Nanocomposite Structure Depending on the Degree of Surface Treatment of Layered Silicate

DUCK JONG SUH, O OK PARK

Center for Advanced Functional Polymers and Department of Chemical Engineering, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Kusong-dong, Yusong-ku, Taejon 305-701, South Korea

ABSTRACT: Nanocomposite structures depending on the degree of surface modification of montmorillonite (MMT) were studied. To change the degree of surface modification, MMT was treated with a controlled amount of stearylamine. The structures of MMTs and nanocomposites were investigated by X-ray diffraction. To confirm the extent of surface coverage of the stearylamine as a organophilic modifier, TGA and elemental analysis experiments were performed. Different structures (intercalated or exfoliated) of a polymer/clay nanocomposite were obtained according to the interfacial characteristics between the polymer chains and the clay by controlling the degree of surface coverage. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2143–2147, 2002

Key words: clay; nanocomposites; structure; interfaces; surfaces

INTRODUCTION

Layered-silicate-based polymer nanocomposites have become an attractive set of organic–inorganic materials not only for their obvious potential applicability as advanced materials, but also for providing a convenient microscopic system to study fundamental scientific issues concerning confined and tethered polymers. Studying the formation, structure, and dynamics of these nanocomposites can lead to a better understanding of organic–inorganic hybrids, polymers in a confined environment or at a solid surface, and polymer brushes.[1] One promising way to fabricate polymer nanocomposites is by intercalating polymers in layered inorganic hosts. Graphite, transition-metal chalcogenides, metal phosphates, complex oxides, oxychlorides, and mica-type layered silicates are typical examples of layered solids capable of intercalation. The structure and properties of the resulting nanostructure can be conveniently mediated by controlling subtle guest–host interactions.[1,2]

Depending on the degree of penetration of the polymer into the mica-type layered silicate framework, hybrids are obtained with structures ranging from intercalated to exfoliated. Polymer penetration resulting in a finite expansion of the silicate layers produces intercalated hybrids consisting of well-ordered multilayers with alternating polymer/silicate layers and a repeat distance of a few nanometers. Extensive polymer penetration resulting in delamination of the silicate layers produces exfoliated hybrids consisting of individual nanometer-thick silicate layers suspended in the polymer matrix. In contrast, if the polymer and the silicate are immiscible, macrocomposites instead of nanocomposites are formed. These macroscale hybrids consist of agglomerates of the layered silicate surrounded by a polymer and resemble conventional filled rubbers and plastics.[3]

Mica-type layered silicates possess the same structural characteristics as those of the well-

known minerals talc and mica. Their crystal structure consists of two-dimensional layers formed by fusing two silica tetrahedral sheets with an edge-shared octahedral sheet of nominally aluminum or magnesium oxide. Stacking of the layers leads to a van der Waals gap or gallery between the layers. The galleries are normally occupied by cations that balance the charge deficiency that is generated by isomorphous substitution within the layers. Commonly, hydrated alkali metal and an alkali earth cation balance the layer charge, creating a hydrophillic interlayer environment.

Organically modified layered silicates (OLSs) are produced by a cation-exchange reaction between silicate and an alkylammonium salt (surfactant molecule). Because the negative charge originates in the silicate layer, the cationic head group of the alkylammonium molecule will preferentially reside at the layer surface and the aliphatic tail will radiate away from the surface. The presence of these aliphtic chains in the galleries renders the originally hydrophilic silicate organophilic. Whether an admixture of polymer and OLS produces an exfoliated or intercalated or a conventional macrocomposite depends critically upon the intercalation characteristics between the polymer and the OLS. These characteristics depend on the nature of the polymer as well as the type, packing density, and size of the organic modifiers on the silicate surface. Unfortunately, existing guidelines as to the optimum polymer–OLS combination have proven unsatisfactory and, at times, contradictory. Consequently, hybrid synthesis is currently a tedious trial-and-error process.[4] In this study, we report a nanocomposite structure depending on the degree of surface treatment of the layered silicate.

