

Synthesis and Properties of Silicone Rubber/Organomontmorillonite Hybrid Nanocomposites

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Received 10 October 1997; accepted 22 January 1998

ABSTRACT: In this article, silicone rubber/organomontmorillonite hybrid nanocomposites were prepared via a melt-intercalation process. The resulting hybrid nanocomposites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). The results proved that the organomontmorillonite could be exfoliated into ca. 50-nm thickness and uniformly dispersed in the silicone rubber matrix during the melt-intercalation process. Furthermore, the mechanical properties and thermal stability of the hybrids were very close to those of aerosilica-filled silicone rubber. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1557–1561, 1998

Key words: silicone rubber; organomontmorillonite; hybrid nanocomposite

INTRODUCTION

Nanocomposites are a relatively new kind of materials which exhibit ultrafine phase dimensions, typically in the range of 1–100 nm. Because of the nanometer-size effect, nanocomposites have unique properties not shared by their conventional microcomposite counterparts. In most cases, the synthesis of polymer/clay hybrid nanocomposites was reported via either an intercalation polymerization process or a melt intercalation process.^{1–6} The melt intercalation compounding process is one of promising new approaches of synthesizing polymer/clay nanocomposites by using organosilicate and the conventional twin-screw extrusion compounding process. This process does not need any solvent. So, it is easy to be applied in industry. Layered mica-type silicates such as vermiculite, smectite, and montmorillonite are suitable fillers for this process.⁷

The layer structure of montmorillonite (MMT) consists of two silica tetrahedral sheets to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Stacking of the layers of ca. 1-nm thickness by a weak dipolar force leads to interlayers or galleries between the layers. The galleries are normally occupied by cations such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and Cs^+ , by which is easy to form the organosilicate by an alkylammonium ion-exchange reaction. The organosilicates can be broken down into their nanoscale building blocks and uniformly dispersed in the polymer matrix to form exfoliated nanocomposites during the melting-compounding process.

Silicone rubber is one of the most important types of high-temperature-resistance 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, most silicone rubber is reinforced by aerosilica, which is more expensive than are other fillers. Aerosilica, with a very small particle size (5–20 nm), is easy to aggregate and is difficult to disperse in the rubber matrix. Aerosilica particles

Correspondence to: Z. Qi.

Contract grant sponsor: National Natural Science Foundation of China.

Journal of Applied Polymer Science, Vol. 69, 1557–1561 (1998)

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CCC 0021-8995/98/081557-05

are liable to be inhaled into the human body and do harm to the worker's health, for example, causing "silicosis."⁸

Burnside and Giannelis reported on polydimethylsiloxane/organo-MMT nanocomposites using melt intercalation.⁹ In their report, the organosilicate was prepared by ion exchanging Na^+ -MMT with dimethyl ditallow ammonium bromide and the hybrids were prepared by a sonicating method. Furthermore, no mechanical properties or structures of the nanocomposites have been reported so far. In the present article, the organosilicate was prepared by ion exchanging Na^+ -MMT with hexadecyltrimethylammonium bromide and the silicone rubber/organo-MMT hybrids were simply prepared by a mechanical mixing method. We here first report the nanometer structure features and the mechanical properties of silicone rubber/organo-MMT hybrid nanocomposites. The results indicate that silicone rubber/organo-MMT nanocomposites have a potential for industry.

EXPERIMENTAL

Materials

Na^+ -MMT with a cation-exchange capacity of 100 mequiv/100 g and a nominal particle size of 40 μm was obtained from Institute of Chemical Metallurgy, Chinese Academy of Sciences (China). Hydroxyl-terminated polydimethylsiloxane (PDMS) with a number-average molecular weight of 68,000, room-temperature vulcanized silicone rubber, was produced by the Beijing No. 2 Chemical Factory (Beijing, China). Aerosilica, #2 (SiO_2), tetraethyl orthosilicate [$\text{Si}(\text{OEt})_4$], and dibutyltin dilaurate $\{\text{Bu}_2[\text{Sn}(\text{OCOC}_{11}\text{H}_{23})_2]\}$ were industry products, chemical pure grade.

Synthesis

Preparation of Organo-MMT

Na^+ -MMT was dissolved in distilled water with concentration of about 5 wt % and excess hexadecyltrimethylammonium bromide was added. The mixed solution was stirred for 1 h at 80°C, filtered at room temperature, and then repeatedly washed with distilled water to a very low concentration of Br^- where no white precipitate was observed in the filtrate when tested by a 0.1N AgNO_3 solution. The product obtained was then vacuum-dried to a constant weight at ambient temperature and grinded into powder (organo-MMT).

