

## Mechanical properties, flame retardancy, and smoke suppression of lanthanum organic montmorillonite/poly(vinyl chloride) nanocomposites

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**ABSTRACT:** A dimethyl dioctadecyl ammonium chloride modified organic montmorillonite (OMMT-<sub>L44P</sub>)/poly(vinyl chloride) (PVC) nanocomposite and anionic-surfactant-modified lanthanum organic montmorillonite (La-OMMT)/PVC nanocomposites (with three different anionic surfactants for the La-OMMTs) were prepared via melt-intercalation technology. The effects of the La-OMMTs and OMMT-<sub>L44P</sub> on the mechanical properties, flame retardancy, and smoke suppression of PVC were studied. X-ray diffraction characterization showed that the La-OMMTs were exfoliated in the PVC matrix. The mechanical properties of the nanocomposites were enhanced by the incorporation of the La-OMMTs. Cone calorimetry and gas chromatography–mass spectrometry analyses indicated that the incorporation of the La-OMMTs enhanced the flame retardancy and smoke suppression of the PVC nanocomposites. Scanning electron microscopy photos further showed that the residual char surfaces of La-OMMT/PVC were all intact and, thus, provided better barriers to energy and smoke transport. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43951.

**KEYWORDS:** clay; flame retardance; mechanical properties; poly(vinyl chloride)

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### INTRODUCTION

Poly(vinyl chloride) (PVC) is a kind of general resin with comprehensive applications, such as in daily products, packaging materials, and decoration materials, because of its considerable corrosion resistance, excellent insulating characteristics, and price advantage. Particularly, PVC products, such as pipe, floor, and window profiles,<sup>1</sup> have been widely used as building materials. However, its poor thermal stability, brittle properties, and flame-spreading and heavy smoke hazards during house fires, have put PVC under attack.<sup>2</sup> Different types of additives, such as thermal stabilizers, plasticizers, toughening agents, flame retardants, and smoke suppressants, have been reported to improve these problems.

Montmorillonite (MMT) is a kind of layered silicate inorganic material. Because of the characteristics of inorganic materials and its nanoscale lamellar structure, considerable research has proven that MMT could be an effective flame retardant for polymers and can lead to a significant reduction in the peak heat release rate (PHRR).<sup>3</sup> Moreover, the incorporation of

MMT also enhances the physical properties and thermal stability of nanocomposites.<sup>4–6</sup>

To enhance the chemical compatibility of MMT with the polymer matrix, organic modifications of MMT have also been given extensive attention. The normal organic modification method of MMT is cation exchange with a quaternary ammonium salt cationic surfactant. These surfactants can be inserted into the layer of MMT to expand the layer spacing. Quaternary ammonium salt cationic surfactant modified MMT can improve the thermal stability and flame retardancy of polymers such as polystyrene, ethylene-co-vinyl acetate (EVA), and polypropylene.<sup>7–9</sup> Quaternary ammonium salt cationic surfactant modified MMT shows chemical effects on the polymer matrix through acid sites, which form during the Hofmann degradation reaction. The acid sites catalyze the carbonization of the polymer, and the clay-enriched char layer provides a mass- and heat-transfer barrier. Although quaternary-ammonium-modified MMT can improve the thermal stability of PVC to a certain extent, the existence of H<sup>+</sup> catalyzes the initial dehydrochlorination of PVC chains, and this further affects the discoloration

and mechanical properties of PVC during processing.<sup>10</sup> Therefore, quaternary-ammonium-modified MMT is not the most suitable candidate for the preparation of PVC nanocomposites.

Silane coupling agents or titanate coupling agents have been proven to be effective modifiers for MMT organic modification.<sup>11,12</sup> They form a film around the MMT edges by the formation of covalent bonds with hydroxyl groups, which show strong interactions and prevent the polymer chain from contacting the clay. However, Song and Sandi<sup>13</sup> found that organosilanes were fixed with hydroxyls on the outer surface of MMT rather than inserted into the gap of the layers; this prevented the swelling and expansion of MMT layers in the nanoscale.

In comparison with modification by quaternary ammonium salt, the organic modification of MMT with an anionic surfactant seems to be a possible path<sup>14</sup> for the preparation of MMT/PVC nanocomposites. An anionic surfactant could offer compatibility with the PVC matrix and prevent accelerated dehydrochlorination at the same time.

To insert the negatively charged anionic surfactant into the interlayer spaces of MMT, a proper counter ion is necessary in the modification of MMT with an anionic surfactant.<sup>15</sup> Lanthanum ion could be a good candidate for the following reasons.  $\text{La}^{3+}$  has higher valence and larger volume than  $\text{Na}^+$  or  $\text{Ca}^{2+}$ ; this would facilitate the expansion of the layer spacing and could form stronger interactions by coordination and precipitation with the anionic surfactant.<sup>16</sup> The anionic surfactant could enter interlayer spacing of MMT and form a stable organic montmorillonite (OMMT) structure. Moreover, it has been reported in the literature that lanthanum enhanced the thermal stability of PVC through the inhibition of the elimination process of hydrogen chloride.<sup>17</sup>

PVC combustion is a thermal degradation process that is divided into two steps. During the primary degradation process, conjugated polyenes are formed because of dehydrochlorination. The secondary processes are about crosslinking, cyclization, scission, and oxidation with the presence of oxygen.<sup>18,19</sup> Our previous results prove that anionic-surfactant-modified lanthanum organic montmorillonites (La-OMMTs) with three different anionic surfactants effectively improved the thermal stability of PVC.<sup>16</sup> As a continuation of our previous work, the determination of the influence of three kinds of La-OMMTs with different types of anionic surfactants on the thermal degradation of PVC on the flame retardancy and smoke suppression would be very meaningful.

