EFFECT OF TRIHEXYLTETRADECYLPHOSPHONIUM ON THERMAL DEGRADATION PROPERTIES OF LOW LINEAR DENSITY POLYETHYLENE/MONTMORILLONITE NANOCOMPOSITES

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ABSTRACT

Low linear density polyethylene/organo-montmorillonite (LLDPE/OMMT) nanocomposites at 1–5 wt% OMMT loading were prepared by the melt intercalation technique. The OMMT was synthesized via an ion exchange reaction by replacing the interlayer of sodium ions (Na^+) in the repeating unit of silicate layers of montmorillonite (MMT) with the cationic surfactant in the form of trihexyltetradecylphosphonium (THTDP) ions. The obtained OMMT and its nanocomposites were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, and elemental and thermogravimetric analyses. The interlayer spacing of MMT expanded from 1.41 to 2.29 nm due to the accommodation of THTDP ions in the intergallery of OMMT. The introduction of THTDP in the interlayer of OMMT rendered better dispersion of OMMT layers in the LLDPE/OMMT nanocomposites and significantly improved the thermal degradation properties of nanocomposites as compared to the pristine LLDPE.

Keywords: Melt intercalation; Nanocomposites; Organo-montmorillonite; Thermal degradation

1. INTRODUCTION

Polymer/montmorillonite (MMT) nanocomposites have attracted attention recently; in fact, materials engineers have focused on them based on the need to overcome the limitations of traditional micrometer-scale composites (Livi et al., 2011; Abdullah et al., 2010). The term "nanocomposite" describes phases of MMT dispersed in the polymer matrix at the nanometer level. Systems in which the inorganic particles make up the individual layers of a lamellar compound most typically smectite clay or nanocomposites of a polymer embedded among layers of silicates exhibit dramatically altered physical properties relative to the pristine polymer. Polymer-silicate/clay nanocomposites are suitable for industrial applications, such as high-barrier packaging for food products and electronics (Malucelli et al., 2007).

Notably, MMT is among the most common minerals on the earth's surface, and it has been used by man for centuries. In the preparation of low linear density polyethylene/organoclay composites, modification of MMT from hydrophilic to organophilic is necessary for compatibility with the organic LLDPE.

To change the character of MMT from hydrophilic to organophilic, a surfactant is used to alter the structure of MMT before mixing it with the polymer. The surfactant reduces the surface energy of the inorganic host and improves its wetting characteristics when mixed with the polymer. The ion exchange between the organic surfactant and sodium ions in the interlayer of MMT expands the interlayer space, allowing large polymer molecules to enter. This process improves the miscibility of MMT with organic polymers, thereby achieving a good dispersion of MMT in the polymer matrix (Naveau et al., 2011; Zhao et al., 2010).

Common modification treatment for MMT utilizes inorganic cations, such as sodium or calcium which located in the interlayer of MMT. It involves the exchanging of these cations with the organic cationic surfactants, for instance alkylammonium cations. However, alkylammonium cations has low thermal stability, hence the obtained organoclay could suffer decomposition following the Hofmann elimination reaction (Zanetti et al., 2001; Xie et al., 2001) during the melt intercalation process. The resulting products from this decomposition process would then catalyze the degradation of polymer matrixes (Qin et al, 2004). The clay itself also can catalyze the degradation of polymer matrixes as well (Xie et al., 2001; Zanetti et al., 2001). The latter two actions would be expected to reduce the thermal stability of polymer-clay nanocomposites.

In this study, sodium montmorillonite (Na^+-MMT) was modified with the thermally stable organic cationic surfactant, trihexyltetradecylphosphonium (THTDP), to form an organoclay of MMT-THTDP (OMMT). Subsequently, the synthesized OMMT was introduced to LLDPE, forming the composites. Effects of the organoclay addition on the thermal degradation properties of newly formed composites were investigated.

