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Natural photo-aging degradation of polypropylene nanocomposites

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Abstract

The natural photo-aging degradation of polypropylene (PP), PP/$CaCO_3$ and PP/SiO_2 nanocomposites were studied outdoor for up to 88 days. The chemical structure characterized by Fourier transform infrared spectroscopy (FTIR) and pyrolysis gas chromatography–mass spectroscopy (PGC–MS) showed that PP nanocomposites are much more susceptible to photo-degradation than unfilled PP. And the oxidation rate is faster with more filler amount. There are lots of chain scissions happened in PP nanocomposites, accompanied with the formation of ketone, alcohol, ester and unsaturated double bond. This severe chain scission led to great decrease of M_n and M_w, and the consequent small fragments would re-crystallize and increase the crystallinity of the nanocomposites. However, these effects do not relate to the ultraviolet character of the two nano fillers.

Keywords: Polypropylene; Nanocomposites; Photo-oxidation; Chain scission; Re-crystallization

1. Introduction

Since the successful development of montmorillonite reinforced polyamide nanocomposite by the Toyota group [1], polymer nanocomposites have received considerable attentions. Studies have shown that polymer nanocomposites exhibit remarkable properties, including high heat distortion temperatures, enhanced flame resistance, high modulus, perfect barrier properties and decreased thermal expansion coefficient, which may lead to applications in the automobile industry as well as the aircraft industry where materials with light weight but high heat-resistance are desirable.

The durability of polymer nanocomposites, as well as mechanical and thermal property, is also of great importance from the application point of view. Knowledge on aging behavior and mechanism of these materials is of great help for anti-aging research. Researchers studied photo-degradation behavior of different kinds of polymer/clay nanocomposites [2–5] and found opposite effect of clay on different polymer matrix. In polycarbonate (PC)/clay nanocomposites, clay helped to improve PC's light stability [4], while in polyethylene (PE)/clay, polypropylene (PP)/clay and ethylene–propylene–diene monomer (EPDM)/clay nanocomposites, clay decreased these polymers' light stability [2,3,5]. However, the aging research is quite scarce compared to numerous reports on the modification of polymer nanocomposites. And limited works nearly all surround polymer/clay nanocomposites.

For PP nanocomposites, although in the past decades, researchers have done numerous work and obtained a good understanding about photo-degradation mechanism and photo-degradation products of PP [6–8], relatively few research reported on photo-aging of PP nanocomposites. Similarly, PP/clay nanocomposite occupied most of these reports. Mailhot et al. [5] studied the photo-chemical behavior of PP/clay nanocomposites. Tidjani and Wilkie [9] prepared PP/clay nanocomposites and studied their photo-oxidation stability. Qin et al. [10] investigated the photo-oxidation behavior of the PP/montmorillonite (MMT) nanocomposites upon ultraviolet exposure. They concluded that PP nanocomposites degraded much more rapidly than pure PP. The photo-oxidation of PP-based nanocomposites at wavelengths above 300 nm produced the same species and the same quantities of photoproducts as those of pure PP.

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Apart from clay, nano-$CaCO_3$ and SiO_2 are often used to improve the mechanical properties of PP as well. However, there is hardly any report on the outdoor durability of these nanocomposites. Leong et al. [11] studied the natural aging of conventional PP/$CaCO_3$ composite. Their result showed that the composite had a better retention in mechanical properties with some degree of surface degradation as well. Would the nano fillers have the similar effect as the conventional ones? In this work, the natural aging degradation of PP/$CaCO_3$ and PP/SiO_2 nanocomposites was carried out and the effects of these two nano fillers were evaluated.

2. Materials and experiments

2.1. Materials

Isotactic polypropylene F1002 (commercial grade, with melt flow index 1.7 g/10 min, from Yanshan Petrochemical Co. Ltd, Beijing, China) was used as received. Nano-$CaCO_3$, 15 ± 5 nm in diameter, was supplied by Beijing University of Chemical Technology; nano-SiO_2, about 40 nm in diameter, was supplied by Zhejiang Zhoushan Mingri Nanomaterial Co.