EXPERIMENTAL

Materials and Film Preparation

Poly(9-vinyl carbazole) (PVK) with a molecular weight of 100,000 was obtained from Aldrich (Milwaukee, WI). The Kunimine Co. provided the purified MMT under the trade name Kunipia-F (Tokyo, Japan). This MMT was treated in our lab with stearylamine by known procedures.[5] First, 20 g of MMT was dispersed into 400 mL of water. A controlled amount of stearylamine was dissolved in the mixture of 100 mL of water and 100 mL of ethanol and it was treated with HCl. Then,

Table I   Sample Codes and Amount of Organophilic Surface Modifier

Code	Feed[a]	Data from TGA[a]	Data from Elemental Analysis[a]
MMT50	50	51.0	47.5
MMT75	75	62.7	64.6
MMT100	100	91.7	96.3

[a] Composition unit is mol percent based on the CEC of MMT.

the stearylamine solution became transparent. It was poured into the MMT–water solution with vigorous stirring for 1 h at 70–80°C using a homogenizer. The precipitates were collected through filtering the above mixture and redispersed in the ethanol/water (50/50 vol %) solution for 1 h. Then, the mixture was filtered and freeze-dried to yield an organophilic MMT. The codes and compositions of each sample are summarized in Table I.

PVK with MMT of 1 wt % was dissolved in chlorobenzene for 1 day under stirring with a magnetic bar. Composite films were made by casting onto glass substrates from the PVK/MMT/chlorobenzene solution at a temperature of 30°C and left to dry overnight.

Measurements

X-ray diffraction (XRD) patterns were obtained by using a Rigaku X-ray diffractometer equipped with Cukα radiation and a curved graphite crystal monochromator. Samples were prepared by casting the dissolved mixture in film form onto a slide. All XRD data were collected by an X-ray generator equipment with $\lambda = 1.5406$ Å. Bragg's law, $\lambda = 2d \sin \theta$, was used to compute the crystallographic spacing (d) for the untreated and treated MMT. Measurement of the organophilic modifier loading into the OLS was carried out by thermogravimetric analysis (TGA). A 1–10–mg mass of the OLS sample was heated to 900°C at a heating rate of 30°C/min under an argon atmosphere. Elemental analysis was performed by an EA1110-FISONs elemental analyzer to measure amount of the organophilic modifier in the OLS.

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns for untreated MMT (UTMMT) and PVK/UTMMT. The peaks of the
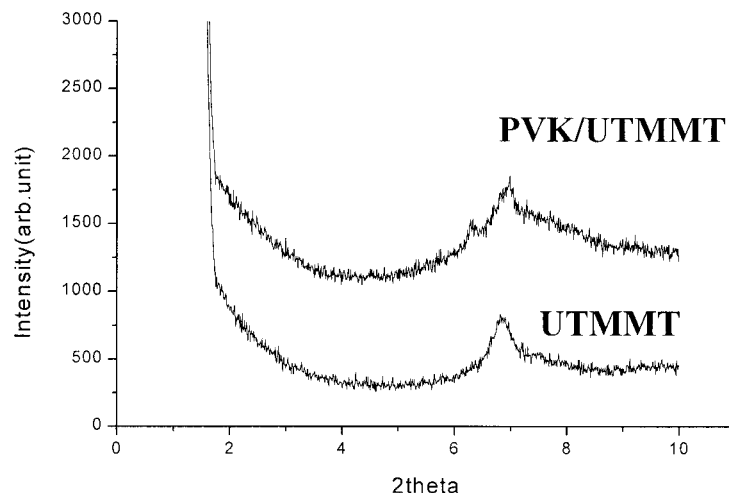
Figure 1 X-ray diffraction patterns for the PVK/UTMMT and UTMMT.

XRD patterns for PVK/UTMMT and UTMMT are observed at the same position. This means that the interlayer spacing of MMT does not change in the process of solution blending of PVK/UTMMT. Therefore, PVK/UTMMT has a conventional composite structure. The PVK is immiscible with UT-MMT, because the PVK has a hydrophobic character and the surface of UTMMT is hydrophilic.

