Polymer Bulletin 41, 511–518 (1998)

Polymer Bulletin

Synthesis and properties of polystyrene-organoammonium montmorillonite hybrid

Jae Goo Doh, Iwhan Cho*

Department of Advanced Materials Engineering, Korea Advanced Institute of Science and Technology, P.O. Box 201, Cheongryang, Seoul 130-650, Korea

Received: 4 June 1998/Revised version: 10 September 1998/Accepted: 15 October 1998

Summary

Styrene monomer was mixed with quaternary ammonium montmorillonites(org-MMTs) and polymerized in the presence of radical initiator. The resulting materials showed an expansion of interlayer distance. These hybrid materials exhibited higher thermal stability compared with the virgin polystyrene(PS) or PS/pristine-MMT microcomposite. PS/Bz-MMT, containing benzyl-unit similar to styrene in org-MMT, exhibited higher decomposition temperature even for MMT loading as low as 0.3wt.% compared with other PS/org-MMT hybrids. It was found that the structural affinity between styrene monomer and the organic group of org-MMT plays an important role in the structure and the properties of hybrid materials.

Introduction

Recently, polymer/clay hybrid materials have received significant attention because the mutual interactions between polymer and clay are considered to affect their properties. Hybrids based on a thermoplastic matrix containing a nano-scale dispersion of the layered silicates are the materials with greatly improved physical and mechanical characteristics. Since the properties of the hybrid materials are directly related to the morphology of these systems, the state of dispersion of the inorganic phase is very important(1,2,3). These nanostructured hybrids exhibit the properties dramatically different from those of conventional microcomposites offering the possibility to find the materials of high performance(3,4,5).

Montmorillonite(MMT) is a hydrated alumina-silicate clay composed of the units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The silicate layers of MMT are planar, stiff, about 10 Å in thickness, about 2000 Å in length, and do not occur as isolated individual units but aggregate to form crystalline structures(5,6,7,8,9). The efficiency of the MMT in improving the properties of the polymer materials is primarily determined by the degree of its dispersion in the polymer matrix, which in turn depends on its particle size. However, the hydrophilic nature of the MMT surface impedes their homogeneous dispersion in the organic polymer phase. To overcome this problem it is often necessary to make the surface organophilic prior to its use(2,10,11). Although in pristine layered MMT the interlayer cations are usually hydrated Na^+ or K^+, ion exchange reactions with organic cations (e.g. alkylammonium cations) can render organophilicity to the normally hydrophilic MMT surface. The role of organic cation in the org-MMT is to reduce the surface energy of the MMT surface improving the wetting characteristics by the polymer or

---

* Corresponding author

monomer(5,12). Successful formation of a hybrid is, to a great extent, determined by the miscibility of individual component of the system.

Since the miscibility of monomer with organic cation in the organophilic MMT is important in determining the subsequent hybrid preparations(10,11,13), it is the objective of this study to investigate the effect of the chemical structures of various organophilic MMT on the process of various PS/MMT hybrid preparation. In the present work, PS/MMT-based hybrids were prepared by direct polymerization of monomer in various organophilic MMT phases. The impregnation of styrene monomers into quaternary ammonium MMT was followed by the polymerization by radical initiator.

Experimental

Pristine sodium-montmorillonite(Na-MMT) and organic-modified montmorillonite (org-MMTs) used in this study were generously donated by Southern Clay Products, Inc. The org-MMT was prepared by ion exchanging Na-MMT with alkylammonium cations, $(CH_3)_2N^+$(hydrogenated tallowalkyl)R, where R is hydrocarbon chain (tallow is composed predominantly of octadecyl chains with small amounts of lower homologue s). The org-MMTs used in polymerization were dimethyl hydrogenated tallowalkyl benzyl ammonium montmorillonite(Bz-MMT), dimethyl dihydrogenated tallowalkyl ammonium montmorillonite(Ta-MMT), and dimethyl hydrogenated tallowalkyl 2-ethyl hexyl ammonium montmorillonite(Eh-MMT).

In a 50mℓ glass flask were placed 0.2g of org-MMT, 0.3g of *N,N*'-azobis(isobutyronitrile)(AIBN) as radical initiator, and 20g of styrene monomer. This mixture was stirred at room temperature for 30min, and polymerized at 50°C for 72 hrs to obtain the PS/org-MMT hybrid. The polymerized PS/org-MMT sample was removed from the flask, crushed, and dried in vacuum at 80°C overnight.

