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Novel clay treatment and preparation of Poly(ethylene terephthalate)/clay nanocomposite by *In-situ* polymerization

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Summary

Novel clay treatment was proposed for poly(ethylene terephthalate) (PET)/clay nanocomposite and the clay dispersed trimellitate ester oligomers were prepared by esterification with 1, 2, 4-Benzenetricarboxylic anhydride (TMA, trimellitic anhydride) and montmorillonite (MMT) dispersed ethylene glycol (EG). The structure, interlayer distance and thermal stability of the clay dispersed trimellitate ester oligomers were investigated by NMR, WAXD, SAXS and TGA techniques.

Introduction

Polymer/clay nanocomposites are commonly based on polymer matrices reinforced by nanofillers such as layered polysilicates and silica-titania oxides, silica beads, cellulose whiskers, zeolites as well as colloidal dispersion of rigid polymers and many others [1-4]. Polymer/clay nanocomposites have several advantages such as lightweight, enhanced mechanical properties and barrier properties. The mechanical properties are potentially superior to fiber reinforced polymers since the reinforcement from the inorganic layers occur in two dimensions rather than in one dimension. The nanocomposites also exhibit outstanding diffusional barrier properties without requiring a multi-polymer layered design [5]. Besides, adding a small quantity of these inorganic clay (0.5 - 5 %) can increase various properties of polymer materials, including rigidity, heat resistance, UV resistance, and flame retardancy, and can lower water absorption and thermal expansion coefficient while at the same time maintaining transparency and allowing better recycling, when compared to their micro- and macro-composite counterparts [6-7].

The poly(ethylene terephthalate) (PET)/clay nanocomposite have been studied since early 1991's. There are many companies developing PET nanocomposites (PCN) having enhanced gas barrier properties, but commercialization is still to come. The major drawbacks in PCN commercialization are discoloration, haze, I.V. drop, side reactions and agglomerated clay particles in PET matrix [8-13].

The objective of this study is to develop proper clay system for enhancing PCN properties. The novel clay treatment first proposed in this paper is focusing on improvement of the dispersibility in the PET matrix. The novel clay treatment is based on trimellitate ester oligomers (TEO) which are synthesized by esterification of TMA and EG swollen montmorillonite (MMT).

Experimental

Materials

1, 2, 4-Benzenetricarboxylic anhydride (TMA, Aldrich Chemical Co., Inc., 97%) and ethylene glycol (EG, Honam Petrochemical Corp., Korea) were used as received. And the pristine MMT for the novel clay treatment was Cloisite® Na^+.

Purified terephthalic acid (PTA, Samsung Petrochemical Co. Ltd., Korea) and EG were used as received for PET polymerization. Antimony(III) oxide (Sb_2O_3, Aldrich Chemical Co., Inc., USA, 99%) was used as a polycondensation catalyst and triethyl phosphate (TEP, Aldrich Chemical Co., Inc., USA, 99%) was a thermal stabilizer in the polymerization process. Cobalt(II) acetate tetrahydrate (CoAc, Merck Ltd., Korea) was used as a color inhibitor.

Novel clay treatment

This novel clay treatment was proposed for simplification of organoclay preparation and enhancement of intercalant's reactivity with PET. First step of the novel clay treatment was swelling of the pristine MMT in EG. The pristine MMT and EG was stirred by mechanical agitator in resin kettle under nitrogen atmosphere for 2 hours at 170 °C. Second step was addition of TMA into the MMT dispersed EG. When the TMA was completely added to the resin kettle, the temperature was elevated to 200 °C by 10 °C/min. rate and the esterification between TMA and EG was initiated at 200 °C. The reaction was lasted for 2 hours. The equivalent ratio of the reactants can be changed from 1 equiv. of TMA and 1.5 equiv. of EG to 1 equiv. of TMA and 3.0 equiv. of EG. The amount of the pristine MMT in the total reactant was 6.5 wt% and 12 wt%. The clay dispersed TEO by this novel clay treatment was directly added in the preparation of PCN.

