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Various organo-clays based nanocomposites of poly(ethylene terephthalate-co-ethylene naphthalate)

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Summary

Poly(ethylene terephthalate-co-ethylene naphthalate) (PETN) hybrid films with four different organo-clays have been compared in terms of their thermal stabilities, mechanical properties, and morphology. Hexadecylamine-montmorillonite (C_{16}-MMT), dodecyltrimethyl ammonium-MMT (DTA-MMT), Cloisite 25A, and Cloisite 30A were used as organo-clays. In hybrid, Cloisite 25A was exfolated and dispersed homogeneous into the copolyester matrix. We found that the addition of only a small amount of organo-clay was enough to improve the thermal stabilities and mechanical properties of PETN/clay hybrid films.

Introduction

Recently, considerable attention has been devoted to the polyester hybrids with pristine clay and chemically modified organo-clay [1,2]. It has been generally recognized that incorporating clay into the polymer matrix will improve the heat distortion temperature, modulus, toughness, and crystallization rate while decreasing the gas permeability [2,3].

Polyester is a large volume plastic that has been in use for fibers and films for many years. But research on polyester/clay nanocomposite is at an early stage and to date no products have entered the market. However, a number of companies are busy with development and have been issued numerous patents over the last few years [2]. There are very few examples in the literature of the preparation of PET nanocomposites by melt compounding. Claytone APA, a commercial organo-clay available from Southern Clay Products, was melt compounded into PET and an improved modulus was observed [4]. Another report describes the incorporation of montmorillonite (MMT) into PET by in-situ polymerization [5].

Previous work in our laboratory [6] has demonstrated the possibility of a nano-scaled composite in a polyester with alkyl ammonium modified montmorillonite. This work deals with the thermal characterization and mechanical properties of polyester/hybrids with increasing clay loading from 1 to 6 wt %. In this paper, we will examine thermal characterizations and mechanical properties of poly(ethylene terephthalate-co-ethylene naphthalate) (PETN) hybrids with different clays. Four intercalation agents were used to chemically modify the surface of the pristine clay. Thermal and tensile properties of the hybrids in film form were studied as a function of clay content in the matrix polymer. The structure and properties of the hybrids studied were dependent upon a modification of the intercalation agents. We also examined the relationship between properties and structure for PETN/clay nanocomposites through wide-angle X-ray diffraction measurements. The morphological properties of the hybrids have been examined with electronic microscope (TEM).

Experimental

Materials

Source clays, Kunipia-F (Na^+-montmorillonite) was obtained from Kunimine Ind. Co. By screening Na^+-montmorillonit (Na^+-MMT) with a 325-mesh sieve to remove impurities, we obtained a clay having a cationic exchange capacity of 119 meq/100g for montmorillonite. Cloisite 25A and 30A were supplied by Southern clay Co. Hexadecylamine and dodecyltrimethyl ammonium bromide were purchased from Aldrich Chemical Co. and used as received. Commercially available solvents were purified by distillation; N,N,-dimethylacetamide (DMAc) was purified and dried over molecular sieves before use. PETN, composed of 92 mole % of ethylene terephthalate content, was supplied by Kolon Co., Korea. Common reagents were used without further purification.

Preparation of organo-MMT and PETN/organo-MMT hybrid films

A dispersion of Na^+-MMT was added to the solutions of ammonium salt of hexadecylamine (C_{16}-) and dodecyltrimethyl ammonium bromide (DTA-), respectively. Modification of MMT by hexadecyl ammonium chloride and dodecyltrimethyl ammonium bromide were obtained through multi step route [7], and has been termed C_{16}-MMT and DTA-MMT, respectively. Since the synthetic procedures for PETN/C_{16}-MMT, DTA-MMT, Cloisite 25A, or Cloisite 30A hybrids with different weight % organo-clay were very similar, only a representative example for the preparation of the PETN/C_{16}-MMT (2 wt%) is given. A mixture of 50.0g of the DMAc dispersion of 0.4g C_{12}-MMT, 8.0g of PETN solution and excess DMAc was stirred vigorously at room temperature for 1 hr. The solution was cast onto glass plates, and solvent was evaporated in a vacuum at 50 °C for 1 day. The films were then cleaned in an ultrasonic cleaner three times for 5 min each. These films with solvent removed were dried again in a vacuum oven at 50 °C for 1 day. The film thickness was 10-15 μm.