X-ray diffractograms of MMTs revealed peak-shifting depending on the amount of the surface modifiers as shown in Figure 2. The UTMMT showed a peak at 7.07°, corresponding to the (001) plane. The interlayer spacing of UTMMT is 12.5 Å. The gallery spacing of MMT50, MMT75, and MMT100 is broadened with the amount of the surface modifier. The peaks for MMT50, MMT75, and MMT100 are shown at 5.14°, 4.97°, and 4.68°, respectively. These 2θ values correspond to interlayer spacing of 17.2, 17.7, and 18.9 Å, respectively.

To confirm the extent of the surface coverage of the stearylamine as an organophilic modifier, TGA and elemental analysis experiments were performed. Figure 3 shows the weight loss of OLS
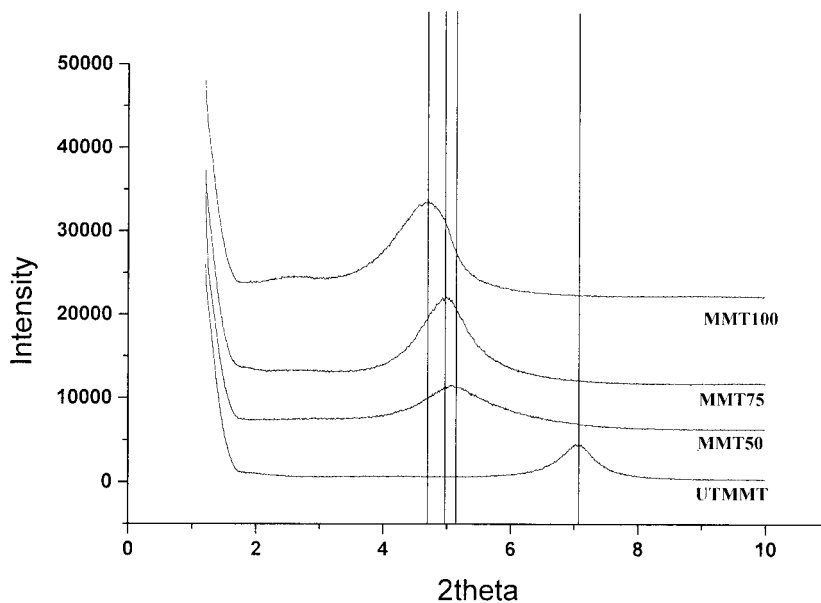

Figure 2 X-ray diffractograms of MMTs with different amounts of the surface modifiers.
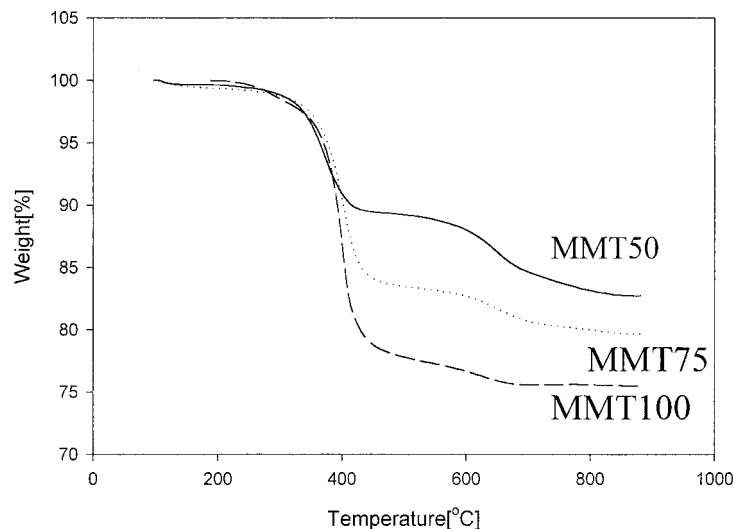
Figure 3   Weight loss of organophilically treated silicates with temperature.

samples with the temperature. The weight loss for MMT50, MMT75, and MMT100 is 17.0, 20.3, and 24.5 wt %, respectively. We assumed that the thermal decomposition of OLS took place only in the organic modifier. The lost weight was converted to mol percent for the cationic-exchange capacity (CEC) of MMT and is summarized in Table I. For comparison, the results of the elemental analysis are also listed in Table I.