2.2. Nanocomposite preparation

The PP/$CaCO_3$ and PP/SiO_2 nanocomposites were prepared with a twin-screw extruder (TE-34 Jiangsu Keya Chemical Equipment Co. Ltd). The operating temperatures of the extruder zones were maintained at 200, 220, 220, 220, 220 and 210 °C from hopper to die, respectively. The screw speed was maintained at 50 r/min. After cooling in water, the extrudates were pelletized. The nanocomposites pellets were dried and then hot-pressed to films (about 120 μm in thickness) with pressure of about 10 MPa at 210 °C. The natural aging test was carried out outdoor for 88 days. After that, PP nanocomposite samples were broken into pieces. The compositions of the samples are listed in Table 1.

Table 1
Composition of PP nanocomposites

Sample number	Composition
PP-C-1	PP/$CaCO_3$ = 100/1
PP-C-3	PP/$CaCO_3$ = 100/3
PP-C-5	PP/$CaCO_3$ = 100/5
PP-S-2	PP/SiO_2 = 100/2
PP-S-3	PP/SiO_2 = 100/3
PP	PP

2.3. Characterizations

The Fourier transform infrared spectra were obtained using a Nicolet 560 FTIR spectrometer. Samples were analyzed by signal averaged from 32 scans at resolution of 4 cm^{-1} in the wavenumber range of 4000–400 cm^{-1}. It is used to monitor the variation of molecular structure of PP during weather aging. In order to remove the influence of the sample thickness, peak at 2720 cm^{-1} was used as reference [12].

The UV spectra of samples were collected by using a Shimadzu UV 2100S ultraviolet–visible spectrophotometer in the wavelength range of 200–800 nm.

The possible volatile molecules formed during the natural photo-oxidation in PP composites were analyzed with a pyrolysis gas chromatograph–mass spectrometer (PGC–MS) (SHIMADZU GCMS-QP5050A equipped with PYR 4A pyrolyzer). The flash evaporation technique was used to separate fragments due to chain scissions of PP molecules from the macromolecules. A sample was flash-heated at 300 °C for 30 s to evaporate only the fragments, while PP chain would not be broken at this temperature. The mixture of these products was carried through the fused silica capillary column (DB-5 25 m × 0.25 μm i.d.) by the carrier gas He and separated at the same time. Finally, each component was detected by the MS detector.

High temperature gel permeation chromatography (HGPC, Waters, Alliance GPCV2000, USA) was used for the characterization of molecular weights and molecular weight distributions of polypropylene fractions. The samples before and after light exposure were dissolved into 1,2,4-trichlorobenzene at 150 °C to make a very dilute solution with concentration of 0.1% by weight. Molecular weight was calculated based on the universal calibration curve of standard polystyrene.

The crystallinity of PP and its nanocomposites before and after exposure was determined by using a differential scanning calorimetry (DSC2910, TA Instruments). About 2.5 mg sample was heated from 50 to 200 °C at a rate of 10 °C/min under a nitrogen flow of 50 ml/min. The crystallinity was defined as follows:

$$X_c = \Delta H / (\Delta H_0 \rho) \qquad (1)$$

where ΔH was the measured melting enthalpy and ΔH_0 was the enthalpy of fusion of a 100% crystalline polypropylene ($\Delta H_0 = 209$ J/g [13,14]); ρ was the content of polypropylene in matrix.

3. Results and discussion

Fig. 1 shows the IR spectra of PP and PP nanocomposites at different aging times. Since PP-C-3 and PP-S-3 broke into pieces after 88 days of exposure, comparison after longer exposure was not carried out. A new broad band appeared at about 1715 cm^{-1} after exposure, which belongs to a mixture of different carbonyl species [5]. The second new band at about 3400 cm^{-1} belongs to hydroxyl group, which indicates the generation of hydroperoxide and hydroxyl species. In addition, the intensity of the carbonyl and hydroxyl bands grew with increasing exposure time. The increasing rate of these bands of pure PP was lower than those of PP nanocomposites. For pure PP, the obvious oxidation occurred after 80 days, and developed slowly. For PP-C-3, although obvious oxidation was observed after 80 days, the band at 1711 cm^{-1} increased sharply. For PP-S-3, oxidation evidence could be seen