In view of the relationship between the thermal stability, flame retardancy, and smoke suppression, more investigations have been performed on the basis of our previous work. The mechanical properties, flame retardancy, and smoke suppression of dimethyl dioctadecyl ammonium chloride modified organic montmorillonite (OMMT<sub>I,44P</sub>)/PVC, and three kinds of La-OMMT/PVC nanocomposites with different types of anionic surfactants were studied systematically. The layer conformation of OMMTs in the PVC matrix was characterized by X-ray diffraction (XRD). The mechanical properties of the PVC nanocomposites were characterized by tensile testing. The flame retardancy and smoke suppression of the OMMT/PVC nanocomposites were

analyzed by cone calorimetry, gas chromatography–mass spectrometry (GC–MS), and scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

The type of SG-5 suspension-grade PVC resin was provided by Xinjiang Tianye (Group) Co., Ltd. (China). Dioctyl phthalate was supplied as a plasticizer by Dongfang Chemicals Co., Ltd. (China). Titanium dioxide and composite lead salt heat stabilizers were acquired from Mingxin Plastic Chemical Co., Ltd. (China). The synthesis method of the La-OMMT samples was described in our previous article.<sup>16</sup> The La-MMTs modified by sodium dodecanoate (SDD), sodium lauryl sulfonate (SDS), and sodium monododecyl phosphate (SMDP) were denoted La-OMMT<sub>SDD</sub>, La-OMMT<sub>SDS</sub>, and La-OMMT<sub>SMDP</sub>, respectively. The MMT modified by dimethyl dioctadecyl ammonium chloride (I.44P), OMMT<sub>I,44P</sub> (Nanacor, Beijing East-West Technology, Ltd., China), was used as a comparison sample. All of the materials were used without further purification.

### Preparation of the OMMT/PVC Nanocomposites

The OMMT/PVC nanocomposites were prepared precisely by the mixture of PVC with 5-, 5-, 5-, and 3-phr dioctyl phthalate, titanium dioxide, lead salt, and OMMT, respectively. All of the samples were premixed with a high-speed stirrer (SHR-5A, China) for 15 min until the temperature reached 120 °C. Subsequently, the samples were prepared on two-roll mills [X(S)K-160, China] at  $168 \pm 3$  °C for 6 min. The samples were compressed to 4 mm at 170 °C and 10 MPa for 10 min with a plate vulcanizing machine (XLB-D/Q 400 × 400, China). Afterward, the samples were cooled to room temperature, and the pressure was released. Tensile test specimens were cut from the molded sheets.

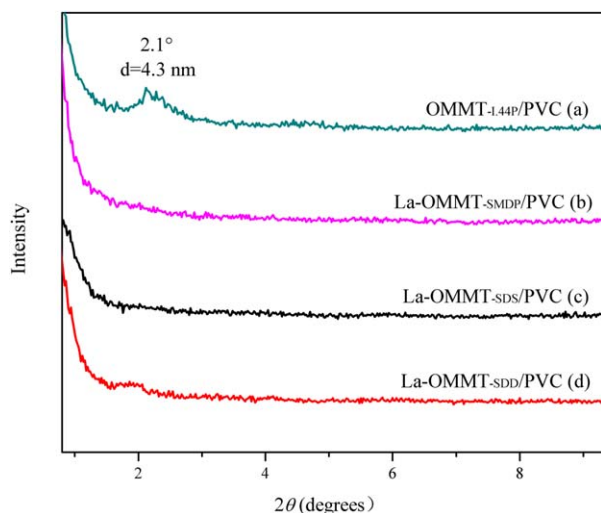
### Measurements and Characterization

XRD was used to characterize the layer conformation of the OMMTs in the PVC matrix on a X-ray diffractometer (Bruker D8 Advance, Germany) with Cu K $\alpha$  irradiation (1.5406 Å) at a scanning rate of 2°/min at 40 kV. Layer spacing was calculated by Bragg's equation within the 2 $\theta$  range 1–10°.

Tensile tests were done on a tensile machine (Instron 3366, United Kingdom) with a crosshead speed of 10 mm/min at room temperature. Dumbbell strip samples (115 × 10 × 4 mm<sup>3</sup>) were prepared according to GB/T 1040-2006. The notched impact strength was measured with an impact testing apparatus (XJJ-50, China) on rectangular samples with a notch depth of 2 mm and dimensions of 80 × 10 × 4 mm<sup>3</sup>, as suggested in GB/T1043.1-2008. The impact velocity was maintained constantly at 2.9 m/s. Five samples were used for each test, and the data are presented in the form of the mean value plus or minus the standard deviation.

