

# Preparation and Properties of Chlorosulfonated Polyethylene/Organomontmorillonite Nanocomposites

Zheng Gu,<sup>1,2</sup> Guojun Song,<sup>2</sup> Weisheng Liu,<sup>1</sup> Jianming Gao,<sup>2,3</sup> Wei Dou,<sup>1</sup> Ping Lu<sup>2</sup>

<sup>1</sup>Department of Chemistry and State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

<sup>2</sup>Institute of Polymer Materials, Qingdao University, Qingdao 266071, China

<sup>3</sup>Qingdao TKS Sealing Industry Company, Qingdao 266071, China

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**ABSTRACT:** Chlorosulfonated polyethylene (CSPE)/organomontmorillonite (OMMT) nanocomposites were prepared by a melt intercalation method. The microstructure of the nanocomposites was characterized by transmission electron microscopy and X-ray diffraction. The effects of the OMMT content on the mechanical properties and swelling behavior of the nanocomposites were investigated. The improvement in the thermal stability of the nanocomposites was determined by thermogravimetric analysis. Transmission electron microscopy and X-ray diffraction showed that CSPE was

intercalated into OMMT. When the OMMT content was lower than 12 wt %, the nanocomposites showed excellent tensile properties, which was attributed to nanometer-scale dispersion. The introduction of a small amount of OMMT also improved the thermal stability and swelling behavior, which was attributed to the gas barrier action of the OMMT layers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3365–3368, 2010

**Key words:** mechanical properties; nanocomposites; organoclay; swelling

## INTRODUCTION

Since the Toyota Co. invented layered silicate/polyamide nanocomposites,<sup>1,2</sup> clay mineral/polymer nanocomposites have greatly attracted the interest of researchers around the world in both industry and science. Compared to microcomposites or macrocomposites, this kind of nanocomposite exhibits excellent properties because of the fine particle dimensions and special structure.<sup>3</sup> In general, this kind of nanocomposite has superior mechanical properties, thermal stability, flame retardancy, and gas barrier properties.<sup>4–6</sup>

Polymer/clay nanocomposites can be prepared by many methods, such as *in situ* melt interaction, polymerization interaction, solution interaction, coagulation of rubber latex, and from aqueous clay dispersions.<sup>7</sup> Melt intercalation is considered a promising method of fabricating clay/polymer nanocomposites because of the use of existing processing equipment and reduced environmental pollution.<sup>8</sup>

Chlorosulfonated polyethylene (CSPE) is obtained via the simultaneous chlorination and chlorosulfonation of polyethylene. It is a polymer that consists of a modified polyethylene backbone with chloro and sulfonyl chloride side groups. Crosslinking can be

achieved with different curing methods (e.g., sulfur, peroxides, maleimide, and others) to produce a commercial generic Hypalon rubber.<sup>9</sup> CSPE is an important and widely used rubber. CSPE is commonly used as a sheath material in electrical cables that are used in nuclear power facilities. CSPE is also used in auto supplies, life-saving equipment, building materials, and so on. In this study, CSPE/organomontmorillonite (OMMT) nanocomposites were prepared by the melt intercalation method first. The structure and properties of the nanocomposites were then investigated.

## EXPERIMENTAL

### Materials

Bentonite was obtained from a clay mine in the Shandong Province of China. The sodium montmorillonite (Na-MMT) of the bentonite had a cation-exchange capacity of 119 mequiv/100 g. The dimethyl ditallow ammonium modified montmorillonite (OMMT) was produced by the Institute of Polymer Materials at Qingdao University, China. CSPE, Carom CSM type (Romania), contained 33.6 wt % chlorine, 1.3 wt % sulfur, and 1.4% molar unsaturation. The other materials were commercial products.

### Preparation of the CSPE/OMMT nanocomposites

CSPE/OMMT nanocomposites were prepared in an open two-roll mill (SK-160B, Shanghai Light Industry Machinery Co., Ltd.) at room temperature.

Correspondence to: W. Liu (liuws@lzu.edu.cn).

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OMMT was mixed with the elastomer. Then, the vulcanization agents were added. The amounts of OMMT added to CSPE were 0, 3, 6, 9, 12, and 15 wt % rubber. The recipe for the CSPE/OMMT compounds was 100-phr CSPE, 10-phr MgO, 1-phr SA (stearic acid), 2-phr DTTT (dipentamethylenethiuram tetrasulfide), and 1-phr (dibenzothiazole disulfide) DM. The specimens were cured at 175°C in an electrically heated hydraulic press (QLB-350 × 350 × 2, Shanghai Rubber Machinery Factory, China) for 10 min.

