

Synthesis of Polypropylene Oligomer–Clay Intercalation Compounds

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ABSTRACT: The synthesis of polypropylene (PP) oligomer–clay intercalation compounds was studied by using three kinds of PP oligomers and organophylic clay. PP oligomers were two types of maleic-anhydride-modified PP oligomers containing different amount of maleic anhydride groups and one type of hydroxy modified PP oligomer. Organophylic clay was sodium-ion-exchanged montmorillonite with octadecylammonium ion (C18–Mt). PP oligomer was mixed with C18–Mt at 200°C. Maleic-anhydride-modified PP oligomer, which was of high acid value type, and hydroxy-modified PP oligomer were intercalated between silicate layers of clay; and PP oligomer–clay intercalation compounds were synthesized successfully. But maleic-anhydride-modified PP oligomer, which was of low acid value type, was not intercalated. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1781–1785, 1997

Key words: hybrid; intercalation; montmorillonite; oligomer; clay

INTRODUCTION

In recent years, smectite clays (e.g., montmorillonite) intercalated by polymers have attracted great interest to researchers since they exhibit novel physical properties.^{1–11} In our previous work, we successfully synthesized a nylon 6–clay hybrid (NCH) in which 10 Å thick silicate layers of montmorillonite are dispersed in the nylon 6 matrix on a nanometer level.⁵ The NCH exhibits various excellent properties, such as high strength, high modulus, high heat distortion temperature, and low gas permeability, compared to nylon 6.^{6–7} Based on the same concept, we synthesized various polymer–clay hybrids, such as polyimide,⁸ epoxy resin,⁹ polybutadiene,¹⁰ acrylic polymer,¹¹ to date. However, it was difficult to disperse silicate layers of montmorillonite at the nanometer level in nonpolar polymers. Vaia et al. reported that for polystyrene melt intercalation into the clay gallery, only single polymer layers

intercalated; so the dispersion of silicate layers of clay at the nanometer level was not achieved.¹² Recently, we reported the new approach of synthesis of polymer–clay hybrid using an oligomer with functional groups.¹³ In this synthesis, at the first stage, a polyolefine oligomer with polar telechelic OH groups (PO–OH) was inserted into the clay gallery in toluene, using a montmorillonite modified with dioctadecyldimethylammonium ion (DSDM–Mt). The basal spacing of the clay increased, and, as a result, the interaction of the layers should be weakened. At the second stage, polypropylene (PP) was inserted into the DSDM–Mt–PO–OH intercalation compound gallery by the mixing the intercalation compound with PP, and the PP–clay hybrid was obtained.

In this article, we studied the synthesis of PP oligomer–clay intercalation compounds without solvent by using three kinds of PP oligomers. PP–MA-1010 is maleic-anhydride-modified PP oligomer (acid value = 52 mg KOH g⁻¹). PP–MA-110TS is also maleic-anhydride-modified PP oligomer (acid value = 7 mg KOH g⁻¹). PP–OH-1210 is hydroxy-modified PP oligomer (OH value = 54 mg KOH g⁻¹). These oligomers are miscible with

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Table I Characterization of Polypropylene Oligomers

Grade	Characterization ^a			
	Acid Value (mg KOH g ⁻¹)	OH Value (mg KOH g ⁻¹)	Softening Temperature (°C)	GPC ^b (<i>M_w</i>)
PP-MA-1010	52	—	145	30,000
PP-MA-110TS	7	—	145	12,000
PP-OH-1210	—	54	143	20,000

^a The data were obtained from Sanyo Chemical Industries.

^b Gel permeation chromatography.

PP, and these oligomer-clay intercalation compounds are expected to be intermediates for preparing PP-clay hybrids.

We will report the preparation of PP-clay hybrids using these oligomer-clay intercalation compounds.¹⁴⁻¹⁵

EXPERIMENTAL

Materials

The materials used for the synthesis of the PP oligomer-clay intercalation compounds are purified sodium montmorillonite (Kunipia-F) from Kunimine Mining Industries Co., Tokyo, Japan, octadecyl amine from Wako Pure Chemical Industries Co., Osaka, Japan, and polypropylene oligomers (Table I) from Sanyo Chemical Industries, Kyoto, Japan.