2. EXPERIMENTAL
Na^+-MMT, with cation exchange capacity of CEC 119 meq/100 g, was purchased from Kunimine Industries, Japan. The OMMT was prepared via an ion exchange between sodium ions of Na^+-MMT and THTDP ions. Further, 20 g of Na^+-MMT was dispersed into 1000 mL of water at 80ºC and stirred continuously for an hour. The solution of diethyl ether containing THTDP chloride was then poured into the suspension and stirred vigorously for 12 h to flocculate MMT. The solution was then warmed to 60°C to evaporate the diethyl ether. The resulting solution was filtered, and the precipitate of OMMT was washed in hot water (80°C). The resulting OMMT paste was mixed with petroleum ether, dried, ground, and sieved to obtain the final products with particle sizes of less than 100 µm. The resultant OMMT was used for the preparation of composites. The LLDPE was mixed with either Na^+-MMT or OMMT with an internal mixer that was equipped with roller rotors. Composites were prepared by the intercalation technique at a temperature of 180°C and a rate of 80 rpm for 20 min.

Powder X-ray diffraction (XRD) was used to examine the nature of MMT using CuKα radiation with a wavelength λ equal to 1.540562 Å at a scan rate of 2°/min. Fourier transform infrared (FTIR) spectra were recorded at room temperature using the KBr disk method. The CHNS-932 elemental analyzer was used to determine the quantitative elemental composition of carbon (C) and hydrogen (H) in MMT before and after modification. A thermogravimetric analysis (TGA) was carried out in a Pyris 6 PerkinElmer instrument with a nitrogen atmosphere heated from room temperature to 800°C at a rate of 20°C/min.

3. RESULTS AND DISCUSSION
In this study, OMMT enhanced by the addition of THTDP was synthesized and used as the precursor for the preparation of LLDPE/OMMT nanocomposites. It was determined that a cationic surfactant of THTDP could change the hydrophilic character of MMT to become

organophilic; thus, LLDPE/OMMT nanocomposites were formed. The standard methods for the characterization of organoclay and their nanocomposites are X-ray diffraction, FTIR, and elemental and TGA. XRD gives information about the gallery structure of the silicate in the nanocomposite and the amount of non-exfoliated, ordered stacks of clay (Naveau et al., 2011). For this research, the XRD patterns of the nanocomposite LLDPE/OMMT containing 1–5 wt% organoclay were compared.

The diffraction peak at $2\theta = 5.95^o$ belonged to the (001) planes of Na^+-MMT, which is the characteristic peak of pure MMT with basal spacing of 1.41 nm (Figure 1). The value of 2θ that corresponded to the (001) planes of OMMT was 4.03^o with basal spacing of 2.29 nm. It is clear that the basal spacing of the silicate layers of OMMT was larger than that of pure MMT and the location of the (001) plane had shifted to the lower 2θ angles. Hence, it can be concluded that the THTDP surfactant had been intercalated into the silicate layers of MMT, thus increasing the basal spacing due to the larger molecular size.
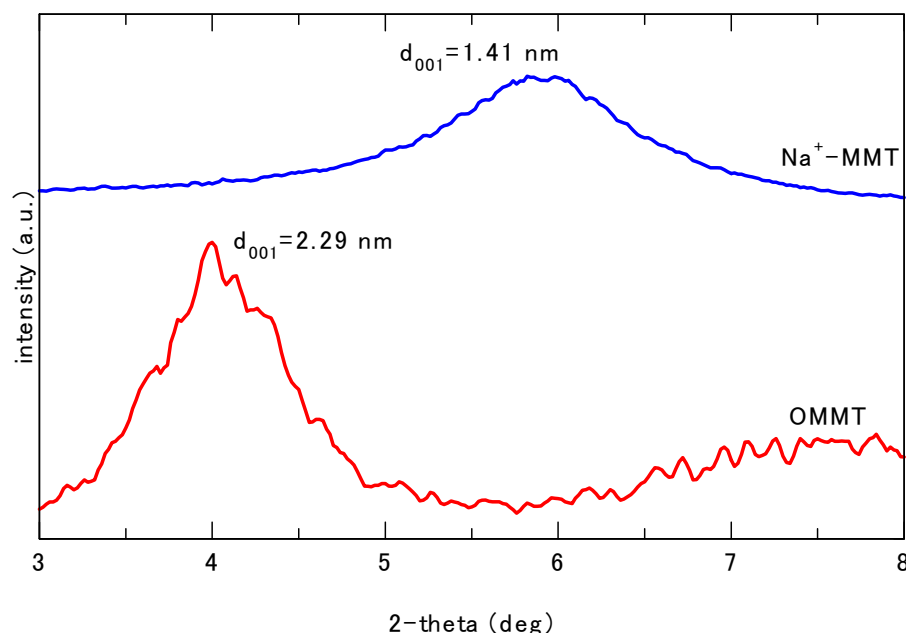

