elongation at break is 513.9%. The analogous TGA curves also reflect the synergistic flame retardant

mechanism by using MVMQ/OMMT nanocomposites mainly due to the physical process in condensed phase.

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