Clay orientation effect on the thermal stability of polyethylene–nanoclay nanocomposites

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ABSTRACT

This paper explores the effect of nanoclay orientation on the long term thermal stability of a polyethylene (PE)/nanoclay nanocomposite. Nanoclay morphology and orientation in an injection molded PE–clay nanocomposite bar were examined using transmission electron microscopy and simultaneous small angle X-ray scattering (SAXS)/wide-angle X-ray diffraction (WAXD). These nanocomposites were aged at elevated temperatures for various periods of time, and the relative amount of antioxidant (AO) was monitored using an oxidative induction time test. The presence of 4 wt% nanoclay accelerates AO depletion, particularly at the surface region of the sample. AO concentration profiles along different directions of the sample bar were constructed based on SAXS/WAXD results, and were correlated with the clay orientation. A detailed AO depletion mechanism is discussed.

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1. Introduction

Since first reported in 1993 [1–3], nanoclay has become one of the most commonly used fillers in polymer nanocomposites to enhance the mechanical, thermal and barrier properties [1,4–9]. While most of the current research in polymer nanocomposites are focused on the morphology, structure–property relationship, and mechanical performance of these materials [4,10–15], little attention has been paid to their durability. Antioxidant (AO) is one of the critical components in polymer products as it protects the polymer from thermal oxidation, and has a great impact on the lifetime of the polymer. AO depletion in thermally aged polyolefins [16–23] and elastomers [24,25] has been studied by a number of research groups. In the case of polymer–clay nanocomposite, the presence of organo-modified nanoclay has been found to lower AO efficiency and accelerate polymer degradation [26–31]. Morlat-Therias et al. attributed the negative effect of clay on polymer stability to the degradation of the alkyl ammonium cation during the processing step, the catalytic effect of the metal ion in the clay gallery, and/or the immobilization of AOs onto the clay surface [26,27]. Qin et al. reached a similar conclusion and further suggested that the degree

of clay dispersion has little effect on the acceleration of polymer degradation [28]. Most of these studies have focused on the ultraviolet-irradiation induced degradation of the polymer, which is a fast and destructive method. However, the effect of nanoclay on thermal oxidation of the nanocomposite systems has not been adequately addressed.

Our previous work has shown the depletion of two types of antioxidants in medium density polyethylene (MDPE)–clay nanocomposites under oven aging at 85 °C [32]. For nanocomposite containing 0.3 wt% of AO Irganox® 1010, the addition of 4 wt% nanoclay changes the active AO distribution along sample thickness from a typical parabolic profile, which represents a diffusion controlled mechanism, to a "table-top" profile after aging at elevated temperatures for prolonged time. This unique AO depletion profile was attributed to the rates of AO migration and oxygen diffusion as well as AO chemical reaction; the detailed mechanism, however, is not clear. On the other hand, extensive studies have shown that processing conditions and molecular interaction between nanoclay and the polymer matrices, such as nylon-6 [33–36], poly (L-lactide) [37], polyethylene oxide [38], polyolefins [39–42], polyvinylidene fluoride [43] can result in a hierarchical structure of the nanocomposites and preferred orientation of nanoclays, both of which could affect AO depletion of the nanocomposite. In this article, we report on the detailed structural and morphological characterization of injected nanocomposite bars, and the morphological effect on AO depletion of the nanocomposites. The local orientations of clay at different locations of the nanocomposite bar were examined using

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simultaneous 2D small angle X-ray scattering (SAXS)/wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). To accelerate the depletion of AO, the nanocomposite sample bars were aged in an 85 °C forced air oven. They were then sectioned into thin slices for oxidative induction time (OIT) tests to evaluate the local active AO contents in the aged samples. A 3D AO distribution profile of the nanocomposite sample bar was then constructed, and the OIT profiles were correlated with nanoclay orientation. Our results show that nanoclay orientation has a significant effect on AO depletion in the nanocomposites.

2. Experimental section

2.1. Materials and polyethylene−clay nanocomposites fabrication

Medium density polyethylene (MDPE) HHM TR 418 resin fluff with a density of 0.939 g/cm^3 and melt index of 20 g/10 min was supplied by Chevron-Phillips Chemical. A sterically hindered phenolic antioxidant (AO) Irganox®1010 (I-1010) was selected for this study, and the chemical structure is shown in Fig. 1. Modified nanoclay (Nanomer® I.44) consisting of 60% bentonite and 40% dimethyl dihydrogenated tallow ammonium was supplied by Nanocor. Maleic anhydride (Chemtura Polybond® 3009) was added as a compatibilizer to improve the dispersion of nanoclay in the polymer matrix.

