

Synthesis and Structure of Polymethylsilsesquioxane–Clay Nanocomposite via *In Situ* Intercalative Polymerization

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ABSTRACT: Polymethylsilsesquioxane (PMSQ)–montmorillonite (MMT) nanocomposites were prepared by *in situ* intercalative polymerization. The dispersion of the MMT layers within the matrix was verified by X-ray diffraction and transmission electron microscopy, which revealed an intercalated morphology with layer spacing of 3.42 nm. The layer spacing was not increased after annealing at 150°C for 3 h. The reason for this result is explained in light of the molecular structure of PMSQ synthesized in and out of the

nanoconfined environment. The coherent order of the silicate layer was decreased after the annealing, possibly because of the change in the PMSQ molecule during the annealing process. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3708–3711, 2002

Key words: nanocomposites; polymethylsilsesquioxane; intercalative polymerization

INTRODUCTION

In recent years, the synthesis of polymer–inorganic nanocomposites has received considerable attention.^{1–6} One of the promising composite systems would be hybrids based on organic polymers and inorganic clay minerals consisting of layered silicates. Layered materials are potentially well suited for the design of hybrid composites because their lamellar elements have high in-plane strength, stiffness, and a high aspect ratio.⁷ Virtually all families of lamellar element solids share these attributes, but the smectite clays (e.g., montmorillonite) and related layered silicates are the materials of choice for polymer nanocomposite design for two principal reasons. First, they exhibit a very rich intercalation chemistry, which allows them to be chemically modified and made compatible with organic polymers for dispersal on a nanometer length scale. Second, they occur ubiquitously in nature and can be obtained in mineralogically pure form at low cost. The unparalleled ability of smectite clays to boost the mechanical properties of an engineered plastic was first demonstrated in a stunning example by Toyota researchers.^{7–15} Considerable effort has been invested in extending the nanolayer reinforcement concept to polymer systems other than nylon.¹⁶ The term polysilsesquioxanes in this study

refers to all structures with the empirical formulas $(\text{RSiO}_{3/2})_n$, where R is hydrogen or any alkyl, alkylene, or other derivative of organic groups. The use of polymethylsilsesquioxane (PMSQ) is focused on coatings, particularly in electronics and optical devices.^{17,18}

PMSQ–clay nanocomposites remain a completely unexplored field. With the development of aerospace and national defense technology, more rigorous requirements, such as higher heat-resistant properties, are needed in polymers used in these industries.¹⁹ Because nanocomposites can possess combined good electrical, optical, and mechanical properties that may not be achieved with each component separately, PMSQ reinforced by clay is expected to possess highly improved mechanical properties, thermal stability, and barrier properties with low cost, which might find application in heat-resistant coatings. The synthesis of polymer–clay nanocomposites is generally carried out by two methods. The first is *in situ* intercalative polymerization, in which the layered silicate is swollen within the liquid monomer (or a monomer solution) so the polymer formation can occur in between the intercalated sheets. The second is melt intercalation, in which the layered silicate is mixed with the polymer matrix in the molten state. The structure of PMSQ was reported as a ladder-like structure with some branches.^{20,21} Therefore, because of this significant steric hindrance, it is rather difficult to prepare PMSQ–clay by the second method.

In this study, a PMSQ–clay nanocomposite was prepared by *in situ* polymerization, and changes of struc-

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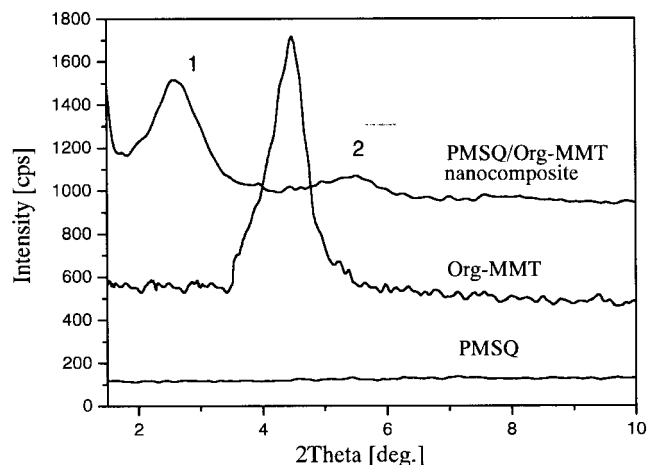