To determine the flame retardancy and smoke-suppression performance, an FTT 0007 cone calorimeter was used according to ISO5660 at a heat flux of 50 kW/m<sup>2</sup>. The exhaust flow rate was 24 L/s. The specimens for cone calorimetry were prepared by their compression molding into 100 × 100 × 4 mm<sup>3</sup> square plaques.

GC–MS (Agilent 5975C) was used to detect the composition of the PVC and its nanocomposites after pyrolysis. To collect the



**Figure 1.** XRD patterns of (a) OMMT-1.44P/PVC, (b) La-OMMT-SMDP/PVC, (c) La-OMMT-SDS/PVC, and (d) La-OMMT-SDD/PVC nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

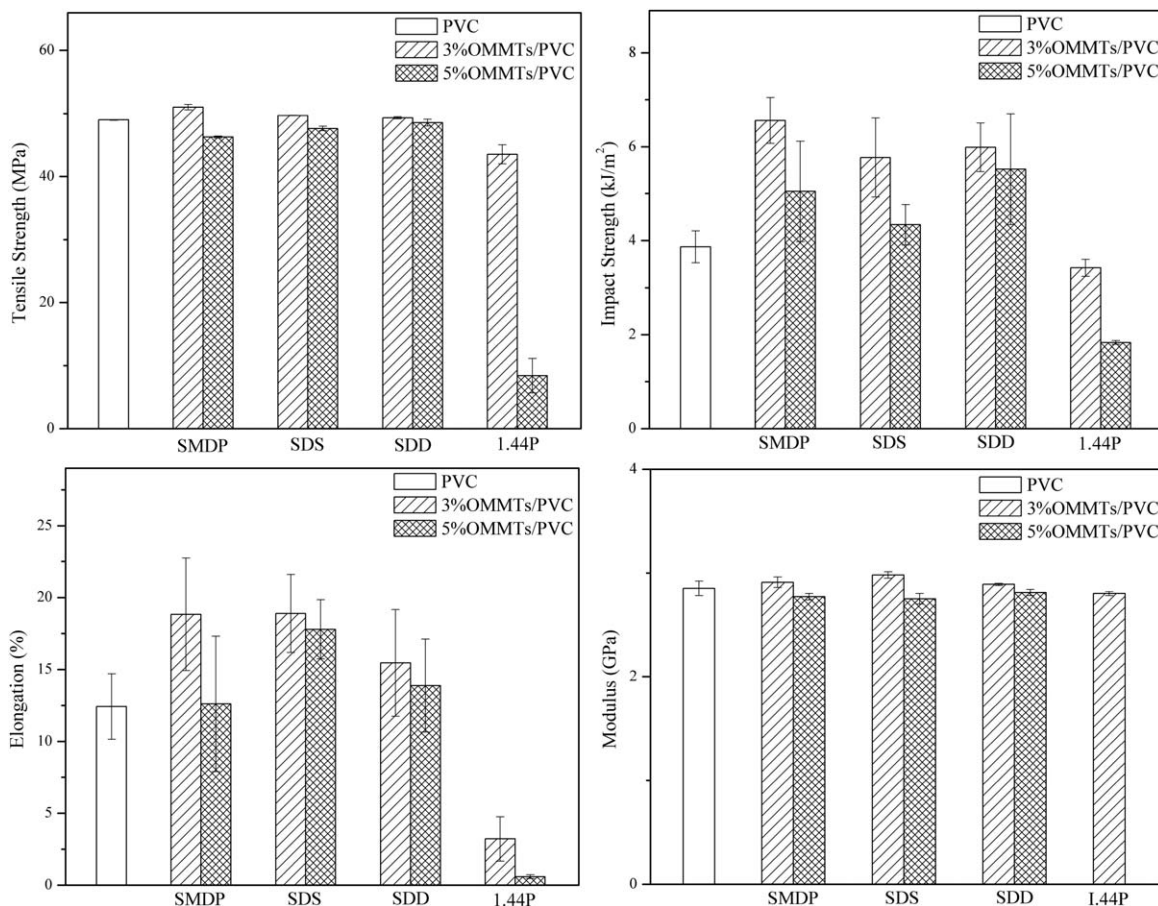
degradation products, about 10 g of sample was placed into a quartz tube and pyrolyzed at 700 °C for 30 min in an N<sub>2</sub> atmosphere. The condensable volatile components were collected with a cold ethyl acetate solution.

Surface morphological images of the residue after pyrolysis were taken by SEM (JSM-5900LV, Japan). All of the sample surfaces were treated with Au deposition. The accelerating voltage of the SEM instrument was 10 kV.

