Available online at www.sciencedirect.com

ScienceDirect

Polymer Degradation and Stability 93 (2008) 252–259

Polymer Degradation and Stability

www.elsevier.com/locate/polydegstab

Thermally stable exfoliated poly(ethylene terephthalate) (PET) nanocomposites as prepared by selective removal of organic modifiers of layered silicate

Jae Woo Chung, Se-Bum Son, Sang-Wook Chun, Tae Jin Kang, Seung-Yeop Kwak*

Department of Materials Science and Engineering, Seoul National University, San 56-1, Sillim-dong, Gwanak-gu, Seoul 151-744, Republic of Korea

Received 2 July 2007; received in revised form 17 September 2007; accepted 23 September 2007
Available online 7 October 2007

Abstract

Exfoliated poly(ethylene terephthalate) (PET) nanocomposite excluding organic modifier (M-$P_{et}LSN_{eom}$) was successfully prepared by the melt processing via solution method with solvent–nonsolvent system. PET nanocomposites including organic modifier (M-$P_{et}LSN_{iom}$ and D-$P_{et}LSN$) as counterpart of M-$P_{et}LSN_{eom}$ were prepared by using the melt processing via solution method without solvent–nonsolvent system and the only conventional direct melt mixing process, respectively. From elemental analysis (EA) and thermogravimetric analysis (TGA), organic modifier in M-$P_{et}LSN_{eom}$ was confirmed to be well removed by solution method with solvent–nonsolvent system. Then, it was found that M-$P_{et}LSN_{eom}$ and M-$P_{et}LSN_{iom}$ had exfoliated structure by wide angle X-ray diffraction (WAXD) and high-resolution transmission electron microscopy (HR-TEM), whereas no expansion of gallery height was observed for D-$P_{et}LSN$. To elucidate the effect of organic modifier on the physical properties of PET nanocomposites, the crystallization behavior, optical transparency, thermal stability, and mechanical properties of M-$P_{et}LSN_{eom}$, M-$P_{et}LSN_{iom}$, D-$P_{et}LSN$, and neat PET were evaluated by differential scanning calorimetry (DSC), UV–visible (UV–vis) spectroscopy, TGA, and universal testing machine (UTM). All of the PET nanocomposites exhibited faster crystallization kinetics and better thermal and mechanical properties compared to neat PET due to the presence of silicate layer in PET. However, M-$P_{et}LSN_{iom}$ and D-$P_{et}LSN$ including organic modifier showed lower crystallization constant rates, longer crystallization half times, and poorer optical, thermal, and mechanical properties than M-$P_{et}LSN_{eom}$. These results were ascribed to the thermal decomposition of the organic modifiers presented in M-$P_{et}LSN_{iom}$ and D-$P_{et}LSN$ during the melt processing.

Keywords: Exfoliated PET nanocomposites; Organic modifiers; PET; Thermal stability

1. Introduction

PET is extensively used for packaging films, beverage bottles, engineering components, and fibers for apparel, on account of its excellent chemical resistance, thermal stability, and mechanical properties [1]. However, the use of PET under more severe conditions requires that its various physical properties, such as optical, thermal, mechanical, and barrier properties, should be much enhanced. Hence, considerable effort has been devoted to improve the various physical properties of PET through blending with high performance polymers [2,3] and mixing with additives such as filler. Recently, the commercial importance of PET in industrial fields has driven intensive investigation into PET-layered silicate nanocomposites ($P_{et}LSNs$), because these composite materials exhibit far superior physical properties to PET blends with micro-sized additives [4–9]. Layered silicates have layers with thicknesses in the order of 1 nm and have very high aspect ratios (e.g., 10–1000), and interlayer spacing between the stacked layers of about 1 nm. The distinctive features of the layered silicates result in the nanocomposites having two possible structures, namely intercalated or exfoliated structures. The

---

* Corresponding author. Tel.: +82 2 880 8365; fax: +82 2 885 1748.
E-mail address: sykwak@snu.ac.kr (S.-Y. Kwak).