Characterization

Thermogravimetric analyzer (TGA) were used on a DuPont 910 instrument with a heating rate of 20 °C/min. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Rigaku (D/Max-IIIB) X-ray diffractometer, using Ni-filtered Co-Kα radiation. The scanning rate was 2°/min over a range of 2θ =2-15°. Tensile properties of the solution cast films were determined using an Instron Mechanical Tester (Model 5564) at a crosshead speed of 2mm/min. The specimens were prepared by cutting strips 5 by 70 mm long. An average of at least eight individual determinations was used. The experimental uncertainties in tensile strength and modulus were ±1 MPa and ± 0.05 GPa, respectively. TEM photographs of ultrathin section of polymer hybrid samples were taken on a Jeol-2000 FX-2 transmission electron microscope using an acceleration voltage of 200 kV.

Results and discussion

Dispersibility of organo-clay in PETN

The X-ray diffraction patterns of pure organo-clays and their hybrids containing 4wt% organo-clay are presented in Figure 1. After the intercalation by organo-clays, the d spacing increased from 25.96 to 31.04 Å for C_{16}-MMT hybrid, from 16.85 to 29.60 Å for DTA-MMT hybrid, and from 17.93 to 29.29 Å for Cloisite 30A hybrid. Examination at this time also revealed that some parts of the organo-clay were agglomerated, and not dispersed homogeneously into the polyester matrix. As previously noted by Pinnavaia [8], increasing n-alkyl chain length of alkylammonium compounds and ion exchange with protonated primary amines resulted in much larger interlayer distances than those found in quaternary amines (25.96 Å for C_{16}-MMT and 16.85 Å for DTA-MMT), although the thickness of montmorillonite (10 Å) was the

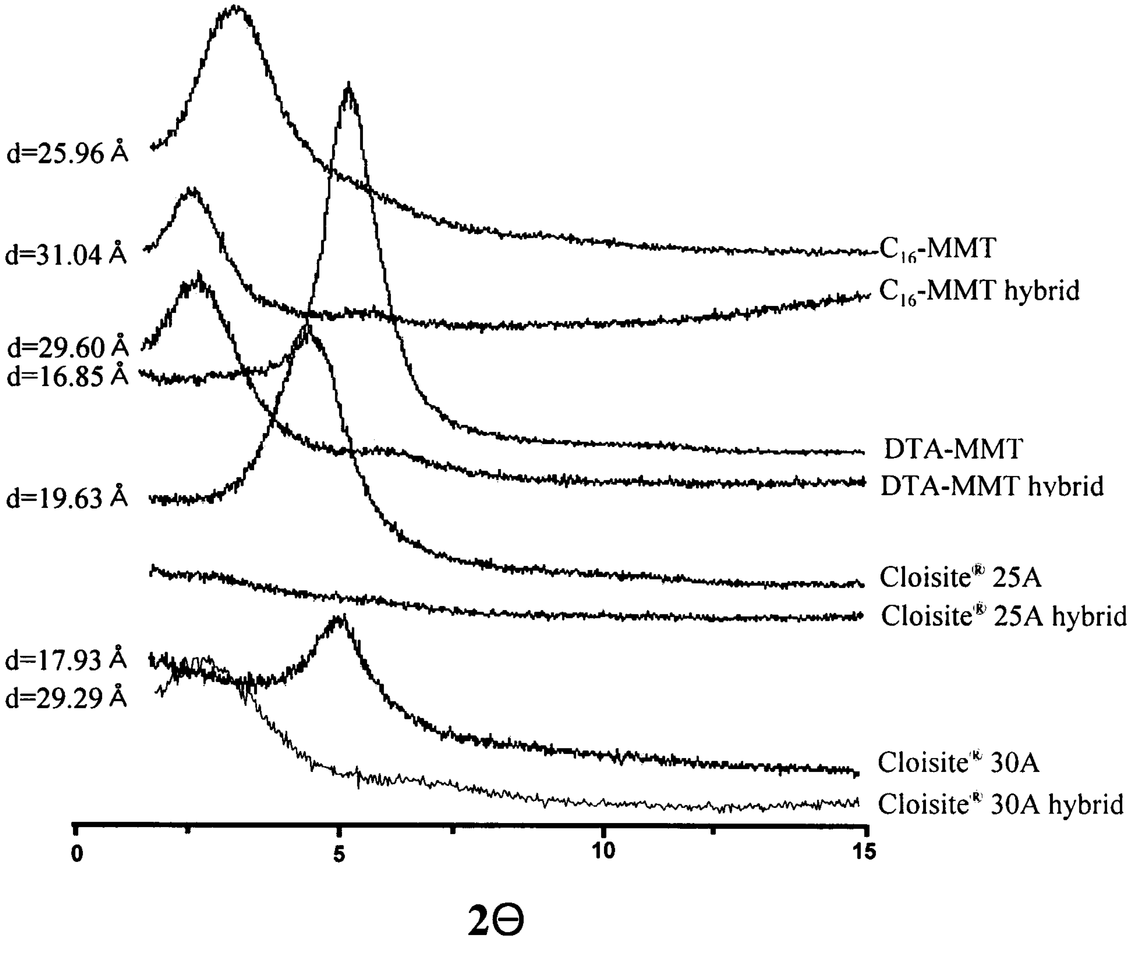

Figure 1. XRD patterns of organo-clays and their hybrids

same. It appears likely that primary amines, in contrast to quaternary ammonium ions, react with matrix polymers to result in advancement products with pendant alkyl side groups, thus enhancing both swelling and compatibility.