In order to get the direct evidence of the nano-structure of this PS/org-MMT hybrid, X-ray diffraction(XRD) and Transmission Electron Microscopy(TEM) were employed(12,14). The XRD measurement was done using a Rigaku RAD-B diffractometer. The CuK α radiation was applied(λ =1.54 Å) in this measurement. The voltage and the current of the X-ray tubes were 40 kV and 40 mA, respectively. Basal spacing of the montmorillonite was estimated from the position of the (001) peak in the XRD pattern. Microscopic investigation was performed on a JEOL TEM 2000EX TEM, with an acceleration voltage of 100 kV. Thermal analysis was performed using TA Instruments TGA 2950 Thermogravimetric Analyzer at a heating rate of 20°C/min under nitrogen atmosphere.

Results and discussion

Typical synthesis of hybrid composites involves intercalation of alkylammonium cation and insertion of a suitable monomer followed by polymerization. The role of the alkylammonium cation is to improve penetration of the organophilic monomers in the MMT interlayers and the role of the monomer is to promote dispersion of the host particles. Since the increased basal spacing associated with hybrid formation arises from the expansion of the interlayer to accommodate the intercalating polymer, the regions of intercalated and unintercalated galleries can be distinguished from the difference in basal spacing(14).

XRD measurements give the values of the basal spacing of Na-MMT, org-MMT(Bz-MMT) and PS/Bz-MMT hybrid as shown in Figure 1. At 2 θ equals to 7.50°, the basal spacing is 11.8 Å for Na-MMT. In Bz-MMT, 2 θ decreases to 4.62° that corresponds to basal spacing of 19.1 Å. This intense reflection of Bz-MMT indicates an ordered intercalated system with alkylammonium cation. And the finite layer expansion associated with polymer intercalation results in the appearance of the new basal reflection(2 θ = 2.60°) corresponding to the larger gallery height. In PS/Bz-MMT hybrid, 2 θ decreases to 2.60° that corresponds to basal spacing of 34.0 Å for new basal reflection. This further increase of basal spacing from 19.1 Å to 34.0 Å is due to the swelling of the interlayer by the styrene monomer and successive polymerization in Bz-MMT interlayers.

Table 1 shows the dispersibility of org-MMTs in styrene monomer. It is particularly notable that Bz-MMT particles dispersed well in styrene monomer. As the structural affinity between styrene monomer and the organic group of org-MMT increases, the dispersibility of org-MMT in styrene monomer increases. Generally, it is known that the penetration of monomers into the lamellae of organophilic MMT can be facilitated by the attractive forces between the org-MMT interlayers and the free monomer molecules. The solvation efficiency of the org-MMT with monomer depends not only on the nature of the organic group intercalated in the MMT and but also on the chemical structure of the monomer used(4).

Table 1 also shows the basal spacing of org-MMTs and PS/MMT hybrids, and the difference(Δd) of basal spacings between them. As the alkyl chain length of the alkylammonium cations in org-MMT becomes larger, the basal spacing(d_{001}) of org-MMT showed be increased. And when monomer is penetrated into org-MMT interlayer space followed by polymerization, the increase of interlayer distance depends on the structure of organic group of org-MMT rather than the chain length of the alkylammonium cation. As shown in Table 1, the basal spacing(d_{001}) and the difference(Δd) of basal spacing for PS/Bz-MMT hybrid were larger than those obtained for PS/Ta-MMT or PS/Eh-MMT. It implies that the amount of PS polymer intercalated in the interlayers of Bz-MMT is much more than that of other PS/org-MMT hybrids. And, the interlayer distance of Eh-MMT was increased by the PS polymer chains polymerized in the interlayers, while that of Ta-MMT was scarcely changed. It seems that the PS polymer chains polymerized in the interlayers of Ta-MMT do not affect the expansion of the interlayers because Ta-MMT has enough space to accommodate the intercalating PS polymer chains without expanding the interlayer. The interlayer space of Ta-MMT is about two times that of Eh-MMT. Because the thickness of MMT layer equals about 10 Å, the interlayer spaces of Ta-MMT and Eh-MMT are 22.7 Å and 10.4 Å, respectively. And the concentrations of alkylammonium cation intercalated on MMT surface are equal, since MMT has an inherent cation exchange capacity(CEC) value. The increase of the decomposition onset temperature of PS/Ta-MMT hybrid comparable to those of other org-MMT hybrids, as shown in Figure 4, indicates PS polymers were intercalated in Ta-MMT interlayers.