0141-3910/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2007.09.009

intercalated nanocomposites show regularly alternating silicate and polymer layers with a repeat distance of a few nanometers, whereas the individual layers in the exfoliated nanocomposites are irregularly delaminated and dispersed in a continuous polymer matrix. Such structural differences play a key role in the enhancement of the nanocomposite properties. Generally, exfoliated nanocomposites have superior mechanical properties to intercalated nanocomposites, because of the larger surface area between the reinforcement phase and the polymer matrix. However, since the substrates of silicate layer are hydrophilic and the gallery height between the silicate layers is very narrow, it is difficult for the hydrophobic PET molecular chain to penetrate into the layered silicates. Therefore, it is necessary to introduce organic modifiers to change the layered silicate substrate from hydrophilic to hydrophobic in order to lead to the insertion of PET molecular chain into the gallery between the layered silicates. This process may provide a favorable way to disperse the layered silicates in the PET matrix [10]. Recently, several methods using organically modified silicate layer have been developed to fabricate the exfoliated polymer-layered silicate nanocomposites (PLSNs) such as in situ polymerization, solution mixing, and direct melt mixing [11–13]. The first two approaches are not appropriate for commercial production on account of difficulties associated with identifying a suitable monomer for the polymerization and a solvent compatible with both the polymer and the silicate. On the other hand, the direct melt mixing method is very useful and simple. In this method, polymers are inserted into the layered silicate at a temperature above the softening or melting of the polymer. However, the main limitations of direct melt mixing method are the localized dispersion of silicate layers into the polymer matrix and the thermal decomposition of the organic modifiers [14–18]. Xie et al. [16,17] reported that the degradation of organic modifiers in PLSNs was correlated with several factors, including the residence time during processing, processing temperature, and the type of ammonium organic modifier used. Davis et al. studied the degradation pathway of PA6/MMT nanocomposites with a focus on the degradation mechanism of organic modifiers in PA6/MMT nanocomposites at high processing temperatures [18]. Then, it was found that significant thermal degradation occurred in the PA6/MMT nanocomposites during processing at 300 °C, and that thermal decomposition may result from hydrolytic peptide scission. Zhang et al. [8,9] developed a new synthetic strategy for the homogeneous dispersion of layered silicate into PET by *in situ* polymerization, but reported that P_{et}LSNs failed to exhibit optical transparency due to thermal decomposition of the organic modifiers in the P_{et}LSNs during the polymerization procedure at 280 °C [7–9], even though the tensile strength increased. Their results revealed that the high processing temperature causes the thermal decomposition of the organic modifiers in P_{et}LSNs. Hence, the main objective of this study is to present a novel approach for the preparation of exfoliated P_{et}LSNs in the absence of the organic modifiers. Additionally, we showed the detailed effects of organic modifiers on the various physical properties of P_{et}LSNs in this study.

2. Experimental section

2.1. Materials

PET with ca. 255 °C of a melting point was obtained from the Huvis Chemical Company (Korea). Organically modified layered silicates (OLS) occupied with organic modifiers (polyoxypropylene methyldiethylammonium cations) between the layered silicate galleries were kindly supplied by Co-op Chemical Co. The OLS had approximately 2.8 nm and 4.4 nm of gallery height. The weight ratio of layered silicates/organic modifiers in the OLS was verified to be about 0.4/0.6 by thermogravimetric analysis (TGA). Chloroform (99%) and methanol (99%) were purchased from Daejung Chemicals & Metals (Korea) and trifluoroacetic acid (TFA) used for removing the organic modifier ionically attached on the layered silicate was purchased from Sigma–Aldrich Co. All materials were used without any additional purification.

2.2. Sample preparation

OLS were added in excess chloroform and stirred at 25 °C for 1 h. TFA was poured in OLS/chloroform solution and stirred for 5 min, and then neat PET was added to OLS/chloroform/TFA solution, and dissolved by stirring for an additional 1 h (neat PET/OLS = 92/8, w/w%). PET/OLS/chloroform/TFA solution was added dropwise to the cold methanol to obtain PET nanocomposite excluding organic modifier (S-$P_{et}LSN_{eom}$), as shown in Scheme 1. Then, precipitated materials were collected by filtration and dried in a vacuum oven at 80 °C for 12 h. On the other hand, PET nanocomposite including organic modifier (S-$P_{et}LSN_{iom}$) was prepared by removing the solvent from prepared PET/OLS/chloroform/TFA solution in a hood at 30 °C for 48 h. Remained white powder was collected and dried in a vacuum oven at 80 °C for 12 h. Acquired S-$P_{et}LSN_{iom}$ and S-$P_{et}LSN_{eom}$, individually, mixed with neat PET by a twin screw extruder (Hakke CTW-100) of co-rotating mode at 270 °C using a screw speed of 80 rpm (neat PET/S-P_{et}LSN = 1/0.333, w/w%). Under these conditions, the mean value of the residence time in the extruder for PET was 350 s. After mixing, obtained materials were cooled in a water bath and then pelletized. Melt processed PET nanocomposite obtained from mixing of S-$P_{et}LSN_{iom}$ and S-$P_{et}LSN_{eom}$ with neat PET is denoted as M-$P_{et}LSN_{iom}$ and M-$P_{et}LSN_{eom}$, respectively. Additionally, PET/OLS (1/0.067, w/w%) mixture (D-P_{et}LSN) was also prepared as counterpart of M-P_{et}LSNs by the direct melt mixing under the same conditions as used for the M-P_{et}LSNs.

2.3. Characterization

The presence and absence of organic modifiers in the S-P_{et}LSNs were determined by elemental analysis (EA) and thermogravimetric analysis (TGA). EA was carried out on an EA 1110 CE elemental analyzer, and TGA was carried out using the TA instruments TGA 2050 thermal analyzer from room temperature to 600 °C at a heating rate of 2 °C min^{-1} under N_2