In contrast, the polyester hybrid containing 4 wt % Cloisite 25A showed no obvious clay peak in the X-ray diffraction curve. This indicated that the clay layers of Cloisite 25A were exfoliated and dispersed homogeneously in the polymer matrix, and offered direct evidence that the polyester/clay formed nanocomposites. Further evidence of organo-clay dispersed in polyester in nano scale can be provided by TEM study.

Morphology

Nanocomposite superstructures were investigated by means of TEM. Typical TEM images are displayed in Figure 2. In contrast to conventional composites, the hybrids with organo-clays showed formation of much smaller nanoscale structures resulting from intercalation. The dark lines are the intersections of the clay layer of 1 nm thickness. In Figure 2 (c), hybrid with Cloisite 25A shows delamination only, whereas all other hybrids are composed of agglomerated nanoparticles. This TEM photograph provides that most clay layers were dispersed homogeneously into the polymer matrix, although some agglomerated particles were also detected. However, as also shown in Figure 2 (d), some clay was not dispersed homogeneously into the polymer matrix when Cloisite 30A was used. Apparently, the hybrid based upon Cloisite 30A posses very poor dispersion characteristics.

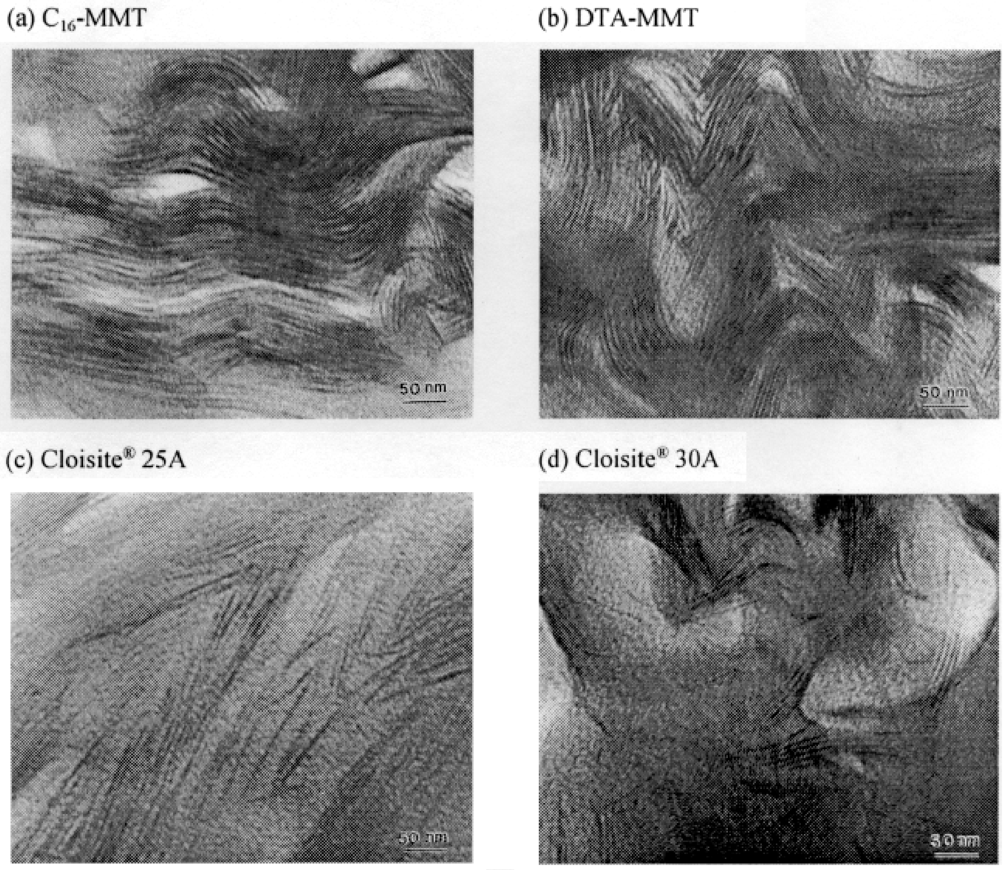

Figure 2. TEM photographs of PETN hybrids containing 4 wt% organo-clay

Many publications have reported attempts to achieve complete delamination of individual clay layers and homogeneous dispersion within the polymer matrix. It appears that delamination assembly, as evidenced by the presence of isotropic laminated clay particles, is the key to improved thermal and mechanical property [2,9]. The next sections will expand upon this idea.