Preparation of PET/clay nanocomposite (PCN)

The PCNs were synthesized by in-situ polymerization. This polymerization process consists of 2-step melt phase polymerization (esterification and polycondensation) in a 5L pilot reactor. In each polymerization, the slurry mixture of the reactants composed of PTA and EG, additives of TEP and CoAc, polycondensation catalyst (Sb_2O_3) was prepared. The mole ratio of EG/PTA was 1.3, and 30 ppm TEP, 40 ppm CoAc were used in this reaction. The 250 ppm Sb_2O_3 was used as a polycondensation catalyst. The slurry mixture was heated to 250 °C under nitrogen atmosphere for 5 - 6 hours in the esterification step. It was transferred to polycondensation reactor when the condensed water by esterification was completely removed. The clay dispersed TEO from the novel clay treatment was added to this polycondensation step. The temperature was raised to 285 °C in the polycondensation reactor under vacuum condition (0.5 torr). The polycondensation step was continued for about 2 hours until the intrinsic viscosity (I.V.) value of the PCNs reached 0.6 dl/g. The I.V. value was checked by the torque value of the agitator in the pilot reactor. When the polycondensation reaction was completed, the final product, PCN was extruded by nitrogen pressure and quenched in water bath and then pelletized. The clay contents in the PCNs were 0.5 wt% and 1 wt%, which were controlled by using the TEO having different amount of clay. In other words, the 0.5 wt% clay added PCN was prepared by adding 6.5 wt% clay dispersed TEO and the 1 wt% clay loaded PCN was prepared by adding 12 wt% clay dispersed TEO.

Characterization

BRUKER AVANCE DRX400 NMR spectrometer was used to confirm the synthesis of the TEO from the novel clay treatment. The NMR spectrum of the TEO was obtained from clay dispersed TEO samples. Clay was separated from TEO by using trifluoroacetic acid at 75 °C and $CDCl_3$ added into the TEO and trifluoro-acetic acid. And then NMR analysis was proceeded at room temperature.

Wide-angle X-ray diffraction (WAXD) measurements were performed at ambient temperature on RIGAKU D/MAX-RC diffractometer with CuKα radiation to measure the d-spacing of the clay in TEO. The scan range was from $2\theta = 1.2 - 10°$ and the scan speed was 2°/min. The d-spacing was calculated by using Bragg's law. Small-angle X-ray scattering (SAXS) was also used to check the d-spacing information near small-angle area for the clay in TEO. The SAXS measurement was performed by RIGAKU SWXD and the scan range was from $2\theta = 0.3 - 6°$.

Thermogravimetric analysis was performed under air atmosphere by using a TA Instruments Auto TGA 2950 to measure the thermal stability of the clay dispersed TEO. The samples were heated to 900 °C at a rate of 20 °C/min.

The morphology of the clay dispersed TEO was investigated by transmission electron microscope (TEM). The TEM micrographs were obtained by a Carl Zeiss Leo EM912 Omega EF TEM using an acceleration voltage of 120 kV. The specimens were also taken by LEICA microtome after molding by Caldofix resin and hardener at 45 °C. The morphologies of the PCNs were investigated by scanning electron microscope (SEM), atomic force microscopy (AFM). SEM micrographs were obtained by a TOPCON SM-701. The vertical section of the PCN pellet was cut by LEICA microtome at room temperature. A POLARON SC7610 sputter coater was used to coat the microtomed surface of the pellet with gold. AFM is a convenient tool compared to SEM and TEM in the sense that the sample preparation is simple and the phase information of the 2D section area could be easily obtained [14]. AFM images were investigated by a Digital Instruments Nanoscope IIIa in Tapping^{TM} mode with the standard etched silicon probe tips. The scanning frequency was 0.5 Hz and scanner was type 'E', all the images shown here are 'Phase' images and have been filtered through the 'Planefit' procedure. SEM specimens were used as AFM specimens before coating treatment with gold.

Results and Discussion

Figure 1 illustrates NMR spectrum of the clay dispersed TEO. The oligomer had characteristic peak near 7 to 9 ppm. And EG was completely reacted with TMA because there was no peak for unreacted EG at about 3.7 ppm. In addition, diethylene glycol (DEG) unit in the oligomer structure existed with a small amount at about

4.2 ppm. DEG unit is generally generated in the main chain by side reaction during esterification.