Figure 1 XRD patterns of PMSQ, Org-MMT, and PMSQ-Org-MMT nanocomposites.

ture before and after annealing were studied by X-ray diffraction (XRD).

EXPERIMENTAL

Materials

Methyltrimethoxysilane was provided by Shin-Etsu Chemical Corporation Limited of Japan.

PMSQ samples were prepared by the polycondensation of the hydrolyzates of methyltrimethoxysilane. A detailed description of the preparation methods can be found elsewhere.²²

Preparation of org-MMT

First, Na^+ -montmorillonite (MMT) was dissolved in distilled water at a concentration of ~ 5 wt % and hexadecyltrimethylammonium bromide was added in excess. 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 with a 0.1 N AgNO_3 solution). The organically modified MMT (Org-MMT) obtained was then vacuum dried to a constant weight at ambient temperature and ground into a powder.

Preparation of PMSQ-org-MMT nanocomposite

First, 10 mL of 0.1 M H_3PO_4 solution, 30 mL of methanol, and 30 mL of chloroform were mixed in a three-necked reactor. Then, 3 g of Org-MMT was immersed in 30 g of chloroform for 10 h. Next, 30 g of methyltrimethoxysilane was added into the solution, which was then sonicated with an ultrasonic generator for ~ 30 min. The mixture, while being vigorously stirred, was then dropped into the reactor at room temperature. At the completion of the reaction, the solution was washed several times with deionized water until no H^+ could be detected. The product was then vacuum dried to a constant weight at $50 \pm 1^\circ\text{C}$ for 10 h.

Characterization

X-ray diffraction spectra (XRD) were collected on a D/max-2400 diffractometer using $\text{CuK}\alpha$ radiation and operating at 40 KB and 40 MA.

Microscopic investigations were performed with a transmission electron microscope (TEM; H-800 TEM) at 120 kV. Extra precautions were taken to minimize sample motion and beam damage of the PMSQ and silicate. The TEM grids were mounted in a liquid-nitrogen-cooled sample holder and the brightness of the electron beam was minimized (low-dose mode). Even with these precautions, the contrast of an area under investigation began to fade after a few minutes of beam exposure. This fading is attributed to destruction of the structure of the silicate layers and possible degradation of PMSQ and interlayer organics by the electron beam. All images were taken before contrast loss was visibly noticeable.

RESULTS AND DISCUSSION

Because of the lamellar structure of the ordered intercalate, XRD is a powerful technique to monitor the formation and structure of these hybrids. Structures of Org-MMT and PMSQ-Org-MMT nanocomposite were characterized by XRD and the results are plotted in Figure 1. The corresponding layer spacing of Org-MMT computed by Bragg's law are listed in Table 1. The XRD pattern of PMSQ, which is plotted as a reference in Figure 1, shows no diffraction peak, signifying that PMSQ made no contribution to the dif-

TABLE I
XRD Data of Org-MMT and PMSQ-Org-MMT Nanocomposites
(standard deviation, 0.002 deg)

Peak	2 θ (deg)	Layer Spacing (nm)	Relative Intensity
Peak of Org-MMT	4.48	1.97	1
Nanocomposite	Peak 1	3.42	0.79
Nanocomposite	Peak 2	~ 1.7	0.21

