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Thermal characteristics of organoclay and their effects upon the formation of polypropylene/organoclay nanocomposites

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Summary

We have examined thermal characteristics of two types of organically modified montmorillonite (OMMT) with different alkylammonium cations and their effects upon the formation of PP nanocomposite, when using a maleic anhydride grafted polypropylene oligomer (maPP) as a compatibilizer. The microstructure of the composite has been characterized by X-ray diffraction (XRD) analysis, transmission electron microscopy and Fourier transform infrared spectroscopy. OMMT showed the decrease of the interlayer spacing at the processing temperature, due to the release of organic ion by thermal decomposition. Thermal characteristics of OMMTs depended greatly on the interlayer structure of OMMT. When the OMMT with small interlayer spacing and less organophilicity was used, PP composite resulted in the only partial exfoliation due to thermal decomposition of the clay layers.

Introduction

Polymer melt intercalation of inorganic clay minerals consisting of layered silicate is a viable approach to synthesize a variety of polymer-clay nanocomposites [1-3]. These nanocomposites exhibit the superior properties such as enhanced strength, reduced gas permeability, and improved flame retardancy. Nanocomposite via melt intercalation is formed by heating a mixture of polymer and clay above the glass transition temperature or melting temperature. Intercalation can be aided by shear(e.g. by mixing in an extruder). The formation of polymer-clay nanocomposite depends upon the thermodynamic interaction between polymer and clay as well as the transport of polymer chain from the bulk melt into the clay layer. Generally, the pristine clay is too hydrophilic to be compatible with most polymers. To render the clay layers organophilic, they are intercalated with organic cations (e.g. alkylammonium cation) by cation exchange reaction[2-5]. The formation of nanocomposite depends largely upon the surface characteristics of the modified clay with an organic ion(organoclay). In addition, since melt intercalation proceeds usually at high temperature, thermal characteristics of organoclay might also affect the formation of the microstructure. However, this effect has been rarely studied in the literatures.

Polypropylene (PP) is one of the most widely used polyolefins. Since PP does not include any polar group in its backbone, the formation of PP nanocomposite was not

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realized even by using an organophilically modified Montmorillonite (OMMT). Recently, Kawasumi et al. have reported a novel approach to prepare PP nanocomposite by using a functional polyolefin oligomer (e.g. maleic anhydride grafted PP oligomer) as a compatibilizer [6,7].

In this paper, we investigated thermal characteristics of different types of OMMT and their effects upon the formation of PP nanocomposite via melt intercalation, when using a maleic anhydride grafted PP oligomer (maPP) as a compatibilizer. We have used two OMMT modified with different alkylammonium ions. Both OMMT possess similar value of cation exchange capability. However, the one of OMMT has the kind of alkylammonium ion with two ethoxy groups, while the other has the organic ion consisting of purely aliphatic chains.

Experimentals

Materials

The materials used for the preparation of polypropylene(PP) nanocomposites are the commercialized PP(H150F) from SK.Co., maleic anhydride grafted PP oligomer from Honam Petrochemical Co. and two different kind of commercialized organophilic montmorillonites(Cloisite® 20A and 30B) from Southern Clay Product, Inc.. Maleic anhydride grafted PP oligomer(maPP) with maleic anhydride of 2 wt.% and M_N of 23,000, and PP with M_N of 72,000 of and M_w of 278,000 were used. Characteristics of organophilic montmorillonites (OMMTs) are listed in Table 1. The basal spacings of (001) plane in Table 1 were measured by X-ray diffraction. Molecular weights and molecular weight distributions of PP and maPP were measured by a Waters 150C gel-permeation chromatography (GPC) in 1,2,4 trichlorobenzene at 140 °C .

Table 1. Characteristics of organophilically modified montmorillonites(Cloisite®)

	organic ion	C.E.C* (meq/100g)	inorganic part* (wt.%)	The basal spacing (nm)
M20A	**Dimethyl dihydrogenated tallow ammonium ion**	**95**	**62**	**2.48**
M30B	**Methyl tallow bis-2 hydroxyl ethyl ammonium ion**	**90**	**68**	**1.84**

*** These data were obtained from Southern Clay Product, Inc..**

Preparation of PP / OMMT composites

The composites consisting of PP, maPP and OMMT were prepared by melt blending. Their compositions and abbreviations are listed in Table 2. All samples contained about 5 wt.% clays as inorganic parts. The mixture of PP, maPP and OMMT were dry-mixed preliminarily and melt-blended at 210 °C for 10 minutes by using a Brabender mixer with 50 rpm. The obtained lumps of the composites were compression-molded into test species(20 mm diameter disk with roughly thickness of 2 mm) at 190 °C, being used for the X-ray diffraction(XRD) analysis and transmission electron microscopy.