Synthesis of Silicone Rubber/Organo-MMT Composite

A given weight of organo-MMT was dispersed in 20 g of PDMS. If necessary, organo-MMT was scattered into a small amount of chloroform before dispersing in PDMS. The mixture was heated for 8 h at 90°C, then cooled to room temperature and 0.25 g of tetraethyl orthosilicate and 0.06 g of dibutyltin dilaurate added. The resulting sample was deaerated and slowly cast into Teflon molds and cured at room temperature for 12 h.

Synthesis of Aerosilica-filled Silicone Rubber

Aerosilica of a given weight was dispersed in 20 g of PDMS. The mixture was added to 0.25 g of tetraethyl orthosilicate and 0.06 g of dibutyltin dilaurate. The resulting sample was deaerated and slowly cast into Teflon molds and cured at room temperature for 12 h as a counterpart for comparison.

Measurements

X-ray Diffraction (XRD)

To measure the change of gallery distance of organo-MMT before and after intercalation, X-ray diffraction data between 1.3° and 40° were collected at 2°/min on a Japan D/max-RB 12 kW diffractometer using $\text{CuK}\alpha$ radiation at a generator voltage of 40 kV and a generator current of 100 mA. Samples were pellets with a smooth surface and a dimension of 1 × 1 × 0.1 cm.

Transmission Electron Microscopy (TEM)

Samples of TEM were embedded in a capsule with an embedding agent polymerized at 60°C for 48 h. The embedded sample was ultrathin-sectioned using a microtome equipped with a diamond knife in a liquid nitrogen trap. The thin sections were 60–100 nm thick. Transmission electron micrographs were obtained with a JEOL-100CX using an acceleration voltage of 100 kV.

Mechanical Testing

According to China Industry Standard GB 528-76, the samples were manufactured as standard dumbbell pieces (a type of GB 528-76) and measured on an Instron 1122 type tensile machine with an extension rate 200 mm/min at room temperature.

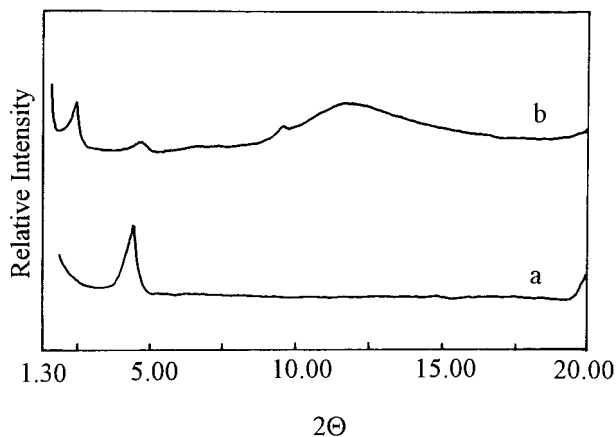


Figure 1 XRD patterns of organo-MMT and silicone rubber/organo-MMT composite with weight ratio of 100 : 10: (a) organo-MMT; (b) silicone rubber/organo-MMT hybrid.

Thermogravimetric Analysis (TGA)

TGA scans from room temperature to 1000°C were obtained on a Perkin–Elmer 7 Series thermal analysis system at a scan rate of 20°C/min in a N₂ atmosphere.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of organo-MMT and silicone rubber/organo-MMT composites (weight ratio of silicone rubber to organo-MMT was 100 : 10) are shown in Figure 1. The XRD pattern of organo-MMT contained a peak at $2\theta = 4.38^\circ$, while a strong peak at $2\theta = 2.38^\circ$ was observed in the XRD pattern of the silicone rubber/organo-MMT composite, which were basal reflections from the silicate layers. The gallery distance can be calculated according to Bragg equation to be 20.2 Å for organo-MMT and 37.1 Å for the composite, indicating that PDMS molecules could be intercalated into the galleries of organo-MMT. The strong diffraction peak at $2\theta = 2.38^\circ$ also suggested that the ordered organosilicate structure of clay was still present in the hybrids, although the gallery distance was enlarged due to polymer chains intercalation, which is different from the XRD featureless patterns in the range 3–9° of Burnside and Giannelis' report and the results about the delaminated hybrids' presence.⁹