## RESULTS AND DISCUSSION

### XRD Analysis

Figure 1(a–d) shows the XRD patterns of the OMMT-1.44P/PVC, La-OMMT-SMDP/PVC, La-OMMT-SDS/PVC, and La-OMMT-SDD/PVC nanocomposites, respectively. The success of the intercalation was mainly verified by measuring the increase in the basal (001) d-spacing. According to our previous work,<sup>16</sup> the initial  $d_{001}$  value of the Na-MMT, La-MMT, La-OMMT-SMDP, La-OMMT-SDS, and La-OMMT-SDD were 1.23 nm ( $2\theta = 7.21^\circ$ ), 1.47 nm ( $2\theta = 6.02^\circ$ ), 3.34 nm ( $2\theta = 2.65^\circ$ ), 3.31 nm ( $2\theta = 2.67^\circ$ ), and 3.36 nm ( $2\theta = 2.63^\circ$ ), respectively. The result proved that the anionic surfactant increased the basal spacing of the clay interlayer obviously. Figure 1(a) shows the small characteristic diffraction peak located around  $2\theta = 2.1^\circ$ . According to Bragg's equation, the basal interlayer spacing was 4.3 nm; this indicated that the majority of OMMT-1.44P was intercalated. For La-OMMT-SMDP/PVC, the disappearance of the characteristic diffraction peak of La-OMMT-SMDP at a  $2\theta$  around  $2.63^\circ$  indicated the significant expansion of La-OMMT-SMDP. This result may have been caused by the large  $d_{001}$  value of the



**Figure 2.** Tensile strength, impact strength, elongation, and modulus results for PVC, La-OMMT-SMDP/PVC, La-OMMT-SDS/PVC, La-OMMT-SDD/PVC, and OMMT-1.44P/PVC.

**Table I.** Cone Calorimetry Data for PVC and Its Nanocomposites

Sample	PHRR (kW/m <sup>2</sup> )	AHRR (kW/m <sup>2</sup> )	ASEA (m <sup>2</sup> /kg)
PVC	156.5	70.3	562.7
OMMT- <sub>I,44P</sub> /PVC	181.3	78.0	575.3
La-OMMT- <sub>SMDP</sub> /PVC	131.5	62.4	456.0
La-OMMT- <sub>SDS</sub> /PVC	147.1	69.5	505.8
La-OMMT- <sub>SDD</sub> /PVC	140.7	66.1	484.7

The cone calorimetry parameters were PHRR, AHRR, and ASEA.

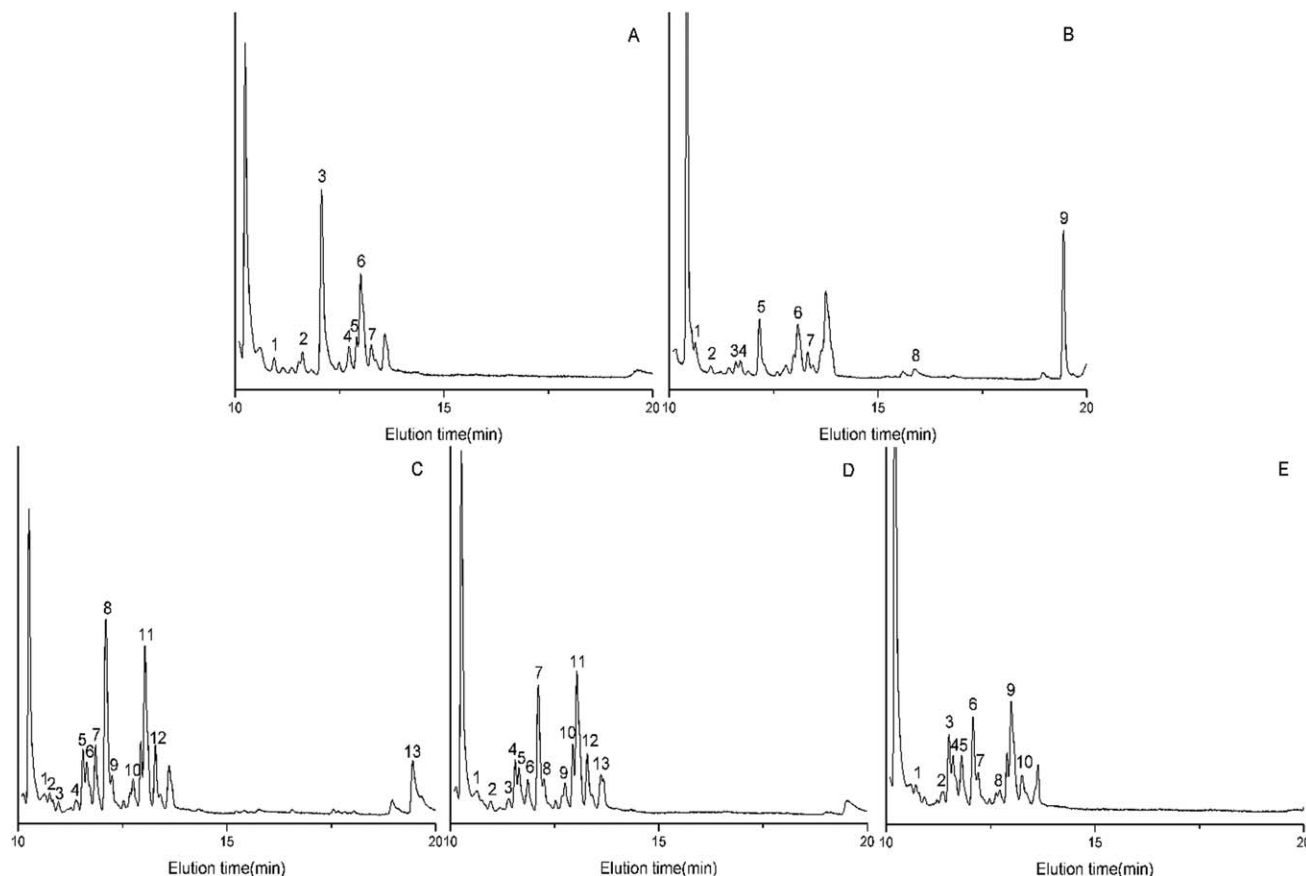
La-OMMTs; this facilitated the swelling and expansion of the La-MMTs in the PVC matrix. The XRD curves of La-OMMT-<sub>SDS</sub>/PVC and La-OMMT-<sub>SDD</sub>/PVC were similar to those of La-OMMT-<sub>SMDP</sub>/PVC. The disappearance of the XRD peak at a low 2θ angle proved that La-OMMT-<sub>SMDP</sub>, La-OMMT-<sub>SDS</sub>, and La-OMMT-<sub>SDD</sub> were dramatically exfoliated in the PVC matrix.<sup>20</sup> The result proves that the La-OMMTs were exfoliated much more obviously than OMMT-<sub>I,44P</sub> in the PVC matrix.