The XRD patterns of the PVK/OLS nanocomposites are presented in Figure 4. Intercalation structures were obtained in PVK/MMT75 and PVK/MMT100. The interlayer spacing of PVK/

MMT100 is broader than that of PVK/MMT75 as was expected. Surprisingly, although the amount of the surface modifier is small, the exfoliated structure is obtained in PVK/MMT50.

To elucidate the different structures in PVK/MMT50 and PVK/MMT75 or PVK/MMT100, the interaction between PVK and MMT should be considered. When PVK is mixed with UTMMT, it is immiscible due to no interaction between PVK and UTMMT. In the case of PVK/MMT100 and PVK/MMT75, it was thought that the surface modifier covered the whole hydrophilic MMT surface. PVK chains could intercalate into the inter-
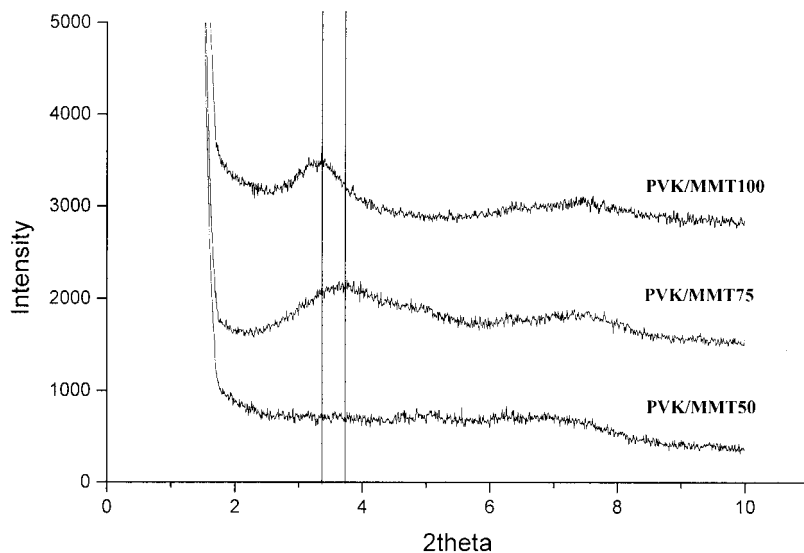

Figure 4   XRD patterns of a PVK/organophilically treated silicate nanocomposite.

layer of the MMT due to the miscibility of the PVK with the surface of MMT. But the surface modifier could not cover the surface of MMT in the case of MMT50. The PVK chains intercalate into the interlayer of the MMT in the surface-treated region and then PVK chains do not have any interaction with the untreated MMT surface. Therefore, they tend to retain their coil-like conformation in the gallery of MMT; this results in forcing the adjacent silicate layers to separate and leads to a fully exfoliated structure. Similar phenomena take place in the graft polymer or copolymer which have a hydrophobic backbone and a hydrophilic functional group such as the PE-*g*-ma/MMT system.[6]

CONCLUSIONS

In this research area, the control of the nanocomposite structure is a not only theoretical but also an experimental issue, because the physical properties of the nanocomposite greatly depend on its structure. In this study, a different structure (in-tercalated or exfoliated) of a polymer/clay nanocomposite was obtained according to the interfacial characteristics between the polymer chains and clay by controlling the degree of surface coverage. Also, an explanation of these phenomena was briefly proposed. This method will be a powerful new approach for the control of a polymer/layered silicate nanocomposite structure.

REFERENCES

1. Giannelis, E. P.; Krishnamoorti, R.; Manias, E. In Polymers in Confined Environments; Granick, S., Ed.; Springer: Berlin, 1999; Chapter 3.
2. Theng, B. K. G. Formation and Properties of Clay–Polymer Complexes; Elsevier: New York, 1979.
3. Vaia, R. A.; Giannelis, E. P. Macromolecules 1997, 30, 8000.
4. Vaia, R. A.; Giannelis, E. P. Macromolecules 1997, 30, 7990.
5. Suh, D. J.; Lim, Y. T.; Park, O. O. Polymer 2000, 41, 8557.
6. Park, O. O.; Lim, Y. T. Rheol Acta 2001, 40, 220.