Figure 1 Diffraction plane of d001 in Na+-MMT and OMMT

The FTIR spectrum of Na^+-MMT shows four main absorption peaks at 3646, 3480, 1655, and 1059 cm^{-1} (Figure 2). The bands between 3500 and 3700 and near 3400 cm^{-1} are indicative of MMT (Patel et al., 2007). Absorption peaks at 3646 and 3480 cm^{-1} are assigned to the –OH in the Si-OH and Al-OH groups of the tetrahedral and octahedral sheets of MMT and water molecules (Avalos et al., 2008). The absorption peak in the region of 1655 cm^{-1} is attributed to the OH bending mode of adsorbed water, while the peak at 1059 cm^{-1} is attributed to the Si-O stretching (in plane) vibration for layered silicates. For the FTIR spectrum of OMMT, the four main absorption peaks can be observed together with the existence of three new peaks at 2941, 2916, and 1472 cm^{-1}. Absorption peaks at 2941 and 2916 cm^{-1} are ascribed to the asymmetric and symmetric vibrations of the methylene group (CH_2) of the aliphatic chain, respectively (Patel et al., 2007); the peak at 1472 cm^{-1} is attributed to the H-C-H stretching vibration. These three absorption peaks are indicative of the alkyl chain in THTDP used for modifying MMT.

In this study, the existence of THTDP in OMMT was supported by elemental analysis. As expected, the percentage of C and H increased dramatically from 0.08 to 32.16% and from 0.81 to 6.50%, respectively, in OMMT. Thus, the presence of the alkyl group in the surfactant of
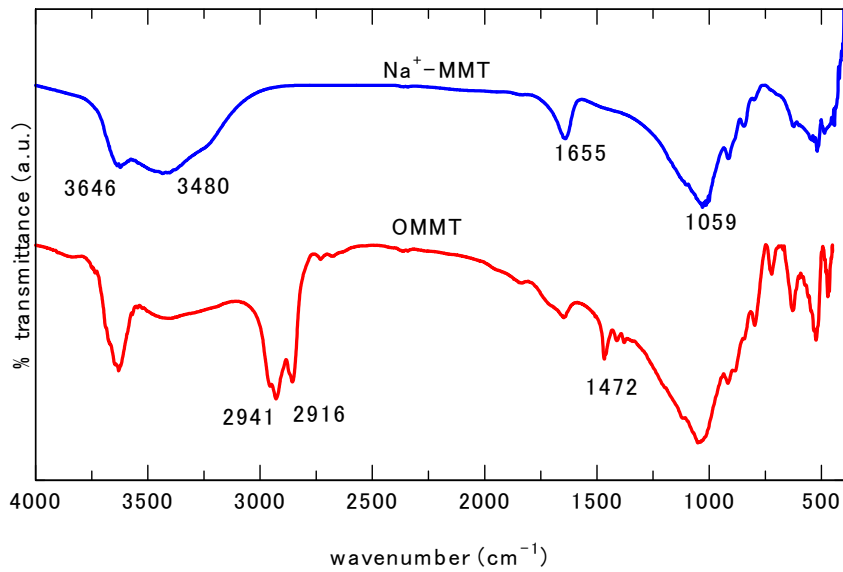
THTDP is shown.