### Mechanical Properties

The mechanical properties data of the PVC and OMMT/PVC nanocomposites are summarized in Figure 2. With the adulteration of 3% OMMT-<sub>I,44P</sub> the tensile strength and impact strength of 3% OMMT-<sub>I,44P</sub>/PVC decreased obviously to 43.5 MPa and





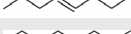
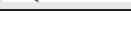
3.4 kJ/m<sup>2</sup>, respectively. However, the tensile strengths of 3% La-OMMT-<sub>SMDP</sub>/PVC, 3% La-OMMT-<sub>SDS</sub>/PVC, and 3% La-OMMT-<sub>SDD</sub>/PVC nanocomposites showed a certain increase from 49.0 MPa (PVC) to 51.0, 49.7, and 49.3 MPa, respectively. The La-OMMT/PVC nanocomposites were also toughened significantly by the incorporation of the La-OMMTs. The impact strengths was increased from 3.9 kJ/m<sup>2</sup> for PVC to 6.6, 5.8, and 6.0 kJ/m<sup>2</sup> for 3% La-OMMT-<sub>SMDP</sub>/PVC (a 69% increase), 3% La-OMMT-<sub>SDS</sub>/PVC (a 49% increase), and 3% La-OMMT-<sub>SDD</sub>/PVC (a 54% increase), respectively. The variation trend was similar to those of the modulus and elongation. For example, the elongation for 3% La-OMMT-<sub>SMDP</sub>/PVC, 3% La-OMMT-<sub>SDS</sub>/PVC, and 3% La-OMMT-<sub>SDD</sub>/PVC increased from 12.42% for PVC to 18.83, 18.89, and 15.46%, respectively. For 3% OMMT-<sub>I,44P</sub>/PVC, the elongation decreased to 3.21%.

Furthermore, when the content of OMMTs increased to 5%, the tensile strengths, impact strengths, and elongation and modulus values of the 5%La-OMMT/PVC nanocomposites showed certain decreases compared with those of the 3% La-OMMT/PVC nanocomposites. This decrease was probably caused by the aggregation of La-OMMTs.<sup>21</sup> For the 5% OMMT-<sub>I,44P</sub>/PVC nanocomposite, the tensile strength, impact strength, elongation, and modulus of OMMT-<sub>I,44P</sub>/PVC decreased obviously, and it even lost mechanical properties. In addition to the aggregation of OMMT-<sub>I,44P</sub> the accelerated dehydrochlorination effects of OMMT-<sub>I,44P</sub> triggered the rapid degradation of PVC.



**Figure 3.** GC-MS curves for the collected volatile components of the degradation products: (A) PVC, (B) OMMT-<sub>I,44P</sub>/PVC, (C) La-OMMT-<sub>SMDP</sub>/PVC, (D) La-OMMT-<sub>SDS</sub>/PVC, and (E) La-OMMT-<sub>SDD</sub>/PVC.

**Table II.** GC–MS Results for PVC (550 and 700 °C)

No.	Compound	Chemical structure	% at 550 °C	% at 700 °C
1	Ethylcyclopentane		—	2.6
2	Hydrogen chloride	HCl	7.2	4.6
3	Toluene		27.8	47.1
4	1-Octene		—	6.7
5	4-Octene(Z)		45.4	5.2
6	4-Octene(E)		9.4	27.6
7	2-Octene(E)		10.2	6.1

The evolved free hydrogen chloride and the changed structure of the PVC molecules exhibited a great influence on the physical and chemical properties of the PVC matrix.<sup>22</sup> The quaternary-ammonium-modified MMT was proven to be unsuitable for PVC in preparation of the nanocomposite. The La-OMMT/PVC nanocomposites would have more practical value than the quaternary-ammonium-modified MMT/PVC when applied to building materials fields.