Preparation of Organophilic Montmorillonite

Sodium montmorillonite (80 g; 119 meq : 100 g cation exchange capacity) was dispersed into 5000 mL of hot water (80°C) by using a homogenizer. Octadecyl amine (31.1 g, 115 mmol) and conc. hydrochloric acid (11.5 mL) were dissolved into 2000 mL of hot water (about 80°C). It was poured into the hot montmorillonite-water solution under vigorous stirring for 5 min by using the homogenizer to yield a white precipitate. The precipitate was collected on a cloth filter, washed with three times with 2500 mL of hot water (80°C), and freeze-dried to yield a montmorillonite intercalated with octadecyl ammonium (C18-Mt). We measured the basal spacing between the layers of the C18-Mt by X-ray diffraction (XRD) and its inorganic content by measuring the weights before and after burning its organic parts. The basal spacing of sodium montmorillonite is 12.3 Å, and that of C18-Mt is 21.7 Å. The inorganic content

of the C18-Mt is 69.5 wt %. These results indicated that the almost quantitative cation exchanging occurred between sodium ion in the clay and octadecyl ammonium ion.

Synthesis of Polypropylene Oligomer-Clay Intercalation Compounds

PP-MAs and PP-OH were melt-mixed with C18-Mt (weight ratio: PP-MA or PP-OH—C18-Mt = 1 : 1) by using a Labo-Plastomil (Toyo Seiki Co.) at 200°C for 15 min. In the case of using PP-MA-1010, PP-MA-1010—C18-Mt = 1 : 3 and 3 : 1 (weight ratios) were also synthesized. We measured the XRD patterns of the powder of the mixtures in order to confirm whether the PP oligomer-clay intercalation compounds were formed. These XRD patterns were obtained by using a Rigaku RAD-B diffractometer with Cu-K α radiation.

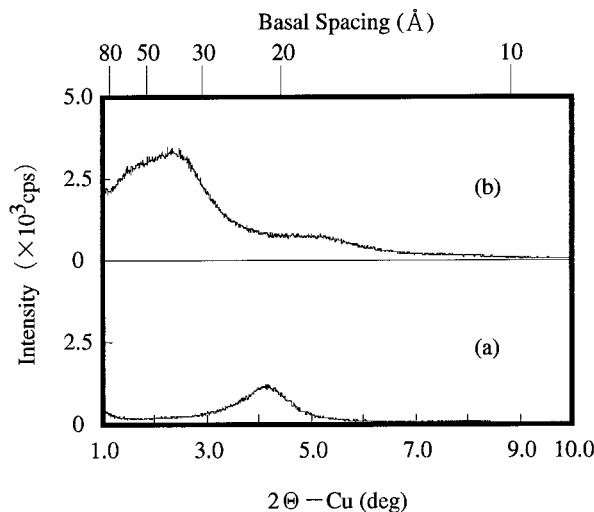


Figure 1 XRD patterns of (a) C18-Mt and (b) the mixture of PP-MA-1010 and C18-Mt (PP-MA—C18-Mt = 1 : 1 by weight) obtained by melt blending.