Table 2. Compositions and abbreviations of PP series

Abbreviations	Weight percent(%) in composite PP	 MaPP	 OMMT
PP-maPP	**74**	**26**	**-**
PP-M20A	**92**	**-**	**8**
PP-M30B	**92.8**	**-**	**7.2**
maPP-M20A	**-**	**75**	**25**
maPP-M30B	**-**	**75**	**25**
PP-maPP-M20A	**68**	**24**	**8**
PP-maPP-M30B	**70.8**	**21.8**	**7.4**

Evaluation of microstructure

The dispersion of the clay layers was evaluated by monitoring the interlayer spacing of the mixtures using an X-ray diffractometer (Rigaku Inc. D/MAX-RC) at room temperature and by observing transmission electron micrographs of the mixtures. Transmission electron micrographs were taken from 60~100 nm thick, microtomed sections of the composites using a JEOL 120 TEM with 120 kV accelerating voltage.

Investigation of thermal characteristics of OMMT

To examine thermal stability of the OMMT, thermal treatment was performed under both air and nitrogen condition in the heating chamber of an ARES rheometer for 10 min at 210 °C, at which the mixtures were melt-mixed. Before and after thermal treatment, OMMT were characterized by measuring the XRD patterns and FTIR spectra at room temperature, and by elemental analysis. Elemental analysis was performed by an EA1110-FISONs elemental analyzer. FTIR spectra were obtained from KBr pellets at room temperature using a BOMEM 102 specrtometer with a nominal resolution of 4 cm^{-1}. For each spectrum, 40 interferograms were collected and co-added.

Result and Discussion

Thermal characteristics of OMMT

We have firstly prepared the mixtures of polypropylene (PP) and organophilic montmorillonite (OMMT) by melt blending. Figure 1 shows the XRD patterns of the mixtures of PP with the two different OMMTs (PP-OMMTs) and OMMTs themselves. As seen in Figure 1, it is clear that no intercalation occurs. But the (001) plane peaks of the composites were shifted to higher angle compared to OMMTs themselves. This indicates that the interlayer spacing decreased. The basal spacing decreased from 2.49 nm to 2.40 nm for PP-M20A and from 1.84 nm to 1.50 nm for PP-M30B. In order to investigate these phenomena, thermal treatments have been performed on OMMTs themselves for 10 min at 210 °C - the melt-mixing temperature - under both air and nitrogen conditions. In Figure 2, the XRD patterns of OMMTs before and after the treatments are shown. In the experiments under both conditions, nearly identical results as those of PP-OMMTs were obtained in view of the interlayer spacing. So, it is reasonable to say that the decrease of the spacing in PP-OMMTs comes mainly from the thermal characteristics of OMMT themselves. In addition, the decrease of the spacing under nitrogen condition confirms that this decrease was mainly attributed to a thermal nature and the environment does not give a significant difference at all.

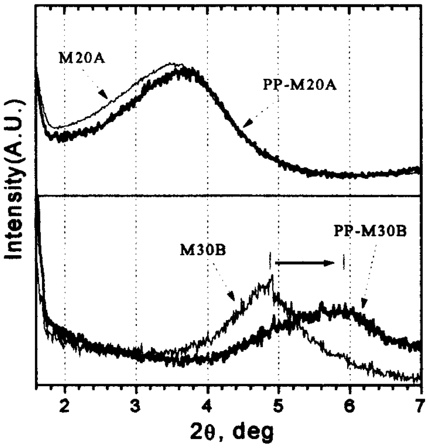


Figure 1. XRD patterns of PP-OMMTs and OMMTs.

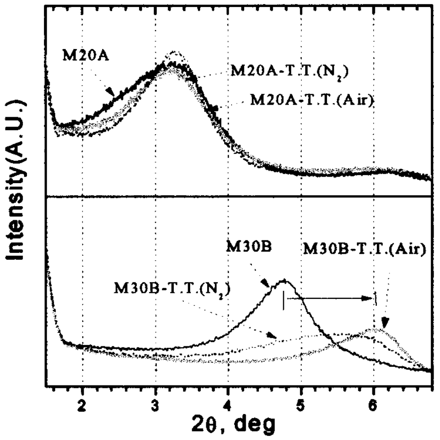


Figure 2. XRD patterns of OMMTs before and after thermal treatment: T.T.(air) and T.T.(N_2) refers to thermal treatment under air condition and nitrogen condition, respectively.