### Characterization of the CSPE/OMMT nanocomposites

The dispersion of OMMT in the rubber was studied by transmission electron microscopy (TEM) and X-ray diffraction (XRD). TEM observation was performed on ultrathin films prepared by cryoultramicrotomy with a JEM-1200EX (JEOL, Japan) at an acceleration voltage of 200 kV. XRD analysis was performed with a Rigaku D/max 2500 VB2+ /Pc. An acceleration voltage of 40 kV and 200 mA was applied with Cu K $\alpha$  radiation.

Tensile and tear tests were done on a DXLL-50000 (Diers Co., China) universal testing machine at a crosshead speed of 500 mm/min. Measurements of the mechanical properties of all of specimens were conducted at 25 ± 2°C according to relevant ISO standards (ISO 37 and ISO 7619).

Samples with dimensions of 20 × 10 × 2 mm<sup>3</sup> were used to determine the swelling behavior of the vulcanized rubber according to ISO1817-198. The initial weight of the samples was taken, and then, they were put into solvent. The samples were periodically removed from the test bottles, the adhering solvent was cleaned from the surface, and the samples were weighed immediately and then placed into ASTM oil no. 1 and ASTM oil no. 3 again. The weight-swelling ratio ( $Q_t$ ) was also determined from the weight of the sample in the unswollen and swollen states:

$$Q_t = [(M_t - M_0)/M_0] \times 100\% \quad (1)$$

where  $M_t$  is the weight of the sample in the swollen state and  $M_0$  is the initial weight of the sample.

Thermogravimetric analysis (TGA) of the samples was performed with a thermogravimetric analyzer (TGA/STDA851, Mettler-Toledo, Shanghai, China) attached to an automatic programmer from ambient temperature to 700°C at a heating rate of 10°C/min in an air atmosphere. A sample weight of approximately 15 mg was used for the measurement.

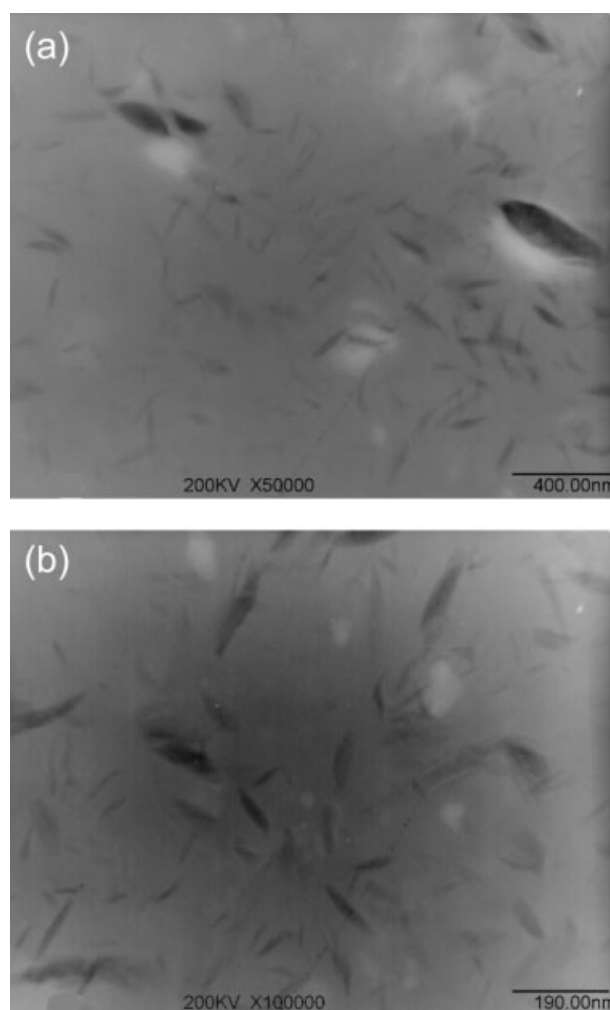
## RESULTS AND DISCUSSION

### Structure of the CSPE/OMMT nanocomposites

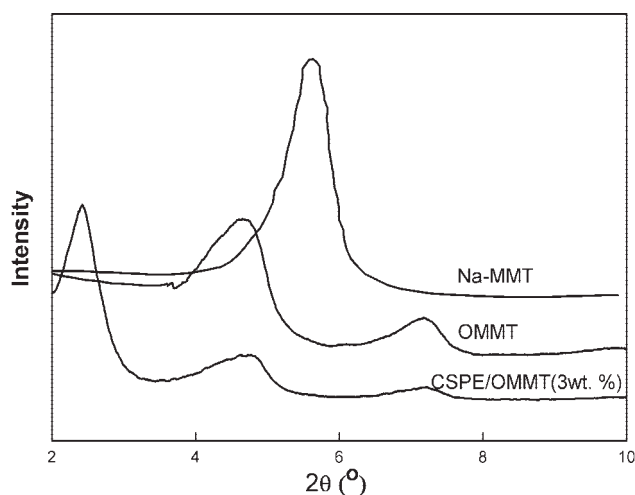
Observation of TEM and XRD were used to observe the type of the prepared nanocomposites. TEM

images were screened at high and low magnifications to observe the dispersion state of OMMT in the matrix. TEM photographs of the CSPE/OMMT nanocomposites are shown in Figure 1. The light color areas are the CSPE matrix, and the dark lines and areas are the OMMT layers and their aggregates. The TEM photographs show that the OMMT layers were homogeneously dispersed in the CSPE matrix. The intercalated and partially exfoliated layers coexisted in the CSPE/OMMT nanocomposites. The thickness of most clay layers was in the range 20–40 nm, and the length was about 100–300 nm. This result shows that intercalated nanocomposites formed.