In addition to XRD, the hybrid materials have been characterized by transmission electron microscopy(TEM). Figure 2 is a micrograph of organically modified layered MMT intercalated with polystyrene. The well-ordered and stacked MMT

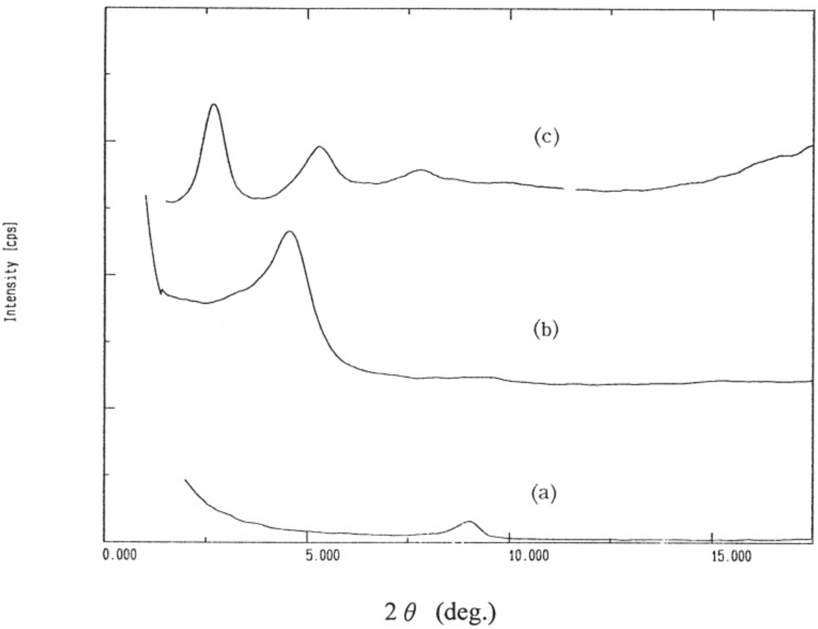

Figure 1. X-ray diffraction patterns of MMT and PS/org-MMT hybrids.
: (a) Na-MMT, (b) Bz-MMT, (c) PS/Bz-MMT

Table 1. Dispersibility of org-MMT in Styrene Monomer and Basal Spacings(d_{001}) of PS/org-MMT Hybrids.

org-MMT	Dispersibility in Styrene Monomer [a]	d_{001} of org-MMT	d_{001} of PS/org-MMT hybrids	Δd [b]
Bz-MMT	◎	19.1 Å	34.0 Å	14.9 Å
Ta-MMT	△	32.7 Å	32.9 Å	0.2 Å
Eh-MMT	△	20.4 Å	28.5 Å	8.1 Å
Na-MMT	X	11.8 Å	14.2 Å	2.4 Å

a) It was judged by the appearance of org-MMT dispersion in styrene monomer. : (◎) perfectly dispersible, (△) partly dispersible, (X) not dispersible

b) Δd represents the difference between the d_{001} of PS/org-MMT hybrid and its org-MMT.

multilayers are dispersed in a continuous PS matrix. The layers of hybrid are shown as regions of alternating narrow, dark and light bands within the particle. The repeat distance is comprised of about 10Å dark bands, corresponding to the MMT layers, separated by about 24Å light bands, corresponding to the polystyrene-containing galleries in agreement with the d-spacing observed by XRD shown in Figure 1. PS/ org-MMT hybrid is multilayered sandwich-like material in which polymer chains are sandwiched between ultrathin sheets of MMT. When polymers are intercalated between MMT sheets, their properties greatly differ from those of the bulk polymers on heating(4).

Figure 3 shows TGA thermograms of the virgin PS, PS/Na-MMT, and the PS/ Bz-MMT hybrid. The TGA curve of hybrid shows delayed decomposition compared to that of the virgin PS or PS/Na-MMT microcomposite. From the TGA data, it is clear that PS/org-MMT hybrids exhibit higher thermal stability compared to PS or PS/Na-MMT composite. It may be attributed to the confinement of PS polymer chains between MMT layers as well as the MMT surface-polymer interactions in the nanostructured hybrid of PS and org-MMT. Therefore, the improvement in the thermal stability will lead to the better service performance of the hybrid composite at elevated temperature.