Thermal stabilities

The thermal stabilities of PETN and PETN/organo-clay hybrids are listed in Table 1. The results of thermogravimetric analysis (TGA) showed that in all cases the initial decomposition temperatures (T_D^i) (at 2 wt % weight loss) of PETN hybrids were higher than the initial decomposition temperature of neat PETN. This increase may be attributable to the clay layer structure, which limits mobility of the small molecules produced during thermal decomposition of the polyester molecules [10].

The maximum decomposition temperatures (T_D^{max}) show almost the same values from 452 to 456 °C regardless of the clay loading and the type of clay. Weight of the residue at 600 °C (wt_R^{600}) increased with clay loading from 1 to 6 wt %, with the increases ranging from 12 to 21 %. A comparison of the thermal stability values leads to the conclusion that the hybrids with higher organo-clay contents are more thermally stable, although all the hybrids show fairy good thermal stabilities.

Table 1. Thermogravimetric analysis of PETN/organo-clay nanocomposites.

Clay	Clay wt%	$T_D^{i\,a}$ ℃	$T_D^{max\,b}$ ℃	$wt_R^{600\,c}$ %
Pure PETN	0	404	453	12
C_{16}-MMT	1	406	452	15
	2	408	452	15
	3	413	454	16
	4	415	454	18
	6	408	453	19
DTA-MMT	1	409	456	14
	2	412	456	16
	3	413	456	16
	4	410	455	19
	6	409	453	21
Cloisite® 25A	1	415	454	16
	2	417	455	18
	3	417	456	18
	4	417	454	18
	6	419	453	20
Cloisite® 30A	1	406	456	12
	2	404	452	13
	3	404	452	16
	4	405	453	18
	6	406	456	18

[a] Initilal weight reduction onset temperature. [b] Maximum weight reduction onset temperature. [c] Weight percent of residue at 600℃.

Tensile properties

The tensile properties with organo-clay loading are listed in Table 2. Tensile properties of PETN hybrids with all organo-clays are substantially higher than those of the pristine PETN. When the organo-clay content is greater than 4 wt % for C_{16}-MMT and DTA-MMT, the ultimate strength of hybrids starts to decrease. It appears that there is an optimal amount of organo-clay needed in the hybrid to achieve the greatest property improvement, and organo-clay domains can agglomerate above certain weight % content in this polyester matrix [7,11]. In the cases of both Cloisite 25A and 30A, the ultimate strength of hybrids increases with increasing organo-clay content. The initial moduli of the hybrids increase linearly with increasing organo-clay contents from 0 to 6 wt %. This enhancement of the modulus can be ascribed to the high resistance exerted by the clay itself. The above results reveal that the tensile properties of Cloisite 30A hybrids were not better than the tensile properties of other hybrids because Cloisite 30A does not disperse effectively in intercalation in a PETN matrix. This was crosschecked by TEM (see Figure 2. (d)).

Table 2. Tensile properties of PETN/organo-clay nanocomposites

Clay	Clay wt%	Ult. Str. MPa	Ini. Modu. GPa	E.B.* %
Pure PETN	0	36	1.57	6
C_{16}-MMT	1	75	3.66	5
	2	79	3.78	5
	3	89	4.12	5
	4	94	4.34	5
	6	66	3.19	2
DTA-MMT	1	60	3.37	3
	2	68	3.84	4
	3	72	4.03	4
	4	73	4.18	3
	6	61	4.22	2
Cloisite® 25A	1	68	3.17	6
	2	71	3.16	6
	3	75	3.28	5
	4	77	4.32	4
	6	96	4.43	3
Cloisite® 30A	1	45	1.61	5
	2	44	1.64	5
	3	45	1.74	4
	4	46	1.79	4
	6	48	2.26	3

*Elongation percent at break.

The percent elongations at the break of all the samples were 3-6%. These values remained constant regardless of organo-clay loading.

Conclusions

Four kinds of copolyester (PETN) nanocomposites were prepared by the solution intercalation method. By combining the observations from TEM and XRD, we determined that the PETN/Cloisite 25A hybrid was an exfoliated nanocomposite. With the exception of the PETN/Cloisite 25A hybrid, all hybrids showed intercalated nanocomposites. Both thermal and mechanical properties of PETN hybrids with all organo-clays are substantially higher than those of the pristine PETN. This can be due to their origin in the uniformly dispersed clay layer.

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