Figure 2 FTIR spectra of Na$^+$-MMT and OMMT

To examine the dispersion of LLDPE into the MMT layers, basal spacing and the diffraction angle of Na$^+$-MMT were used for comparison. As shown in Figure 3, there was an insignificant shift in 2θ values. The values for basal spacing of MMT in the LLDPE matrix showed no difference between the pristine Na$^+$-MMT and its composites with LLDPE (around 1.4 nm). This composite was classified as conventional because there was no insertion of LLDPE into the interlayer of MMT.
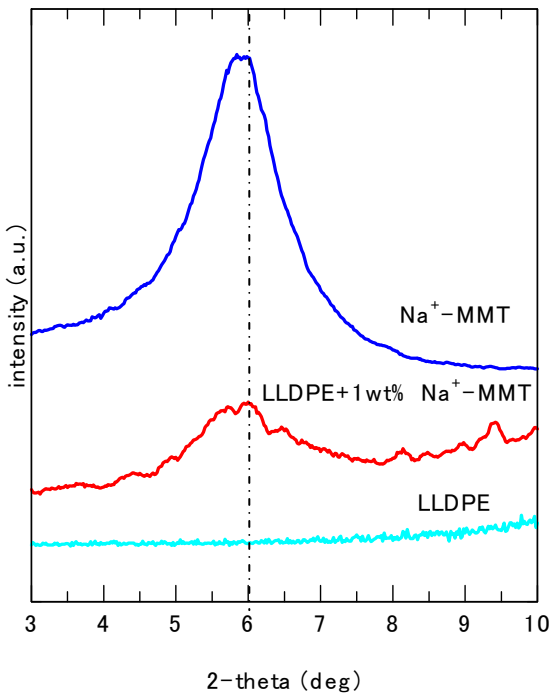

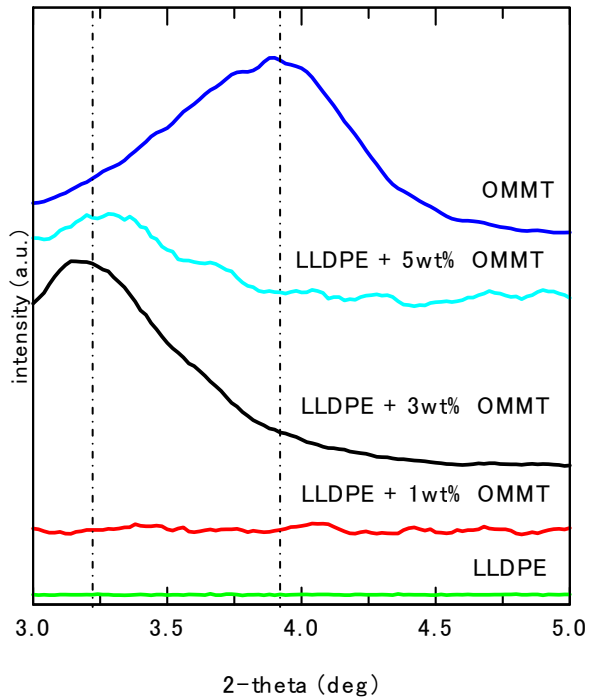Figure 3 XRD patterns for composites of LLDPE and Na$^+$-MMT

Figure 4 XRD patterns for composites of LLDPE and OMMT

Figure 4 shows the (001) diffraction plane of MMT in the LLDPE/OMMT composites shifted to the lower angles compared to the organoclay OMMT. This indicates that the LLDPE was intercalated into the clay layers. For 1 wt% of clay loading, the presence of exfoliated nanocomposites could not be verified even though the peak had disappeared. We observed that a small quantity of OMMT contributed to reducing the intensity peak in XRD spectra. Exfoliated nanocomposites are the best materials based on their improved properties, such as higher heat distortion temperature, enhanced flame resistance, increased modulus, superior barrier properties, and decreased thermal expansion coefficients (Wang et al., 2001). LLDPE/OMMT with 3 and 5 wt% OMMT loading were the intercalated nanocomposites, which were evident from shifting of the (001) diffraction plane toward the lower 2θ angles. For 3 wt% OMMT loading, the basal spacing increased from 2.29 to 2.76 nm. For 5 wt% OMMT loading, the shifting of the peak increased from 2.29 to 2.65 nm.

Degradation temperatures for pure LLDPE and LLDPE/OMMT composites with variations in clay content are shown in Table 1, and the comparison of TGA and derivative thermogravimetric (DTG) thermograms for both materials are shown in Figures 5 and 6. Generally, the degradation temperatures of LLDPE/OMMT composites are higher than those found in the pure LLDPE matrix.