In previous studies about organic/inorganic complexes intercalated with organic ions, it was reported that the decrease of the interlayer spacing with increasing the temperature was due to the release of organic molecules by thermal decomposition of this complex - thermal desorption of organic ion [8] and thermal decomposition of organic molecule itself [9]. To examine the compositional changes of OMMTs with thermal treatment, we performed the elemental analysis for both OMMTs before and after thermal treatment under air condition. Table 3 summarizes the weight of each element after thermal treatment [10]. Both M20A and M30B show the decrease of all constituent elements, which indicates that thermal decomposition occurred as mentioned above. Remarkably, these decrease are roughly proportional to the initial amount of each element. Even though we can not explain the accurate mechanism of this decomposition, it clearly confirms that thermal desorptions of organic ions, which may be the partially decomposed or complete ions, occurs with thermal treatment, resulting in the decrease of the interlayer spacing.

Table 3. weight loss of each element in OMMT after thermal treatment under air condition.

		weight of each element per 100g of OMMT(g)	after thermal treatment	
			weight of each element(g)	change of weight(g)
M20A	Carbon	28.12	25.62	-2.50(9%)
	Hydrogen	6.59	5.96	-0.63(9%)
	Nitrogen	0.84	0.78	-0.06(7%)
	Inorganic*	64.45	64.54	—
M30B	Carbon	19.22	17.23	-1.99(10%)
	Hydrogen	4.32	4.04	-0.28(6%)
	Nitrogen	0.94	0.88	-0.11(12%)
	Inorganic*	75.52	75.52	—

* The content of the absorbed water was ignored and included in the inorganic content

The intercalated chains of organoclay adopt the various arrangements, based on the packing density, temperature and chain length [4,5]. M20A and M30B have the similar value of cation exchange capability (Table 1). But the intercalated chains of M20A consist of two tallow chains, while M30B has the chains with monotallow and two ethoxy groups, so that each OMMT might result in the different interlayer structure. Recently, FTIR was used in conjunction with XRD, to probe the interlayer structure of OMMT [4]. In general, the frequency of asymmetric CH_2 stretching (ν_{as}, CH_2) is sensitive to the gauche/trans conformer ratio and the packing density of the chains. The band shift from lower frequencies, characteristics of highly ordered all-trans conformation, to higher frequencies as the number of gauche conformation along the chain (chain disorder) increases. The methylene in the all-trans ordered state of crystalline $2C18N^{+}2C1Br^{-}$, which is similar as the alkyl chains intercalated into M20A, show a band at 2917 cm^{-1}. The band shifts to 2928.9 cm^{-1} in a liquidlike environment as in $2C18N^{+}2C1Br^{-}/CHCl_3$ solution. Table 4 summarizes the frequencies of ν_{as}, CH_2 of both M20A and M30B at room temperature before and after thermal treatment under air condition. From IR data, for M20A, the alkyl chains seem to adopt a moderately disordered structure and after the treatment, as shown in the band shift to higher frequencies, a more disordered structure, due to the increase of the available space in the interlayer by the release of organic molecules. For M30B, the chains may already adopt a relatively more disordered structure initially, as featured in high frequency of ν_{as}, CH_2, which exhibit relatively little increase of chain disorder after thermal treatment.

Table 4. Frequencies of asymmetric CH_2 stretching (ν_{as}, CH_2) of alkyl chains intercalated into OMMTs at room temperature before and after thermal treatmant

	ν_{as},CH_2	
	Before thermal treatment	**After thermal treatment**
M20A	**2919.2 cm^{-1}**	**2922.5 cm^{-1}**
M30B	**2924.9 cm^{-1}**	**2926.0 cm^{-1}**

Considering the previous theoretical and experimental results [4,5], for M20A, the monolayer, similar as the paraffin-type monolayer but with disordered chain conformations, is most likely, which is consistent with basal spacing (2.49 nm), IR data, the organic content and the size of organic ion, and the lateral bilayer for M30B with basal spacing of 1.84 nm. Considering this structure of bilayer, surface area of M30B per tallow chain is thought to be four times lager than that of M20A [4]. This also confirms that the chains of M30B adopt a more disordered structure originally. After thermal treatment, the chains in M20A seem to still adopt a mortolayer but a more disordered structure as shown in the IR results, while little decrease of the interlayer spacing is observed. On the other hand, in the case of M30B, in which the increase of the chain disorder is relatively small, the structure of the chain aggregation is thought to change from the lateral bilayer to the intermediate (basal spacing 1.47 nm) between the lateral bilayer (~1.8 nm) and monolayer (~1.3 nm) after thermal treatment. These structural changes with thermal treatment are illustrated schematically in Figure 3. Although both OMMT show the considerable amount of the loss of organic ions, M20A exhibits little decrease of the interlayer spacing, while relatively larger decrease is observed for M30B. This difference may result from the difference of the interlayer structure as explained in the above. In addition to decrease of interlayer spacing, the release of organic ions may make the surface character of OMMT less organophilic, which can effect melt intercalation of polymer into OMMT in view of thermodynamic interaction.