#### Combustion Behavior

Cone calorimetry, one of the most commonly used bench-scale methods, was used to study the flammability of materials, and the obtained results from this method can be used to predict the combustion behavior of materials in actual fires.<sup>23,24</sup> The cone calorimetry data of the PVC and 3% OMMT/PVC nanocomposites are listed in Table I.

The PHRR, average heat release rate (AHRR), and average specific extinction area (ASEA) of OMMT-<sub>I,44P</sub>/PVC were higher than those of PVC. On the contrary, the PHRR, AHRR, and ASEA values of the three kinds of La-OMMT/PVC nanocomposites decreased to different degrees. Among the three La-OMMT/PVC nanocomposites, the PHRR, AHRR, and ASEA of

OMMT-<sub>SMDP</sub>/PVC decreased most significantly by 25, 7.9, and 106.7 m<sup>2</sup>/kg, respectively.



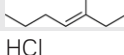

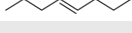




The results indicate that the flame retardancy and smoke suppression of the La-OMMT/PVC nanocomposites improved excellently, but the incorporation of OMMT-<sub>I,44P</sub> showed the opposite effects. For the OMMT-<sub>I,44P</sub>/PVC nanocomposite, some compounds that could produce more heat and smoke might have been present; this caused the flame retardancy and smoke suppression of PVC to deteriorate.

PVC combustion could be considered a process of thermal degradation. Therefore, the thermal degradation products of the OMMT-<sub>I,44P</sub>/PVC and La-OMMT/PVC nanocomposites at high temperature were investigated via GC–MS.


















#### GC–MS Analysis

GC–MS was used to detect the collected volatile components in a cold ethyl acetate solution of degradation products from PVC and its nanocomposites, which were pyrolyzed at a high temperature under nitrogen (Figure 3). The compositions of the volatile components from the GC–MS tests (at 550 and 700 °C) are listed in Tables (II–VI). Compared with PVC, the













**Table III.** GC–MS Results for OMMT-<sub>I,44P</sub>/PVC (550 and 700 °C)

No.	Compound	Chemical structure	% at 550 °C	% at 700 °C
1	1-Chloro-2-methyl-2-butene		—	5.9
2	Ethylcyclopentane		—	1.4
3	3-Methyl-3-heptene		—	2.6
4	Hydrogen chloride	HCl	11.9	19.9
5	Toluene		14.6	14.3
6	4-Octene(E)		19.6	19.8
7	2-Octene(E)		7.3	0.5
8	1,3-Xylene		3.1	2.8
9	2,3,3-Trimethyl-1-pentene		39.2	27.7
10	4-Octene(Z)		4.2	—

**Table IV.** GC–MS Results for La-OMMT<sub>SMDP</sub>/PVC (550 and 700 °C)

No.	Compound	Chemical structure	% at 550 °C	% at 700 °C
1	Hydrogen chloride	HCl	8.0	8.8
2	2,5-Dimethylhexane		2.0	1.4
3	Ethylcyclopentane		—	0.7
4	4-Octene(Z)		2.0	6.0
5	3-Ethyl-3-hexene		—	4.9
6	3,3-Dimethyl-1-hexene		—	5.8
7	2-Methylheptane		9.5	6.8
8	Toluene		—	20.1
9	3-Methyl-5-heptene		4.6	3.2
10	1-Octene		—	3.3
11	3-Octene(Z)		11.0	18.2
12	2-Octene(Z)		27.8	12.6
13	2,3,3-Trimethyl-1-pentene		—	8.1
14	3-Methyl-3-heptene		6.8	—
15	4-Methyl-2-heptene		7.4	—
16	3-Methylheptane		12.0	—
17	4-Octene(E)		6.8	—
18	3,5-Dimethylhex-2-ene		2.2	—

**Table V.** GC–MS Results for La-OMMT<sub>SDS</sub>/PVC (550 and 700 °C)

No.	Compound	Chemical structure	% at 550 °C	% at 700 °C
1	Hydrogen chloride	HCl	4.6	10.5
2	Ethylcyclopentane		—	1.1
3	4-Octene(E)		7.9	8.1
4	5-Methyl-3-heptene		8.5	5.6
5	3,3-Dimethyl-1-hexene		—	6.5
6	2-Methylheptane		6.5	4.9
7	Toluene		12.0	17.2
8	3-Methyl-5-heptene		6.1	4.8
9	1-Octene		—	3.8
10	3-Octene(Z)		33.8	23.0
11	2-Octene(Z)		12.7	7.5
12	3-Octene(E)		—	1.6
13	2-Octene(E)		—	5.4
14	4-Methyl-2-heptene		7.8	—