The maximum thermal degradation temperature (T_{max}) for LLDPE/OMMT showed a similar trend in that the additions of 1, 3, and 5% OMMT resulted in an increase in T_{max} by 9, 10, and 14°C, respectively, as compared to pristine LLDPE. It is believed that higher THTDP concentrations render higher hydrophobic characteristics that enhance compatibility with polymer matrices (Nayak & Mohanty, 2010). In addition, the stable morphology of the dispersed phase and the presence of intercalated silicate layers may be the primary reason for the enhanced thermal stability of the blend nanocomposites (Zhao et al., 2005). This phenomenon can be explained by clay layers which have good barrier action; when dispersed in the nanocomposites, it prevents heat from transmitting quickly and limiting continuous degradation of the nanocomposites (Zhang et al., 2003).

Table 1 Degradation temperatures of LLDPE and its nanocomposites

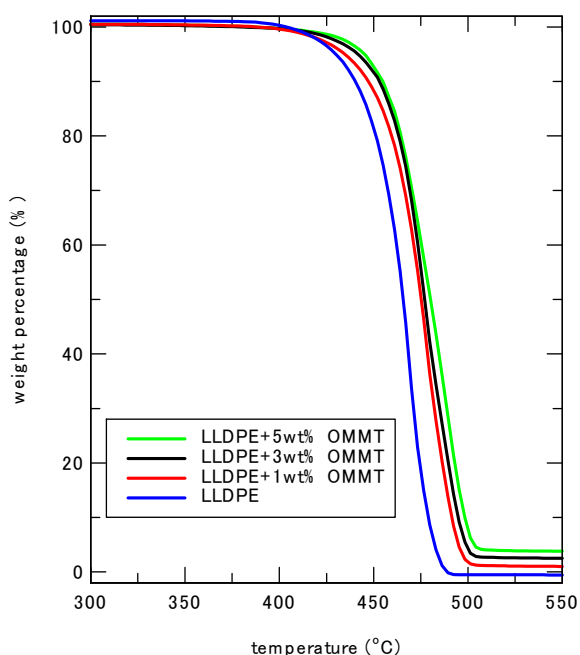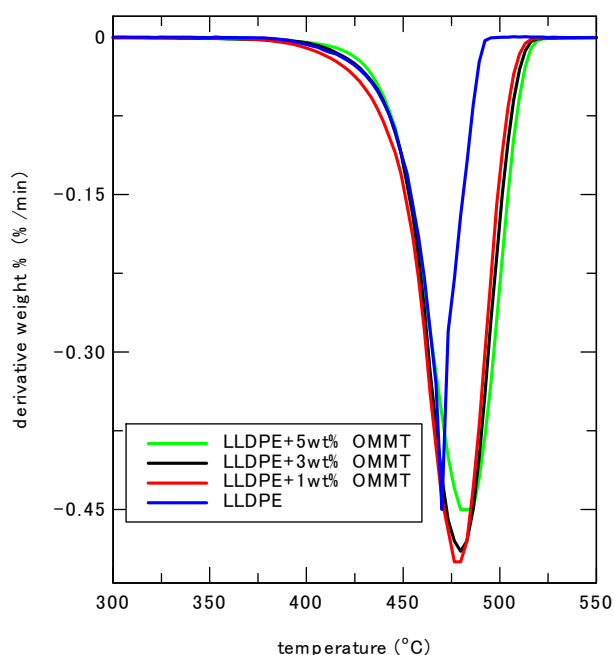| Weight loss (%)	OMMT content (% wt)			
	0	1	3	5
5	430°C	435°C	442°C	445°C
50	466°C	475°C	477°C	481°C
95	482°C	494°C	499°C	504°C
T_{max}	470°C	479°C	480°C	484°C

Figure 5 TGA thermograms of LLDPE /OMMT
nanocomposites

Figure 6 DTG thermograms of LLDPE
/OMMT nanocomposites

4. CONCLUSION

The organophilic character of hydrophilic MMT was attained by replacing Na^+ ions in the interlayer with a cationic surfactant of THTDP. Compatibility with the organic LLDPE material was achieved. The compatibility between organoclay and LLDPE was shown by the formation of the LLDPE/OMMT nanocomposites. X-ray studies showed the LLDPE/OMMT composites were in the intercalated structure at 3 and 5 wt% of OMMT loading. The LLDPE/MMT nanocomposites showed higher thermal degradation levels than those for pure LLDPE based on the barrier action of layered silicates within MMT.

5. ACKNOWLEDGEMENT

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