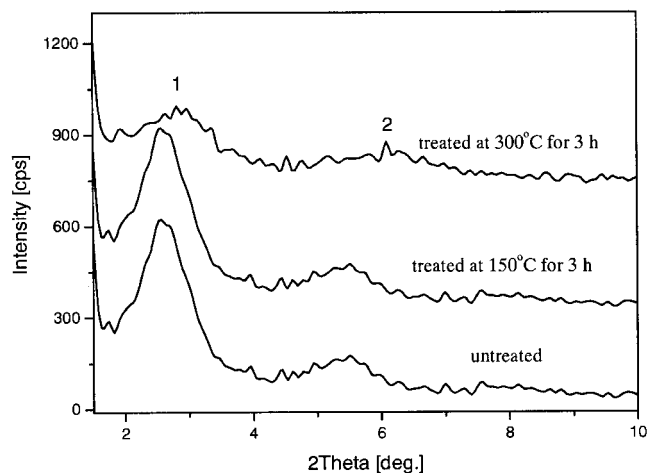


Figure 2 XRD patterns for PMSQ and Org-MMT nanocomposites annealed at different thermal conditions: (a) 0 h, untreated; (b) 3 h, 150°C; (c) 3 h, 300°C.

fraction peak of Org-MMT. A single and large peak at 4.48° was found for Org-MMT, corresponding to an interlayer space of 1.97 nm (shown in Table 1). The XRD pattern of the PMSQ–Org-MMT nanocomposite shows two Bragg reflection peaks. The presence of such peaks in this compound indicates that the nanolayers are largely stacked in crystallographical order in the polymer matrix, but the distance between the nanolayers and the dispersion of the intercalated tactoids with the polymer matrix could be in the range where matrix reinforcement may be expected. The former peak is at 2.58°, corresponding to an interlayer space of 3.42 nm. This increase from 1.97 to 3.42 nm should be due to the intragallery polymerization. The latter peak is around 5.3°, corresponding to a layer spacing of ~ 1.7 nm. These results indicate that layer spacing of some part of Org-MMT was decreased from 1.97 to ~ 1.7 nm, possibly because of the process of methyltrimethoxysilane polymerization. With this process, after dropping the mixture of monomer and Org-MMT, solvent and water molecules would move into the space between the nanolayers and the monomer either polymerized and stayed in the space or moved and polymerized out of the space. It is well known that layer spacing of MMT and Org-MMT are ~ 1 and 2 nm, respectively, due to the existence of Org-MMT between the nanolayers. When the monomer moves out of the space, some organic molecule might be taken out of the space by the moving. Therefore, the layer spacing of some part of Org-MMT was decreased after polymerization. A similar situation was also encountered by Richard A. Vaia when preparing polymer/clay nanocomposite.²

X-ray diffraction patterns for a series of PMSQ–Org-MMT nanocomposites annealed at different temperatures are shown in Figure 2. It could be noted that there is no obvious change of the layer spacing of the

nanocomposite before and after annealing at 150°C. This result is in contrast to research results reported in the literature.^{23, 25} In those cases, polymer–clay nanocomposites, such as PS–clay, were synthesized via static polymer melt intercalation and the layer spacing was increased in the process of annealing. The discrepancy could be explained in light of molecular structure. The dynamics of the linear macromolecule of PS was increased by annealing, which is helpful for the molecule to reach the crystallite edge of Org-MMT and intercalate the gallery from the edge of the crystallites. The molecular structure of polysilsesquoxanes, such as polyphenylsilsesquioxane, was reported as a ladder-like structure with branches.^{20, 21} In this study, polymerization of a trifunctional monomer was conducted in a nanoconfined environment (layer space, several nanometer high) and a sheet-like polymer was formed. On the other hand, when polymerization of monomer was conducted out of the layer space, PMSQ with branches was obtained. When annealing, it is impossible for PMSQ to reach the crystallite edge of Org-MMT and intercalate the gallery from the edge of the crystallites because of the great steric hindrance of PMSQ and the existence of a plate-like polymer in the nanoconfined space. Therefore, the layer spacing was not increased after the annealing at 150°C.