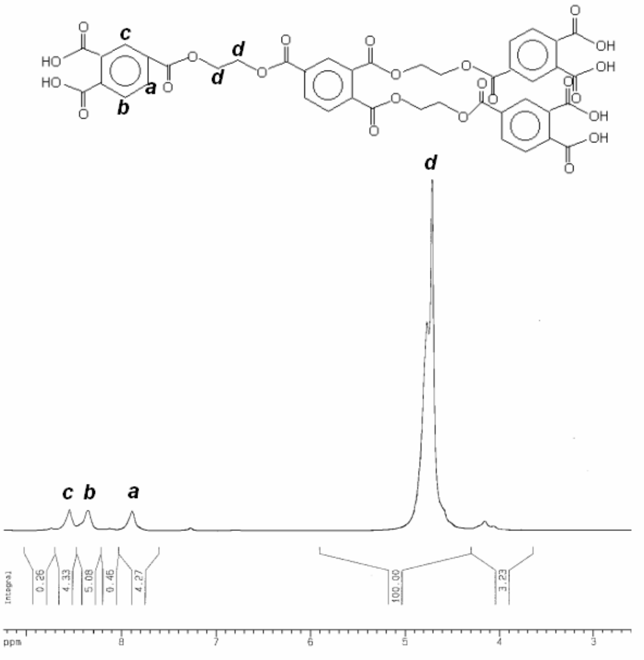

Figure 1. The ^{1}H-NMR spectrum for the clay dispersed TEO

The interlayer distance of the clay dispersed TEO having different equivalent ratio was investigated by WAXD. When the TMA/EG equivalent ratio was changed from 1/3 to 1/1.5 (Table 1), the d-spacing value shifted to small angle which means the interlayer distance increased by incorporating TEO between clay layers. The d-spacing of 1/3 equivalent ratio was 44Å (2θ = 2.01°) and the one of 1/2.5 equivalent ratio was 53Å (2θ = 1.68°). The d-spacing cannot be detected when the equivalent ratio was decreased below 1/2.5. Another d-spacing value was observed in 17 to 18 Å (2θ = 5.2 - 4.9°) be originated from MMT dispersed in EG [15-16]. Therefore, there were 2 parts of d-spacing value in the TEO, one was high value above 50 Å, the other was medium value at about 18 Å. The detailed results are summarized in Table 1 and shown in Figure 2. SAXS analysis of 1TMA/1.5EG TEO was also conducted to confirm the peak in low angle region. The SAXS pattern was very similar pattern with

Table 1. The WAXD information of the various clay dispersed TEOs

Equiv. Ratio (TMA/EG)	1 / 1.5	1 / 2	1 / 2.5	1 / 3
1st d-spacing (Å)	disappeared	disappeared	53	44
2nd d-spacing (Å)	18.1	18.0	17.2	17.2