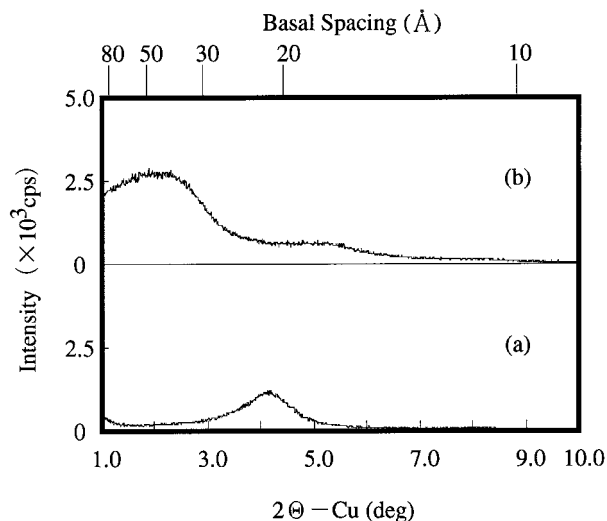


Figure 2 XRD patterns of (a) C18-Mt and (b) the mixture of PP-OH-1210 and C18-Mt (PP-OH-C18-Mt = 1 : 1 by weight) obtained by melt blending.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the mixtures of C18-Mt with PP-MA-1010 (weight ratio: PP-MA-1010-C18-Mt = 1 : 1) and that of C18-Mt itself. The (001) plane peaks of the mixture are observed at a lower angle than those of C18-Mt around $2\theta = 4^\circ$ in the XRD curves. The top of the (001) plane peaks of the mixture is $2\theta = 2.3^\circ$, and this angle indicates that the average of basal spacings is 38.2 Å. Figure 2 shows the XRD pattern of the mixture of C18-Mt with PP-OH-1210. The (001) plane peaks of the mixture are observed lower angle than those of C18-Mt. The top of the (001) plane peaks of the mixture is $2\theta = 2.0^\circ$, and this angle indicates the average of basal spacings is 44.0 Å. The basal spacing of those mixtures are about 20 Å longer than that of C18-Mt. These results indicate that PP-MA-1010 and PP-OH-1210 intercalate into the silicate layers and expand the basal spacing, so PP oligomer-clay intercalation compounds are formed.

Figure 3 shows the XRD pattern of the mixture of C18-Mt with PP-MA-110TS. The plane peaks are slightly shifted to lower angles. The top of the (001) plane peaks of the mixtures of C18-Mt with PP-MA-110TS is $2\theta = 3.8^\circ$, and the average of the basal spacings is 22.9 Å. The basal spacing of that mixture is only about 1 Å longer than that of C18-Mt. This indicates that PP-MA-110TS has few intercalation capabilities into the silicate layers.

These results about PP oligomer intercala-

tion behavior indicate important factors for PP oligomers to be intercalated between silicate layers. The molecular weight (M_w) of oligomer is not concerned with the intercalation capabilities of oligomer since the molecular weight (M_w) of PP-MA-1010 and PP-OH-1210 is larger than that of PP-MA-110TS. The kind of polar functional group is also not of concern because the polar functional group of PP-MA-1010 is maleic anhydride (or COOH group derived from the hydrolysis of maleic anhydride) group, while that of PP-OH-1210 is the hydroxy group. The acid value of PP-MA-1010 (acid value: 52 mg KOH g^{-1}), the OH value of PP-OH-1210 (OH value: 54 mg KOH g^{-1}) is larger than the acid value of PP-MA-110TS (acid value: 7 mg KOH g^{-1}). Calculated from those values, the carboxyl equivalent weight of PP-MA-1010 is about 1070 $g\ mol^{-1}$, and the hydroxyl equivalent weight of PP-OH-1210 is about 1040 $g\ mol^{-1}$. The carboxyl and hydroxyl equivalent weights are smaller than the carboxyl equivalent weight of PP-MA-110TS (about 8010 $g\ mol^{-1}$). Since the molecular weight of propylene unit $-\text{CH}(\text{CH}_3)-\text{CH}_2$ is 42.08 $g\ mol^{-1}$ in calculations, one carboxyl group exists per approximately 25 units of propylene in PP-MA-1010 and one hydroxyl group exists per approximately 25 units of propylene in PP-OH-1210. On the other hand, in PP-MA-110TS, one carboxyl group exists per approximately 190 units of propylene. It is necessary for the intercalation to form the hydrogen bonding between the oligomer's polar functional group and the oxygen

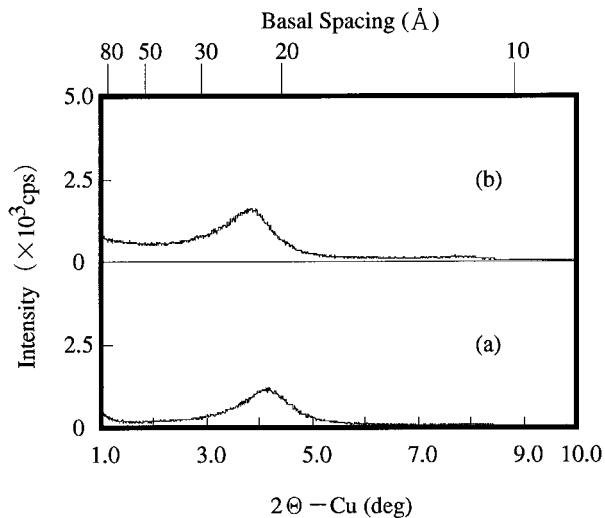


Figure 3 XRD patterns of (a) C18-Mt and (b) the mixture of PP-MA-110TS and C18-Mt (PP-MA-C18-Mt = 1 : 1 by weight) obtained by melt blending.