**Table VI.** GC–MS Results for La-OMMT<sub>-SDD</sub>/PVC (550 and 700 °C)

No.	Compound	Chemical structure	% at 550 °C	% at 700 °C
1	Pentyl vinyl ether		—	2.9
2	4-Octene(E)		6.0	2.4
3	3-Methyl-3-heptene		—	16.5
4	4-Methyl-2-heptene		11.0	10.5
5	2-Methylheptane		15.0	10.1
6	Toluene		—	15.0
7	3-Methyl-5-heptene		—	6.6
8	Hydrogen chloride	HCl	5.7	1.6
9	3-Octene(Z)		23.4	24.0
10	2-Octene(Z)		7.2	10.4
11	3-Ethyl-3-hexene		11.6	—
12	3-Methylheptane		13.8	—
13	2-Methyl-5-heptene		6.4	—

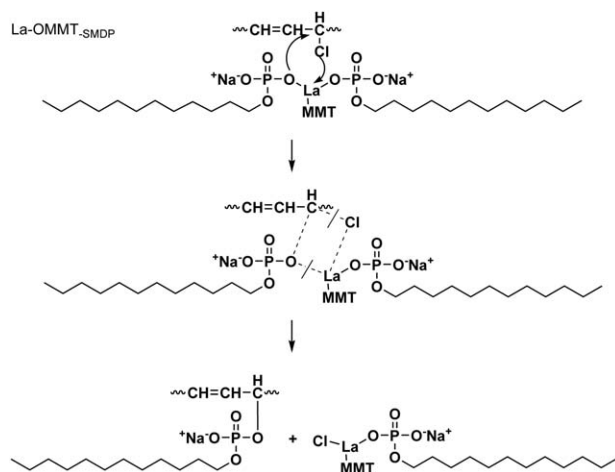
degradation products from OMMT<sub>-I,44P</sub>/PVC and La-OMMT/PVC became more complicated; this means that the incorporation of both OMMT<sub>-I,44P</sub> and the La-OMMTs affected the process of PVC thermal degradation. According to the analysis of the thermal degradation products, the large difference between the composition after the thermal degradation of OMMT<sub>-I,44P</sub>/PVC and La-OMMT/PVC indicated that OMMT<sub>-I,44P</sub> and the La-OMMTs exhibited different effects on the PVC matrix.

Table III shows that 4-octene(z) disappeared when the temperature was increased from 550 to 700 °C in the thermal degradation products of OMMT<sub>-I,44P</sub>/PVC. In addition, more kinds of cyclic compounds were detected by GC–MS because of the formation of cyclic compounds from unsaturated short-chain *cis*-alkenes, such as 4-octene(z), through the cyclization reaction. The unsaturated cyclic compounds produced more heat and smoke; this deteriorated the flame retardancy and smoke suppression of PVC.<sup>2</sup>

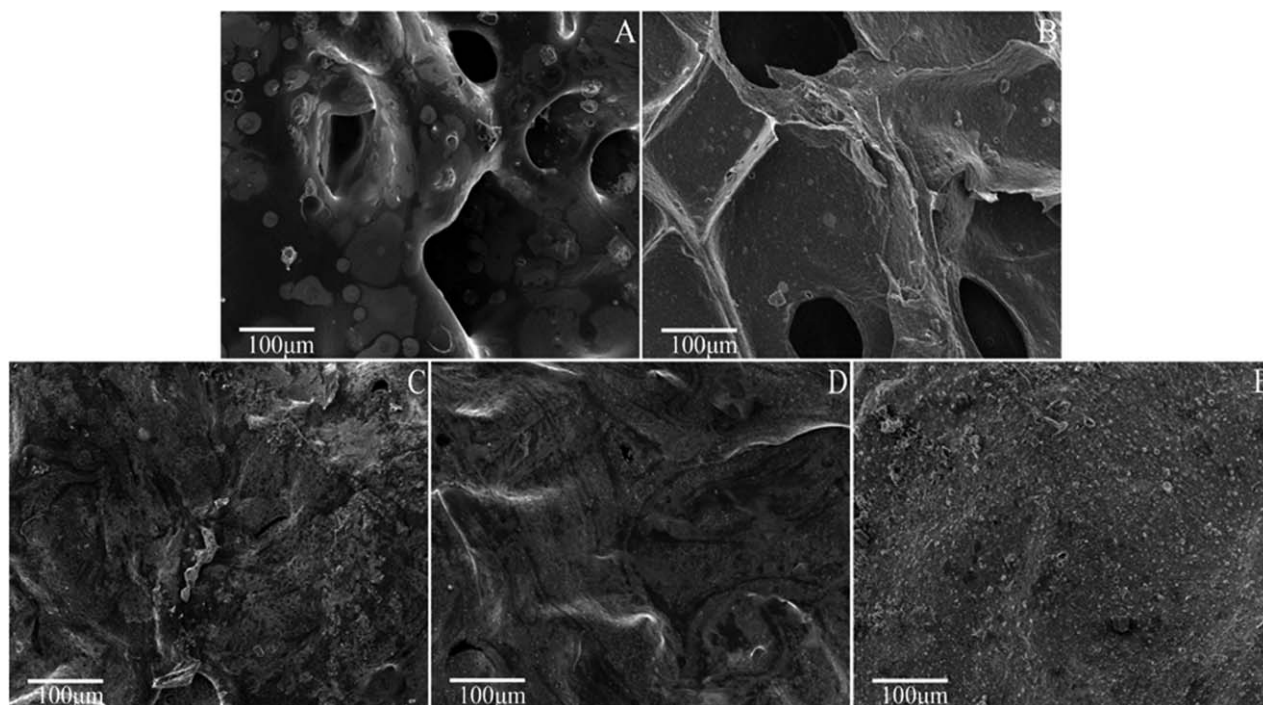
The compositions of the thermal degradation products at 550 and 700 °C from La-OMMTs/PVC are listed on Tables (IV–VI). Compared with PVC, two new kinds of *n*-octene(z) [2-octene(z) and 3-octene(z)] were detected in the degradation products from La-OMMT/PVC. At 700 °C, the kinds of cyclic compounds, ethylcyclopentane, and toluene in the degradation products from La-OMMT<sub>-SMDP</sub>/PVC and La-OMMT<sub>-SDS</sub>/PVC remained identical to those from PVC. The ethylcyclopentane cyclic compounds even disappeared in the degradation products from La-OMMT<sub>-SDD</sub>/PVC. At 550 °C, except for La-OMMT<sub>-SDS</sub>/PVC, no cyclic compounds existed in La-OMMT<sub>-SMDP</sub>/PVC and La-OMMT<sub>-SDD</sub>/PVC. However, toluene and 1,3-xylene were detected in the thermal degradation products of OMMT<sub>-I,44P</sub>/PVC at 550 °C. Combined with the results of combustion behavior, the incorporation of La-OMMTs might have hindered the structural transformation from *n*-octene(z) to cyclic compounds. The La-OMMTs also