XRD spectra of Na-MMT, OMMT, and the CSPE/OMMT nanocomposites (3 wt %) are presented in Figure 2. It is well known that if the intercalation of rubber macromolecules into the OMMT layers occurs, the XRD peak will shift to a smaller angle for the intercalated nanocomposites, and if the layers are exfoliated completely, there will be no diffraction



**Figure 1** TEM photographs of CSPE/OMMT nanocomposites with 3 wt % OMMT.



**Figure 2** XRD spectra of Na-MMT, OMMT, and CSPE/OMMT nanocomposite (3 wt %).

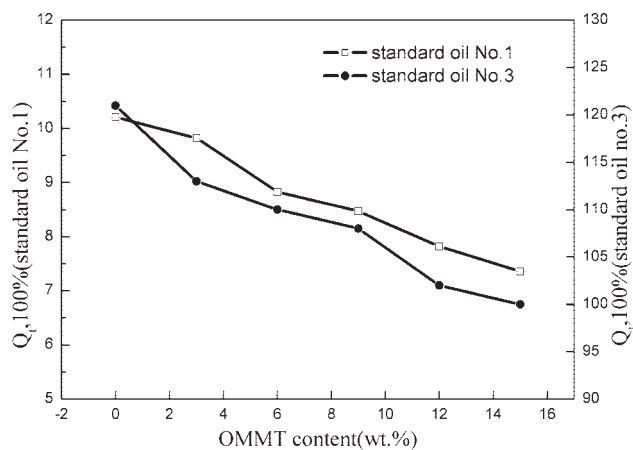
peaks observed because of the disorder of sheets or the larger space of the layers beyond the XRD resolution.<sup>3</sup> Figure 2 shows that the basal spacing of the Na-MMT was 1.58 nm. The OMMT pattern revealed a broad intense peak around  $2\theta = 4.60^\circ$ , which corresponded to a basal spacing ( $d_{001}$ ) of 1.92 nm, whereas the CSPE/OMMT patterns showed that the  $d_{001}$  reflection of the clay shifted to lower angles around  $2\theta = 2.41^\circ$ , which corresponded to a spacing of 3.67 nm, which indicated that the CSPE chains were intercalated into the OMMT. The TEM and XRD results demonstrate the intercalated structure.

### Mechanical properties of the CSPE/OMMT nanocomposites

The mechanical properties of the CSPE/OMMT nanocomposites are shown in Table I. The addition of OMMT effectively improved the mechanical properties of CSPE. When the OMMT content was lower than 9 wt %, the modulus, tensile strength, and elongation at break of the nanocomposites increased with the OMMT content. Compared to pure CSPE, the modulus at 300% and tensile strength of the nanocomposites with 9 wt % OMMT increased by 119 and

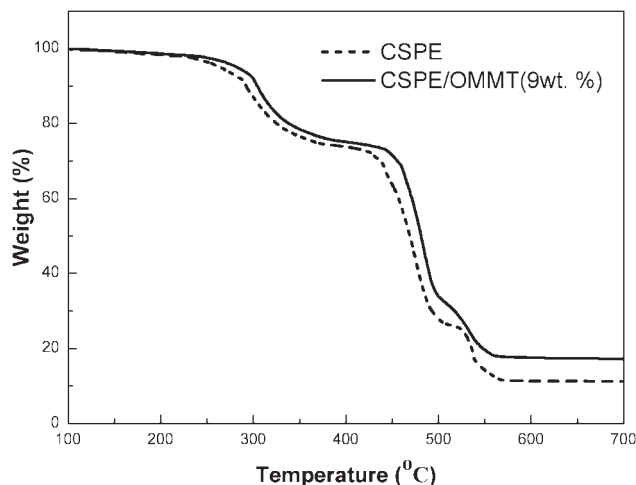
**TABLE I**  
Effect of the OMMT Content on the Mechanical Properties of the CSPE/OMMT Nanocomposites

OMMT content (phr)	Modulus at 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN/m)
0	2.71	22.82	602	55.31
3	4.83	33.73	612	44.82
6	5.21	35.63	633	50.22
9	5.96	38.91	648	43.36
12	7.03	36.92	668	45.07
15	10.55	33.25	680	41.51