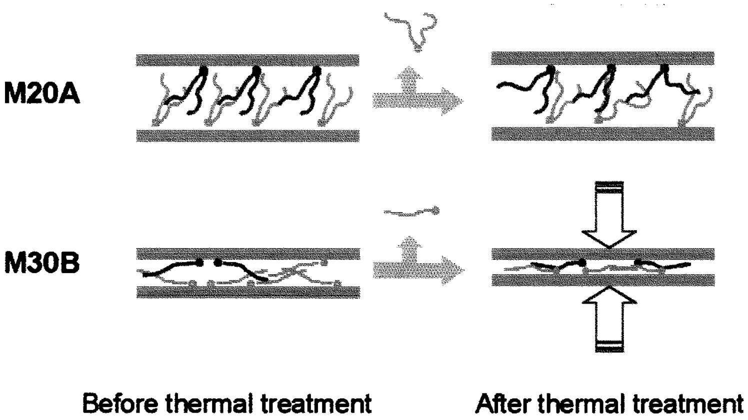


Figure 3. Schematic illustration of the interlayer structures of OMMTs before and after thermal treatment at room temperature

Microstructure of PP nanocomposites

The mixtures of PP and OMMT with maPP were prepared in order to investigate the effect of the type of OMMT upon the formation of nanocomposite. According to the previous studies [6,7], maPP should first intercalate into the interlayer of clay and expand the layers of clays in order to realize the formation of PP nanocomposite with the exfoliated structure. Figure 4 shows the XRD patterns of M20A, PP-M20A, maPP-M20A and PP-maPP-M20A. In maPP-M20A, Peak shifts to lower angles and broadens, indicating that the intensive intercalation occurs. Remarkably, PP-maPP-M20A exhibits the exfoliated structure other than maPP-M20A. This may result from the effects of large shear by PP matrix and the diffusion of PP into expanded clay layers during melt mixing.