group of silicates. Therefore, the number of the carboxyl group in a PP-MA-110TS molecule is not enough to be intercalated, so oligomers should include a certain amount of polar functional groups in a molecule; in the case of PP oligomers, one polar group per approximately 25 units of propylene is necessary for the intercalation.

Figure 4 shows the changes of XRD patterns when the mixing weight ratio of PP-MA-1010—C18-Mt is changed from 1 : 3 to 3 : 1. As the weight of PP-MA-1010 in the mixtures increases, the plane peaks of montmorillonite are shifted to lower angles. When the mixing weight ratio of PP-MA-1010—C18-Mt is 3 : 1, the top of the (001) plane peaks of that mixtures is $2\theta = 1.2^\circ$. The average of the basal spacings is 72.2 Å. Figure 5 presents a schematic representation of PP-MA-1010 intercalation process. A small amount of

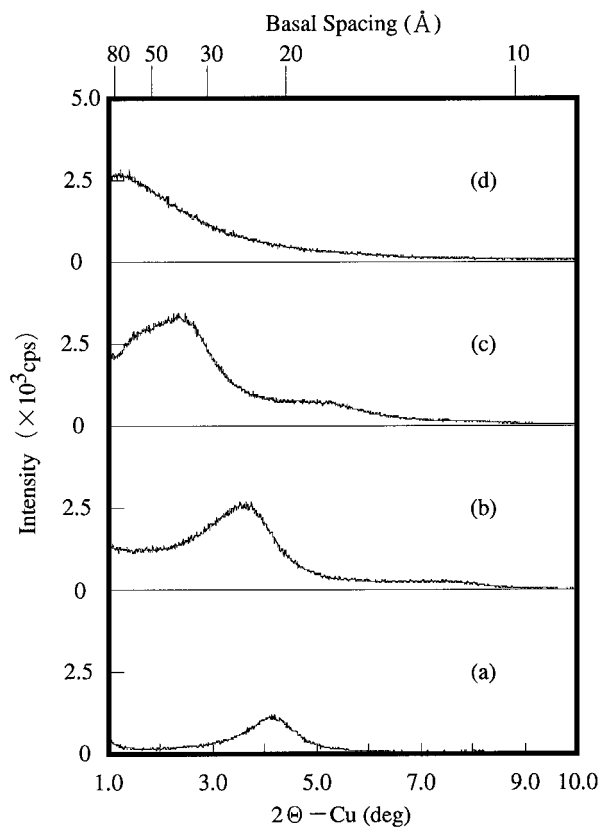


Figure 4 XRD patterns of (a) C18-Mt, (b) the mixture of PP-MA-1010 and C18-Mt (PP-MA—C18-Mt = 1 : 3 by weight) obtained by melt blending, (c) the mixture of PP-MA-1010 and C18-Mt (PP-MA—C18-Mt = 1 : 1 by weight) obtained by melt blending, and (d) the mixture of PP-MA-1010 and C18-Mt (PP-MA—C18-Mt = 3 : 1 by weight) obtained by melt blending.