The width of the peaks, B (measured by the full width at half-maximum, fwhm), is inversely proportional to the coherence length of scattering entities and therefore reflects the coherent order of the silicate layers. As the angular width of the reflection increased, the length over which coherency exists decreases. Initially, the breadth of the (001) reflection from sample annealed at 150°C for 3 h is slightly greater than that from the untreated sample, indicating that the coherency of the intercalated silicate layers of annealed nanocomposite is slightly less than that of untreated nanocomposite. As shown in Table 2, the relative intensity of peak 1 of the sample annealed at 150°C for 3 h is also slightly lower than that of untreated sample. This result might be explained by the continued reaction of methoxide group in the nanoconfined environment at $>100^\circ\text{C}$, which has been shown to contribute to the decrease of the coherency.²⁶ As the annealing progresses, the width of the (001) reflection increases significantly, indicating the coherent order of the silicate layered was mostly vanished. The disappearance could be explained as a result of dehydrogenation and evaporation of the low molecular weight components in and out of the nanoconfined environment at 400°C,²⁷ which decreased the coherent order of the silicate layers. In addition, degradation of the alkyl ammonium material also paid a contribution to the loss of coherent order.

In contrast to the global averaging of XRD, conventional TEM can provide information in real space, in a

TABLE II
XRD Data for PMSQ–Org–MMT Nanocomposite Annealed at Different Thermal Conditions
(standard deviation, 0.002 deg)

Peaks of the Nanocomposite		2 θ (deg)	Layer Spacing (nm)	Relative Intensity
Untreated	Peak 1	2.58	3.42	0.79
	Peak 2	~5.3	~1.7	0.21
Annealed at 150°C for 3 h	Peak 1	2.58	3.42	0.77
	Peak 2	~5.3	~1.7	0.23
Annealed at 300°C for 3 h	Peak 1	~2.9	~3.0	0.66
	Peak 2	~6.0	~1.4	0.34

localized area, on morphology and defect structures. The TEM images of PMSQ–Org–MMT nanocomposites are shown in Figure 3. Because the silicate layers are composed of heavier elements (Al, Si, O) than the interlayer and surrounding matrix (C, H, N), they appear darker in bright field images.² The low magnification view in Figure 3a reveals that the Org–MMT is uniformly dispersed into matrix. The dark lines in Figure 3a are the cross-sections of single or possibly multiple silicate platelets. The platelets are flexible and, thus, show some curvature. A higher magnification picture, shown in Figure 3b, reveals that the layer spacing of Org–MMT is ~3–4 nm, which corresponds to XPS pattern analysis.

CONCLUSIONS

A PMSQ–MMT nanocomposite was prepared by *in situ* intercalative polymerization, and the structure was characterized by XRD and TEM. Layer spacing of PMSQ–Org–MMT decreased after annealing, which is in contrast to the results reported for the conventional polymer–clay system. The explanation was proposed in the light of molecular structure of PMSQ synthesized in and out of the nanoconfined environment.

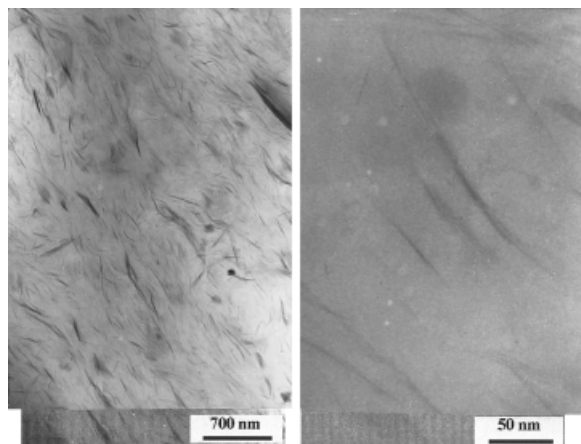


Figure 3 TEM images of PMSQ–MMT nanocomposite.

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