increased the temperature of the cyclization reaction during the process of secondary thermal degradation.

Among the three kinds of La-OMMTs, La-OMMT<sub>-SMDP</sub> exhibited the most excellent flame retardancy and smoke-suppression performances; this might have been caused by its lowest absolute content of cyclic compounds (all of the data in GC–MS results indicate relative contents). The mechanism (e.g., of La-OMMT<sub>-SMDP</sub>) could be explained by a four-center transition-state theory.<sup>17</sup> The La-OMMTs replaced the allylic chlorine in the PVC chain with an anionic surfactant through a four-center transition state. According to steric hindrance theory, an anionic surfactant with a long-train structure will hinder the *n*-octene(z) structural attack of linear *cis*-polyenes to form a cyclic compound structure. The relevant mechanism is presented in Scheme 1.



**Scheme 1.** Reaction mechanism of La-OMMTs with the replacement of allylic chlorine with an anionic surfactant.



**Figure 4.** SEM surface morphological images for the residual degradation products: (A) pure PVC, (B) OMMT-I<sub>44P</sub>/PVC, (C) La-OMMT-SMDP/PVC, (D) La-OMMT-SDS/PVC, and (E) La-OMMT-SDD/PVC.

### SEM Analysis

The SEM surface morphological images of the PVC and its nanocomposites after pyrolysis are shown in Figure 4. The surface of PVC and OMMT-I<sub>44P</sub>/PVC exhibited similar holes in the char residue. By contrast, La-OMMT/PVC showed an intact residual surface. Liu *et al.*<sup>25</sup> found that the well-dispersed nanocomposites were favorable for the formation of continuous char layer after pyrolysis. The char residue acted as the barrier to energy and smoke transport. Therefore, the integrated char residual surface was beneficial for obtaining better PHRR and ASEA. The relevant results agree with the results of combustion behavior.

### CONCLUSIONS

The effects of the three kinds of La-OMMTs on the mechanical properties, flame retardancy, and smoke suppression of PVC were investigated. The XRD characterization proved that the La-OMMTs were dramatically exfoliated; this indicated that the La-OMMT/PVC nanocomposites were prepared successfully. During the melt-intercalation processing, the accelerated dehydrochlorination reaction was increased by the incorporation of OMMT-I<sub>44P</sub>; this reduced the thermal stability of PVC. Consequently, the OMMT-I<sub>44P</sub>/PVC showed weak mechanical properties. On the contrary, the La-OMMT/PVC nanocomposites exhibited outstanding mechanical properties. The flame retardancy and smoke suppression of PVC were investigated through cone calorimetry. The lower values of PHRR and ASEA of La-OMMT/PVC proved that the La-OMMTs had excellent effects on PVC in terms of flame retardancy and smoke suppression. GC-MS analysis showed that La-OMMTs inhibited the cyclization reaction and increased the cyclization reaction temperature.

This could be explained by the four-center transition-state mechanism. The intact char of La-OMMT/PVC also caused the enhancement of flame retardancy and smoke suppression. In conclusion, the La-OMMT/PVC nanocomposites had showed mechanical properties, thermal stability, flame retardancy, and smoke suppression simultaneously. Thus, these nanocomposites should have significant practical potential for building materials fields.

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