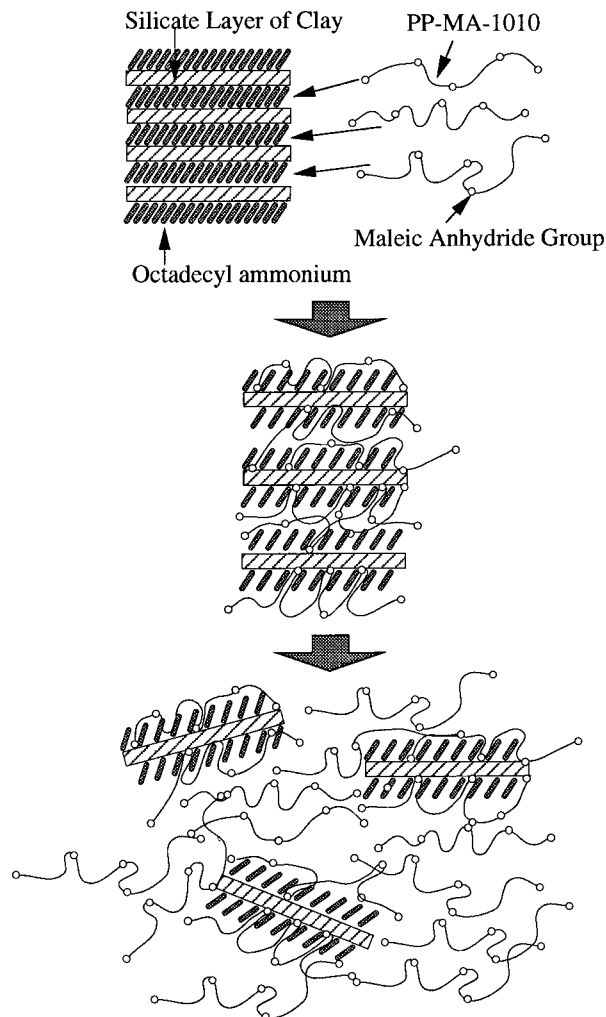


Figure 5 Schematic representation of the intercalation process of PP-MA-1010 into the organized clay.

PP-MA-1010 is intercalated into the silicate layers at the early step of the mixing process, so the silicate layers are coated by PP-MA-1010 and the interaction of the layers should be weakened. Therefore, the remainder of PP-MA-1010 is easily intercalated, and the basal spacing is expanded as the weight of PP-MA-1010 in the mixtures increases.

CONCLUSION

In conclusion, we successfully synthesized PP oligomer-clay intercalation compounds. It became apparent that PP oligomers should include one polar group (i.e., carboxy group and hydroxy group) per approximately 25 units of PP to be intercalated between silicate layers.

REFERENCES

1. A. Okada and A. Usuki, *Mater. Sci. Eng.*, **C3**, 109 (1995).
2. B. M. Novak, *Adv. Mater.*, **5**, 422 (1993).
3. E. P. Giannelis, *Adv. Mater.*, **8**, 29 (1996).
4. R. A. Vaia, K. D. Jandet, E. J. Kramer, and E. P. Giannelis, *Macromolecules*, **28**, 8080 (1995).
5. A. Usuki, M. Kawasumi, Y. Kojima, Y. Fukushima, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1179 (1993).
6. Y. Kojima, A. Usuki, M. Kawasumi, Y. Fukushima, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1185 (1993).
7. A. Usuki, A. Koiwai, Y. Kojima, M. Kawasumi, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Appl. Polym. Sci.*, **55**, 119 (1995).
8. K. Yano, A. Usuki, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Polym. Sci., Polym. Chem.*, **31**, 2493 (1993).
9. A. Usuki, T. Mizutani, Y. Fukushima, M. Fujimoto, K. Fukumori, Y. Kojima, N. Sato, T. Kurauchi, and O. Kamigaito, U.S. Pat. 4,889,885 (1989).
10. K. Fukumori, A. Usuki, N. Sato, A. Okada, and T. Kurauchi, *Proceedings of the 2nd Japan International SAMPE Symposium*, 1991, p. 89.
11. A. Usuki, K. Okamoto, A. Okada, and T. Kurauchi, *Kobunshi Ronbunshu*, **52**, 727 (1995).
12. R. A. Vaia, H. Ishii, and E. P. Giannelis, *Chem. Mater.*, **5**, 1694 (1993).
13. A. Usuki, M. Kato, A. Okada, and T. Kurauchi, *J. Appl. Polym. Sci.*, **63**, 137 (1997).
14. N. Hasegawa, M. Kawasumi, M. Kato, A. Usuki, and A. Okada, *J. Appl. Polym. Sci.*, to appear.
15. M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, and A. Okada, *Macromolecules*, to appear.