For hybrid composites, the layer expansion associated with PDMS intercalation resulted in the appearance of a new basal reflection corresponding to the larger gallery height. Although XRD

allowed for precise measurements of the silicate layer spacing, little could be said about the real spatial position of the layers or any change of structure in the composites. The featureless patterns cannot suggest the presence of delaminated hybrids. Furthermore, it was more difficult when the peak was broadened or the intensity was decreased. So, TEM analysis was added to examine the microstructure of the hybrids. TEM could provide information in real space, in a local area on the spatial distribution of the silicate layers, of the changes of the structure in the hybrids. Figure 2 shows TEM images of an ultrathin section of the PDMS composite with 20 wt % of organo-MMT. Since the silicate layers are composed of heavier elements (Al, Si, O) than are the interlayer and surrounding matrix (C, H, N), they appear darker in the bright-field images. From Figure 2(a), organo-MMT particles were clearly observed, having been exfoliated into nanoscale layers with about 50-nm thickness from their original 40- μm particle size and, furthermore,

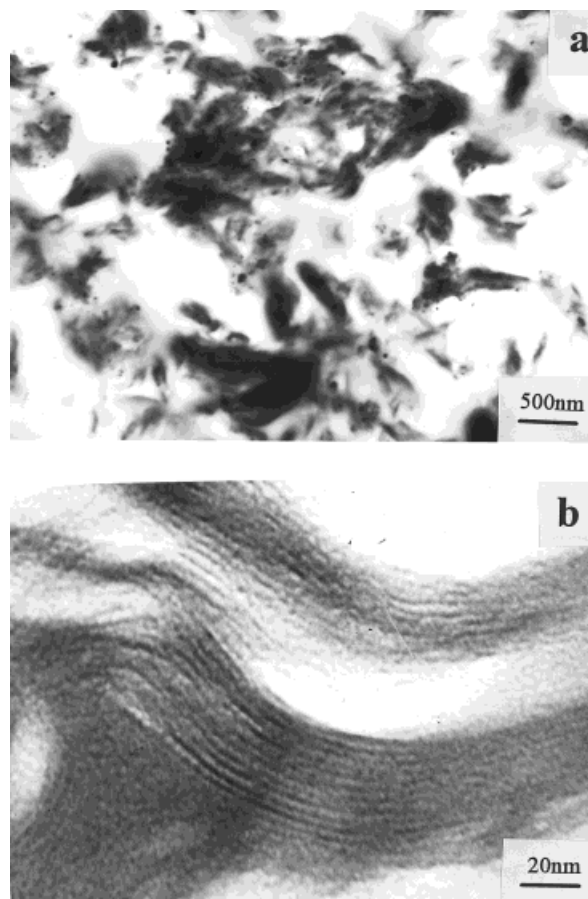


Figure 2 TEM images of PDMS/organo-MMT hybrid composite with weight ratio of 100 : 20.

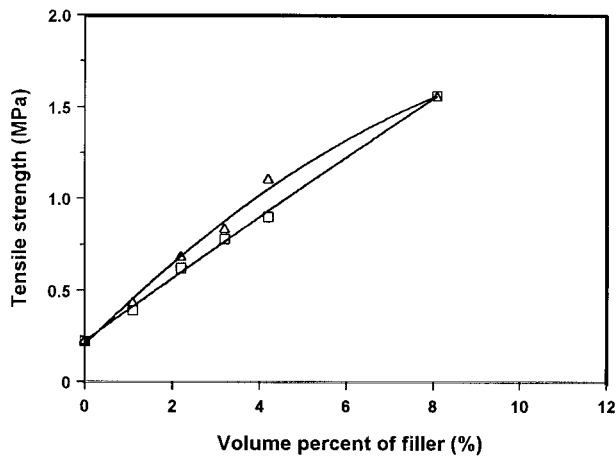


Figure 3 Tensile strength of composites versus volume content of filler: (□) silicone rubber/organo-MMT hybrid; (△) silicone rubber/aerosilica.

these layers were dispersed in silicone rubber matrix uniformly. In Figure 2(b), the scattering contrast in the bright-field mode led to "lattice fringes," corresponding to a periodic stacking sequence of the silicate layers; the layers were separated by galleries and layer spacings corresponded to a 3.6-nm basal repeat distance. The larger repeat distance arose from increases in the gallery height due to PDMS chain intercalation.