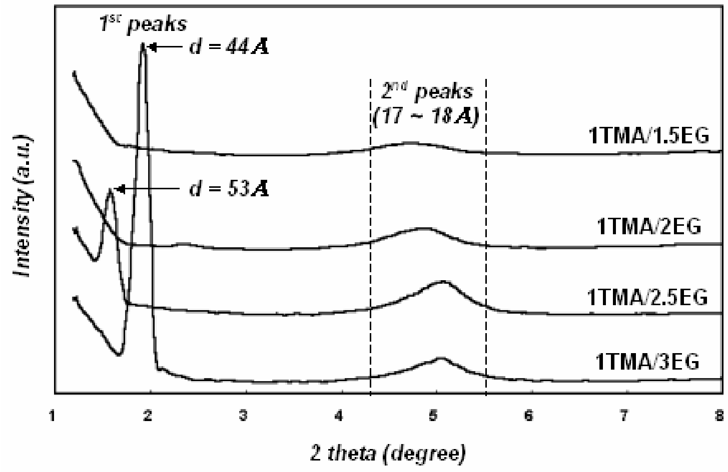

Figure 2. WAXD patterns of the various clay dispersed TEOs

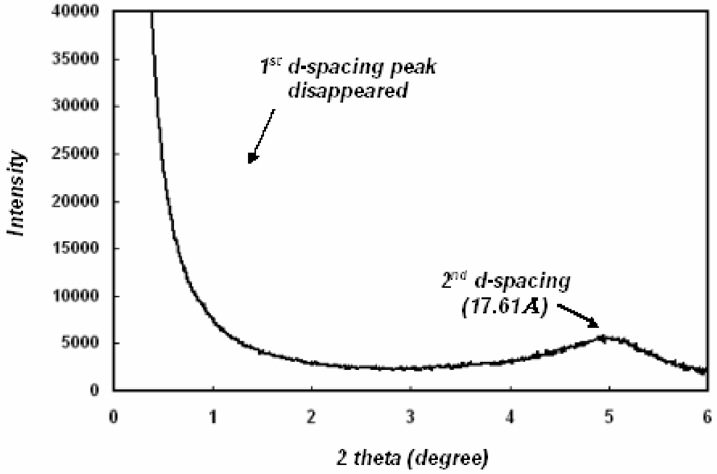

Figure 3. SAXS pattern of the clay dispersed TEO with 1TMA/1.5EG equivalent ratio

WAXD result and no additional peaks at low angle region were observed in the SAXS analysis (Figure 3).

The thermal stability of the various clay dispersed TEO (6.5 wt% clay loading) was investigated by TGA. When the equivalent ratio of TMA/EG in the TEO was varied to 1/1.5, the thermal stability of the TEO increased. The amount of decomposition at 290 °C decreased from 44 % to 8 % and the temperature of maximum decomposition rate for the first stage (T_{d1st}) also increased from 152 °C to 263 °C. The initial temperature of the major decomposition for the TEO (equiv. ratio : 1/1.5) was up to 404 °C which is high enough to resist during PET polymerization. And the TEO without clay had similar decomposition pattern with TEO including clay. There were slightly different from initial decomposition rate and final residue. The detailed results are shown in Figure 4 and summarized in Table 2.

Table 2. TGA results of the various clay dispersed TEOs

Equiv. Ratio (TMA/EG)	$^1T_{d1st}$	$^1T_{d2nd}$	$^1T_{d3rd}$	Weight loss (%) at 290 °C
1 / 1.5	263.4	457.6	519.8	8
1 / 2.0	229.7	431.5	489.7	19
1 / 2.5	182.9	446.0	504.9	31
1 / 3.0	152.1	452.8	510.6	44

[1] The temperature of the maximum decomposition rate for 1st stage, 2nd stage and 3rd stage

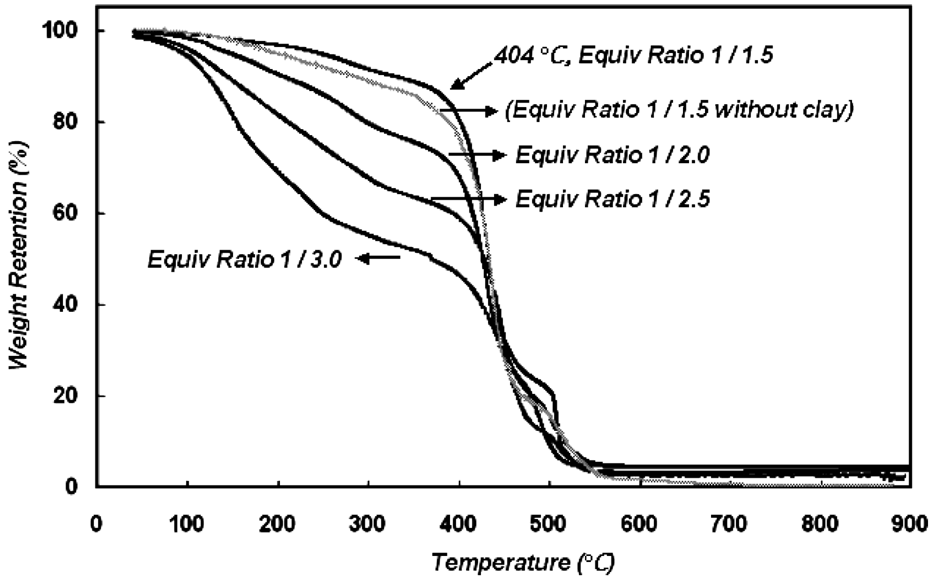

Figure 4. TGA thermograms for the various TEOs

It was estimated that exfoliated structure and intercalated structure of the clay were co-existing in the TEO matrix from the results of the WAXD and SAXS. The real morphologies of the TEOs were confirmed by TEM. Figure 5 shows the TEM micrographs of the TEOs. Many clay particles were delaminated in the TEO matrix and the agglomerated clay bundle size decreased to 20 nm levels. But large agglomerated clay particles with width ranging 100 nm levels were also observed in the TEO matrix. The TEO having high clay loadings (12 wt%) shows images similar to 6.5 wt% clay loaded TEO.