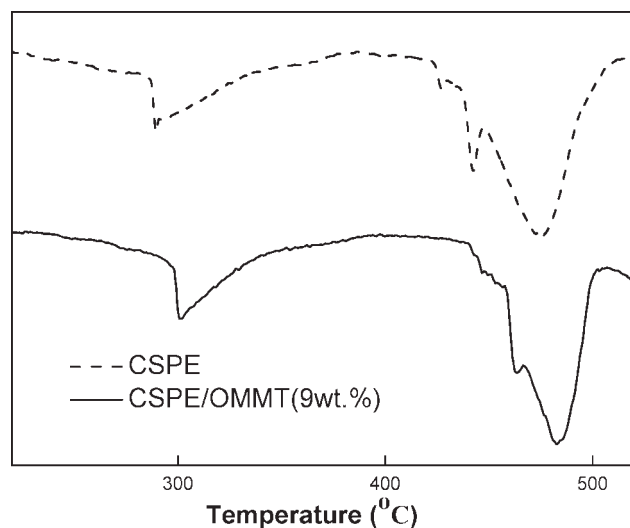


**Figure 3** Swelling behavior of CSPE/OMMT nanocomposites at 150°C for 70 h  $Q_t$  weight-swelling ratio.

71%. The improved mechanical properties were mainly attributed to strong interactions between the nanodispersed OMMT layers and CSPE chains with large contact surfaces.<sup>10</sup> The OMMT layers interacted with the rubber chains to form a network, in which the clay layers acted as physical crosslinking junctions. When the OMMT content increased, the strong interactions between the OMMT and CSPE chains limited the motion of rubber chains so that the modulus and tensile strength increased. When the OMMT content exceeded 9 wt %, the tensile strength decreased because fewer chains intercalated into the OMMT layers, which reduced the crosslinking junctions between the OMMT layers and CSPE chains. It was interesting to observe that the tear strength of the nanocomposites decreased with the addition of OMMT layers. This is a question that needs be resolved by researchers. We think this may have been due to the decrease in crosslinking density.



**Figure 4** TGA thermograms of CSPE/OMMT nanocomposites.



**Figure 5** DTA curves of CSPE/OMMT nanocomposites.

### Swelling behavior of the CSPE/OMMT nanocomposites

The relative swelling behavior of the nanocomposites with various OMMT contents is depicted in Figure 3. It showed that the solvent absorption decreased when the OMMT content increased. The introduction of OMMT led to an obvious decrease in the swelling ratio. The swelling ratio decreased from 0.10 for pure CSPE to 0.08 for CSPE/OMMT (9 wt %) in standard oil no. 1 and from 1.21 for pure CSPE to 1.08 for CSPE/OMMT (9 wt %) in standard oil no. 3. The obvious decrease compared to pure CSPE was due to the good dispersion of OMMT and the strong interactions between OMMT and CSPE chains. The presence of nanodispersed impermeable clay layers with excellent barrier properties decreased the rate of transportation by lengthening the average diffusion path length in the CSPE matrix.<sup>11,12</sup>

### Thermal stability of the CSPE/OMMT nanocomposites

Figure 4 shows the TGA curves of the pure CSPE and CSPE/OMMT nanocomposite with 9 wt % OMMT content. Figure 5 shows the differential thermal analysis (DTA) curves of CSPE and the CSPE/OMMT nanocomposites, which show the maximum decomposition of the composites. The thermal stability of the CSPE/OMMT nanocomposites was better than that of pure CSPE. Figures 4 and 5 show that the onset temperature and the maximum decomposi-

tion temperature were higher than those of pure CSPE and the maximum decomposition temperature increased from 475.3°C (pure CSPE) to 483.4°C (CSPE with 9 wt % OMMT). The results demonstrate that the degradation of the nanocomposites took place at higher temperatures than that of pure CSPE in the presence of OMMT layers, which indicated improved thermal stability. This could have been due to the presence of well-dispersed OMMT layers with good gas barrier properties, which hindered the evaporation of small molecules generated during thermal decomposition and limited the emission of the produced gases or heat.

## CONCLUSIONS

CSPE/OMMT nanocomposites were prepared by melt intercalation. The TEM and XRD analysis indicated the CSPE chains were intercalated into the OMMT layers. OMMT was well-dispersed in the CSPE matrix. The mechanical testing results showed that the tensile strength and modulus at 300% of the nanocomposites containing 9 wt % OMMT were 38.91 and 5.96 MPa, respectively; these were increases of 71 and 119% compared to pure CSPE. This showed the wonderful reinforcement effect of OMMT. The swelling behavior and TGA testing indicated that the oil resistance and thermal stability of the nanocomposites were greatly improved because of the excellent barrier properties of the OMMT layers.

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