From the results above, it was concluded that organo-MMT particles were uniformly dispersed in the rubber matrix and the PDMS chains were intercalated in the galleries of organo-MMT. Intercalation of polymer molecules will offer the hybrids outstanding properties. The tensile strength and elongation at break of the composites and aerosilica-filled silicone rubber are shown in Figures 3 and 4, respectively. With increasing organo-MMT content, the silicone rubber/organo-MMT composite showed a substantial improvement in tensile strength compared to the unfilled silicone rubber. When the content of the organo-MMT was 10 and 20 wt %, the tensile strength of the composite was 0.9 and 1.5 MPa, respectively. With the same contents of tetraethyl orthosilicate and dibutyltin dilaurate, commercial silicone rubber-filled 10 wt % aerosilica exhibited a tensile strength of 1.1 MPa, and silicone rubber-filled 20 wt % #2 aerosilica in this report showed a tensile strength of 1.5 MPa. The traces in Figure 4 illustrated that the above composite and aerosilica-filled silicone rubber exhibited an elongation of about 200%. It was concluded that the mechanical properties of the silicone rubber/organo-MMT

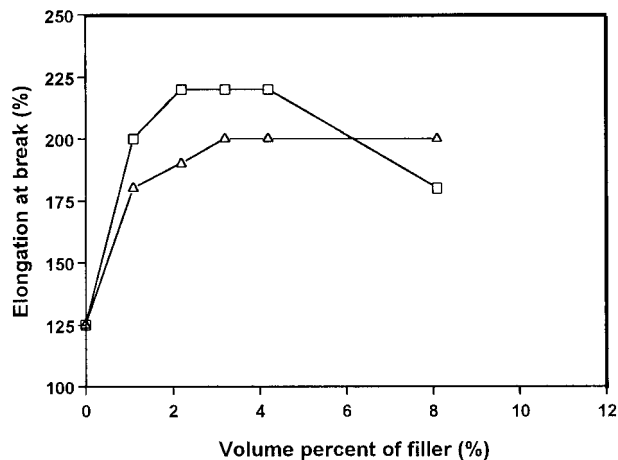


Figure 4 Elongation at break of composites versus volume content of filler: (□) silicone rubber/organo-MMT hybrid; (△) silicone rubber/aerosilica.

composites were close to those of aerosilica-filled silicone rubber.

Silicone rubber shows much better thermal stability than that of other synthetic rubbers. But with polar Si—O bonds and the helical structure of the flexible main chain, silicone rubber decomposes into volatile cyclic silicates above 300°C due to a residual catalyst or water.¹⁰ Figure 5 shows the TGA traces of unfilled silicone rubber and filled silicone rubber with 8.1 vol % of filler (organo-MMT or aerosilica). Decomposition temperatures of the filled silicone rubber were 433°C for the hybrid and 440°C for the aerosilica-filled silicone rubber, both higher than that of the unfilled silicone rubber (381°C). The reasons for the improvement in decomposition temperatures of

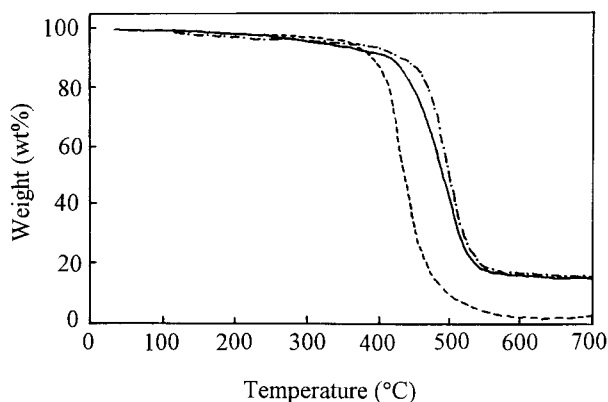


Figure 5 TGA traces for silicone rubber and its composites with 8.1 vol % of filler: (---) silicone rubber without filler; (—) silicone rubber/organo-MMT hybrid; (—●—) silicone rubber/aerosilica.

filled silicone rubber were probably as follows: (1) The active centers of the silicone main chains' decomposition possibly became inactive when they contacted the filler, and (2) the interactions between the filler and silicone rubber increased the physical and chemical crosslinking points which prevented the unbuttoned degrading of the silicone chains.

CONCLUSIONS

1. Organo-MMT particles could be exfoliated into ca. 50-nm thickness and uniformly dispersed in the silicone rubber matrix.
2. PDMS molecules could be intercalated into the galleries of organo-MMT. The interlayer distance of organo-MMT expanded due to the polymer intercalation.
3. Silicone rubber/organo-MMT nanocomposites showed excellent mechanical properties compared with the unfilled silicone rubber, which were very close to those of the aerosilica-filled silicone rubber.
4. The decomposition temperatures of silicone rubber/organo-MMT nanocomposites were

also higher than that of the unfilled silicone rubber.

The financial support of this research by the National Natural Science Foundation of China is gratefully acknowledged.

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