Figure 4 shows the variation in the decomposition onset temperature of the PS/ org-MMT hybrids as a function of the MMT loading. The decomposition onset temperature of the PS/Na-MMT was not greatly affected by the amount of MMT loading, but a remarkable dependency of the decomposition onset temperature of the PS/org-MMT hybrids on the MMT loading was observed. The decomposition onset temperature of PS/org-MMT increased initially with increasing MMT loading and saturated at about 430°C. PS/Bz-MMT, containing benzyl-unit similar to styrene monomer in org-MMT, exhibited higher decomposition temperature even for MMT content as low as 0.3wt.% compared with other PS/org-MMT hybrids. Some works on the properties of polymer/MMT hybrids have also shown that the hybrid materials exhibit impressive thermal properties and permeability at very low MMT loadings(5,7, 15,16). They attributed the increased thermal stability to hindered out-diffusion of the volatile decomposition products. In general, to reinforce a polymer, 10 ~ 30 wt.% of inorganic materials(glass fiber, talk, etc.) are used. As for MMT, about one-tenth of that amount is enough to improve the properties of a matrix polymer. The reason is supposed to be the molecular level dispersion and special geometry(high aspect ratio) of the MMT. As the aspect ratio of inorganic material increases, the effect of improving the properties increases(17). Those facts maximize the available surface area of the reinforcing phase between the MMT and the polymer matrix, and lead to excellent properties.

From above results, it can be concluded that structural affinity between styrene monomer and the organic group of org-MMT is an important factor in preparing hybrid composites. The structural affinity in PS/Bz-MMT hybrid is attributed to the presence of benzyl-unit in alkylammonium cation of Bz-MMT similar to structure of styrene monomer, which improves the thermodynamic compatibility between org-MMT and styrene monomer.

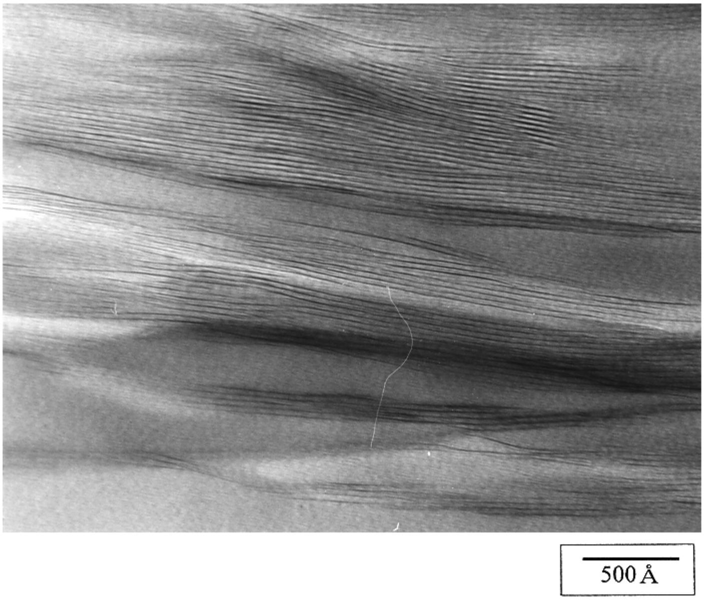

Figure 2. TEM micrograph of PS/Bz-MMT hybrid containing 1 wt% MMT.