A nanocomposite that consists of 93.7 wt% MDPE, 2 wt% compatibilizer, 4 wt% nanoclay and 0.3 wt% AO was prepared by injection molding using a Cincinnati Milacron Vista 33 twin screw extruder. A detailed nanocomposite fabrication procedure can be found in our previous report [32]. The injection molded nanocomposite sample bars have dimensions of 178 mm in length, 38 mm in width and 3.175 mm in thickness.

2.2. Incubation

In order to evaluate AO depletion of PE−clay nanocomposites, sample bars were incubated in a forced air oven at 85 °C to accelerate the thermal-oxidation process. The incubated samples were retrieved from the oven at different time intervals for subsequent tests. All the samples taken from the oven were vacuum sealed and stored in a refrigerator for further tests.

2.3. Characterization

The orientation of clay in the nanocomposite samples was examined by simultaneous 2D WAXD and SAXS using a Rigaku S-MAX 3000 SAXS system. WAXD patterns were collected using an image plate with a 2 mm hole, and the SAXS patterns were collected simultaneously with a 2D multi-wire area detector. Similar setup has been used to study polymer crystallization and liquid crystalline block copolymers [43–46]. Modified nanoclay powder was encapsulated into a 0.7 mm quartz capillary tube while thin sections of 1 mm thick were cut from the nanocomposite
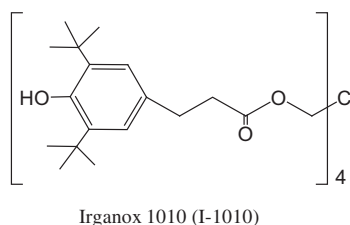
sample bars for the X-ray measurements. TEM characterization of the nanocomposites samples were performed using a JEOL JEM2100 microscope with an acceleration voltage of 200 kV. Thin sections of the samples with thickness of ca. 60 nm were obtained using a Leica EM UC6 ultramicrotome with a DiATOME 35° diamond knife. The samples were then collected on carbon-coated lacey grids for TEM experiments.

The relative amount of active AO in the samples was determined using a TA Instrument Q20 differential scanning calorimeter (DSC), following a standard procedure according to ASTM D3895. The specimens were heated from room temperature to 200 °C at a heating rate of 20 °C/min under a nitrogen atmosphere. The gas flow rate was maintained at 50 ml/min at the gauge pressure of 0.035 MPa. The cell was maintained at 200 °C under a nitrogen gas atmosphere for 5 min and then switched to oxygen gas at the same gauge pressure. The test was terminated after an exothermal peak was detected which signified the oxidation of the polymer. The OIT value was then taken as the time from the initial oxygen exposure to the onset of oxidation. The oxidation onset was recorded following the tangent method, in which the steepest linear slope of the oxidation exotherm and the baseline were extrapolated and their intercept was taken as the oxidation onset. Fig. 2 shows a schematic diagram of a typical OIT thermal curve from the DSC result. In order to determine the OIT profiles within the sample, a small 3 × 3 × 3 mm cubical block was taken from the aged nanocomposite sample bar and sectioned into multiple thin slices with a surface area of 3 mm × 3 mm and thickness between 0.2 mm and 0.5 mm. An OIT test was performed on each slice and the OIT value was then plotted against the position.

3. Results and discussion

3.1. Orientation of clay in nanocomposites

WAXD and SAXS measurements were conducted from three principle directions at different positions of the sample bar to fully understand the structure and morphology of the nanocomposite. 2D WAXD and SAXS patterns from three projections for the unaged nanocomposite sample and the corresponding structures are shown in Figs. 3, 5 and 6. The three principle axes of the sample bar are defined as flow direction (FD), transverse direction (TD, also width direction) and normal direction (ND, also thickness direction), respectively. The schematic drawings of the sample structure in Figs. 3, 5 and 6 are mainly for better illustration and do not representthe actual sample bar dimensions or nanoclay size.

X-ray patterns with the incident X-ray beam parallel to TD were first collected. The meridian of the scattering patterns is parallel to ND, and the specimen locations for the X-ray measurements are shown in Fig. 3g. Fig. 3(a, b), (c, d) and (e, f) are from surface,
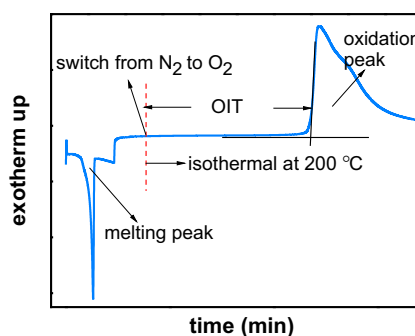

Fig. 1. Chemical structure of antioxidant Irganox®1010.

Fig. 2. DSC trace of a typical OIT test.