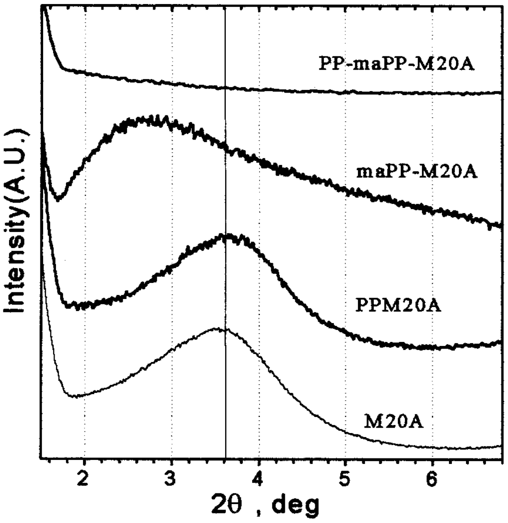


Figure 4. The XRD patterns of the mixtures of PP, maPP and M20A

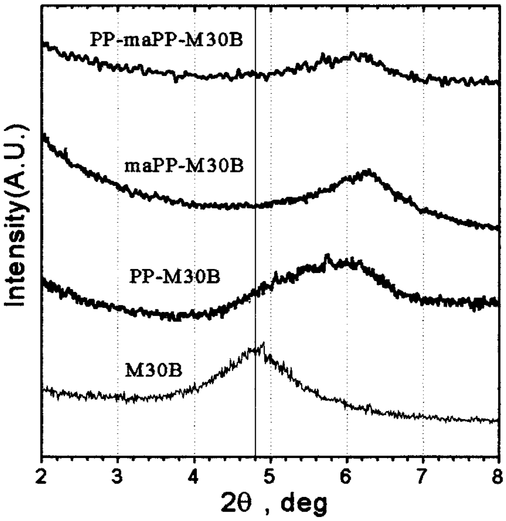
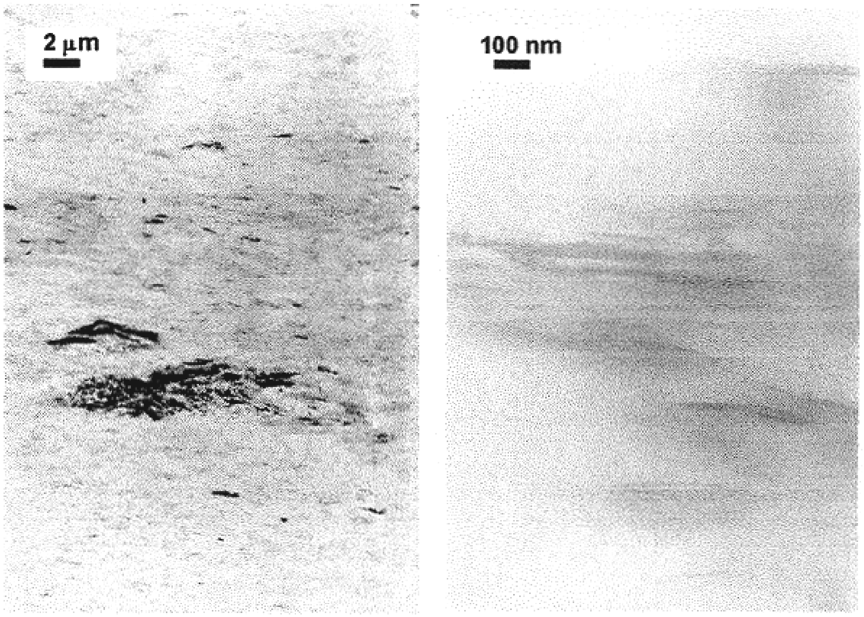


Figure 5. The XRD patterns of the mixtures of PP, maPP and M30B

However, maPP-M30B and PP-maPP-M30B exhibits both the decrease of the interlayer spacing and the gradual increase in the diffraction intensity at low angles (Figure 5). This indicates that maPP-M30B and PP-maPP-M30B might be exfoliated only partially and other clay layers, which were not delaminated, might collapse. As shown in Figure 6, The TEM images of PP-maPP-M03B show this fact more clearly, in which micro-sized particles of clays co-exist with some delaminated clay layers.



(a) (b)

Figure 6. TEM images of PP-maPP-M30B (a) × 2,500 (b) × 50,000

We have expected that the ethanol group of M30B could have the strong favorable interaction with maleic anhydride group of maPP to increase melt intercalation, while unfavorable with the propylene unit of maPP. However, PP-maPP-M30B was exfoliated only partially. The collapse may result from poor thermal stability of M30B as observed previously. M30B has the smaller interlayer spacing and somewhat polar character due to ethoxy groups. To make things worse, thermal decomposition makes the surface character of M30B less organophilic, in addition to the decrease of the spacing that increases the entropical hindrance for polymer confinement. Therefore, considering that both melt intercalation and thermal decomposition occurred simultaneously during melt processing, the clays intercalated only in the initial stage could be delaminated since the thermally decomposed clays do not satisfy the condition for melt intercalation any more. We can not observe the direct effect of the interaction between M30B and maPP on melt intercalation due to thermal decomposition of M30B. However, it may be the evidence of the positive effect of this interaction that at least partial exfoliation could be realized although M30B has such poor thermal stability and initially small interlayer spacing. In the case of M20A, even if the decrease of the spacing is negligible, the release of organic ions will also make the surface character less organophilic like that of M30B. But, since M20A with ditallow chains is more organophilic initially, the condition for melt intercalation, in spite of thermal decomposition, is thought to be still satisfied, resulting in the intensive intercalation or the exfoliation aided by shear.

Conclusion

The surface characteristics of organically modified clay (OMMT) had the great impact on the thermal characteristics of OMMT and the formation of PP nanocomposite via melt intercalation. OMMT exhibited the release of the intercalated ions due to thermal decomposition at the increased temperature, resulting in the decrease of the interlayer spacing and the change of the surface character. Thermal characteristics of OMMT largely depended on not only the type of alkylammonium ions in OMMT but also the interlayer structure. Thermal characteristics, while processing at high temperature, was so important that PP composite was exfoliated only partially when using M30B, which had initially small interlayer spacing and somewhat polar character. This resulted from the decreases of the interlayer spacing and the surface organophilicity due to thermal decomposition of M30B during processing.

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10. These values were calculated from the results of elemental analysis (E.A.) as follows: the weight of each element per OMMT of 100g before thermal treatment = 100 x weight percent of each element before thermal treatment(E.A.); the weight of each element after thermal treatment = 100 x weight percent of each element after thermal treatment(E.A.) x weight percent of inorganic content before thermal treatment(E.A.) ÷ weight percent of inorganic content after thermal treatment(E.A.)