The morphologies of the PCN synthesized with this TEO were investigated by SEM and AFM. Figure 6 shows the micrographs of the PCN including 1 wt% clay by adding the 12 wt% TEO. From the SEM image, the aggregated clays were shown as white particles in the PCN existed as uniform dispersion state with sizes around 1 micron. And the clay dispersion with sub-micron level was also checked by the AFM image. From the result of the microscopic images, it was found that the clay from the novel clay treatment maintained well dispersion state in the PET matrix.

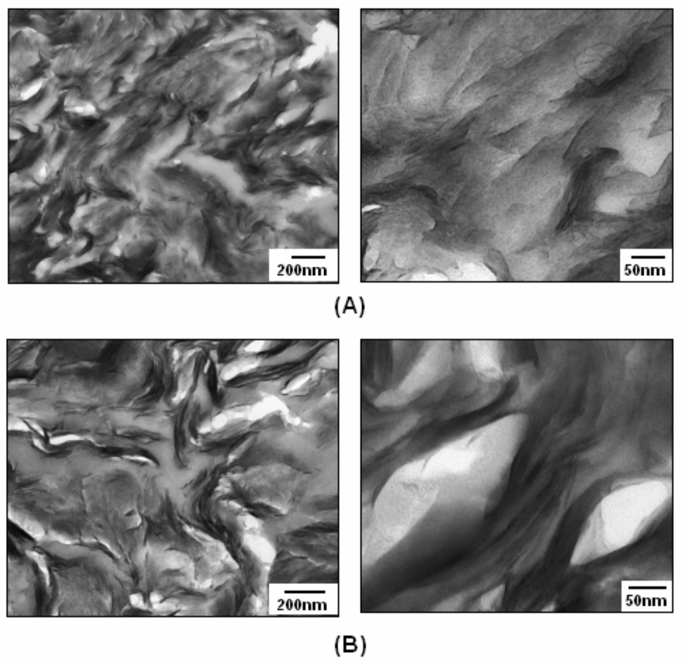

Figure 5. TEM micrographs of the clay dispersed TEOs; (A) 6.5 wt% clay loaded, (B) 12 wt% clay loaded

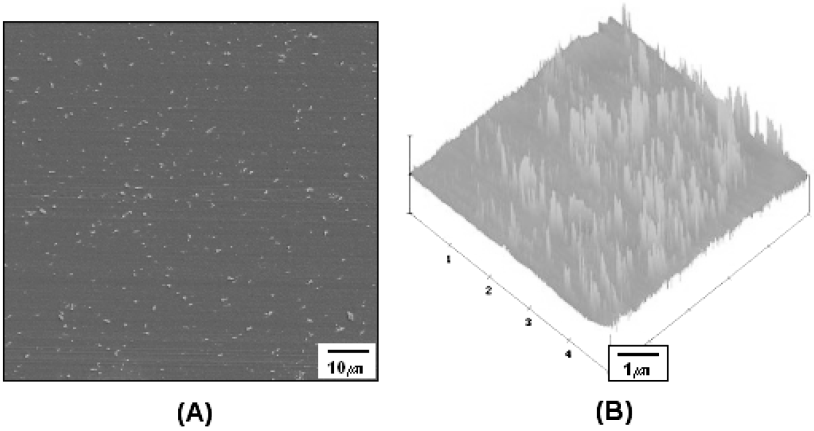

Figure 6. SEM and AFM images of the PCN including 1 wt% clay; (A) SEM micrograph, (B) AFM image

Conclusions

The clay dispersed trimellitate ester oligomers (TEO) by novel clay treatment were prepared by esterification with controlling the equivalent ratio of TMA and EG. The structure of the TEO was confirmed by NMR spectrum. The optimum equivalent ratio of the TEO was 1 TMA / 1.5 EG from the WAXD, SAXS and TGA analysis. The dispersibility of the clay in the TEO matrix was checked by TEM and many layers of the clay were delaminated and well dispersed in the matrix. The PET/clay nanocomposite was prepared using this clay dispersed TEO by in-situ polymerization and its morphology was studied by SEM and AFM. The clay in the PET matrix also maintained well dispersed state in a sub-micron level.

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