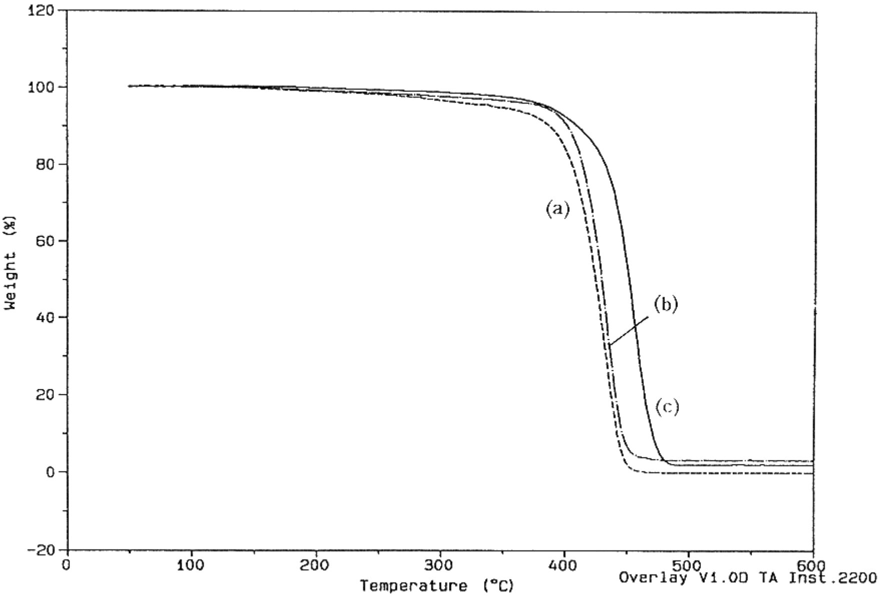

Figure 3. TGA thermograms for (a) PS, (b) PS/Na-MMT, (c) PS/Bz-MMT.

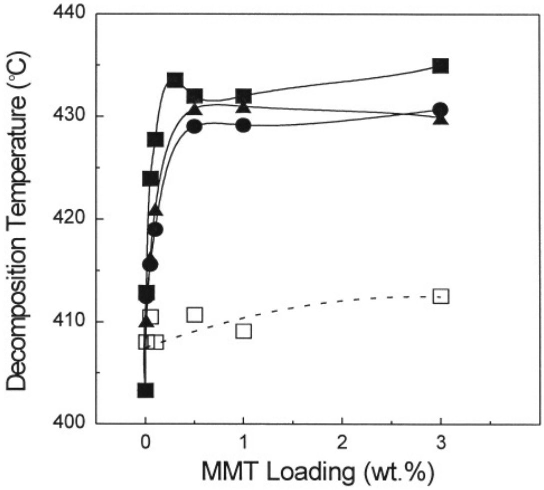

Figure 4. Decomposition onset temperature of the PS/org-MMT hybrids as a function of the MMT loading: (■)PS/Bz-MMT, (●)PS/Ta-MMT, (▲)PS/Eh-MMT, (□) PS/Na-MMT

References

1. Theng B K G (1974) The Chemistry of Clay-Organic Reactions. Adam Hilger, London.
2. Theng B K G (1979) Formation and Properties of Clay-Polymer Complexs. Elsevier, Amsterdam.
3. Solc J, Nichols K, Galobaedes M, Giannelis E P (1997) SPE ANTEC'97 Proceedings, p.1931.
4. a) Akelah A (1995) Nanocomposites of grafted polymers onto layered silicate. In: Prasad P N, Mark J E, Fai T J (ed) Polymer and Other Advanced Materials: Emerging Technologies and Business Opportunities. Plenum Press,New York.
   b) Akelah A, Moet A (1994) J. Appl. Polym. Sci: Appl. Polym. Symp. 55: 153.
5. Giannelis E P (1996) Adv. Mater. 8(1): 29.
6. Blumstein A (1965) J. Polym. Sci.: Part A 3: 2653.
7. Burnside S D, Giannelis E P (1995) Chem. Mater. 7(9): 1597.
8. Sikka M, Cerini L N, Ghosh S, Winey K I (1996) J. Polym. Sci.: Part B: Polym. Phys. 34: 1443.
9. Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O (1993) J. Polym. Sci.: Part A: Polym. Chem. 31: 1755.
10. Akelah A, Moet A (1996) J. Mater. Sci. 31: 3589.
11. Moet A, Akelah A (1993) Mater. Lett. 18: 97.
12. Krishnamoorti R, Vaia R A, Giannelis EP (1996) Chem. Mater. 8: 1728.
13. Kato C, Kuroda K, Takahara H (1981) Clays and Clay minerals 29(4): 294.

14. Vaia R A, Jandt K D, Kramer E J, Giannelis E P (1996) Chem. Mater. 8: 2628.
15. Lan T, Kaviratna P D, Pinnavaia (1994) Chem. Mater. 6: 573.
16. Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O (1993) J. Polym. Sci.: Part A: Polym. Chem. 31:2493.
17. Yano K, Usuki A, Okada A (1997) J. Polym. Sci.: Part A: Polym. Chem. 35: 2289.