Available online at www.sciencedirect.com
ScienceDirect
Polymer Degradation and Stability 92 (2007) 53–60
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Maleated polypropylene OMMT nanocomposite: Annealing, structural changes, exfoliated and migration

Yong Tang, Menachem Lewin*

Polytechnic University, Polymer Research Institute, Department of Chemical and Biological Sciences, 6 Metrotech Center, Brooklyn, NY 11201, USA

Received 13 July 2006; received in revised form 19 September 2006; accepted 21 September 2006
Available online 13 November 2006

Abstract

Annealing of maleated polypropylene/organoclay nanocomposites is studied at a range of temperatures from 180 °C to 300 °C under a stream of nitrogen and nitrogen/air mixtures. The study comprises determinations of the migration of clay to the surface by the use of attenuated total reflectance Fourier transform infra red (ATR-FTIR) spectra. The extent of migration is shown to increase with the increase in the percent of maleic anhydride (MA) grafted onto the PP and with the percentage of air added to the nitrogen gas used for purging of the samples during annealing. The extent of migration increases with temperature up to 225 °C. At temperatures of 250–300 °C, the extent of migration decreases. Simultaneously, a change in the structure of the nanocomposites is observed by small-angle X-ray diffraction (XRD), showing a conversion of the nanostructure to the non-colloidal microcomposite. The study conforms to previous findings and indicates that the migrating moiety is composed of exfoliated clay particles. The effect of the decomposition of the grafted MA groups and the evolution of CO_2 on the rate of oxidation and migration are observed and discussed. The effect of the evolved CO_2 on the stability of the clay particles is pointed out. The role of migration in the elucidation of the structure of nanocomposites is discussed along with other mechanistic considerations.

Keywords: PP; Nanocomposites; Clay; Migration; Exfoliation; Microcomposite

1. Introduction

Polypropylene (PP) is the most widely used polymer in the preparation of nanocomposites. It is preferable to other polymers due to its ready availability and relatively low cost and many possible applications [1,2]. The apolarity and low surface tension of PP present difficulties in the dispersion of the hydrophilic clay in this hydrophobic polymer [3]. Several systems have been designed and developed to overcome these difficulties. These systems include the addition of polar functional groups to the PP macromolecules. In one system, styrene monomers were copolymerized with PP. In other systems, OH, NH_2, and carboxyl groups were incorporated and in a recent development, ammonium ion-terminated PP was prepared [1,2]. All approaches described until now, however, did not find any practical application due to difficulties in preparation and relatively high cost. At present, the only modification applied to PP for use in the preparation of nanocomposites is maleation, i.e., grafting of maleic anhydride (MA) groups onto the polymeric chain. The maleation treatment is connected with a number of complications including such side reactions as β-scission, chain transfer, and coupling and above all, severe decrease of the molecular weight [4–6]. Although interesting modifications of the maleation process were suggested recently, such as the preparation of the borane-terminated intermediate that is prepared by hydroboration of the chain-end unsaturated PP, these modifications have not yet been commercially applied [4–6]. The maleation process is the only one used at present and is being widely studied for a range of applications, such as metal– plastic laminates for structural use, polymer blends, and lately nanocomposites [7,4].

---

* Corresponding author. Tel.: +1 718 260 3163.
E-mail address: mlewin@duke.poly.edu (M. Lewin).

0141-3910/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2006.09.013

In previous communications from this laboratory, special interest was devoted to the phenomenon of the migration of clay to the surface upon annealing at elevated temperatures [8–15]. The reasons for this migration were assumed to depend on the way the nanocomposite samples were heated. For unidirectional heating, such as that applied in the cone calorimetry testing, the rate of migration would increase with decrease in the distance of the surface of the sample from the heat source. The temperature gradient as well as the viscosity gradient created during such heating will accelerate the migration of the clay. In multidirectional or environmental heating, such as applied in closed furnaces, two other reasons for migration were postulated. The gases and bubbles formed in the pyrolysis and combustion of the organic surfactant in the organoclay as well as of the polymeric matrix will drive the clay to the surface. However, in the absence of such gases or bubbles, i.e., at temperatures below the onset of the decomposition of the surfactant and of the polymer, the driving force will be thermodynamic, stemming from surface-free energy differences between the matrix and the interfacial tension between the matrix and the clay [11,14]. The interfacial surface tensions were shown to be much lower than those of the polymeric matrices. The moiety migrating to the surface will thus be a clay particle and some matrix molecules adhering to it. Since the intercalated moieties of nanocomposites exist in the form of relatively large and heavy stacks, they will not be expected to migrate to the surface [12]. The migrating moiety is postulated to be the exfoliated form of the nanocomposite, i.e., the single clay layers to which the surfactant as well as matrix molecules are attached. The extent of migration is thus dependent on the extent of intercalation and consequently of exfoliation in the nanocomposite. In the case of PP, intercalation occurs only when some polarity is imparted to the polymer. As discussed above, in a previous communication, we have shown that oxidation during annealing such as that occurs when air is used to purge the annealing sample greatly enhances the extent of migration. Indeed, we demonstrated that in the absence of a suitable compatibilizer for the PP no migration occurs without oxidation [12].

The present study deals with the behavior of nanocomposites prepared from maleated polypropylene with organically treated MMT (PPMA) upon annealing at a range of temperatures above the melting point of PPMA. The study involves the effects of the concentration of MA in the nanocomposite, as well as the presence of air in the nitrogen stream used for purging the samples during annealing, and also on the exfoliation and migration phenomenon.

2. Experimental

2.1. Materials and preparation of samples

A polypropylene homopolymer, Petrothene PP 31KK01, having melt flow rate of 5 g/10 min, was obtained from Equistar Chemicals (Houston, Texas), and was used as received. The maleic anhydride-modified PP (MAPP) was Polybond X5140, which was received from Crompton Corporation. The MA is 1.5 wt%. The clay used in the study is NANOMER®-I.44P. It is an onium ion modified montmorillonite clay containing 60% MMT (CAS no. 1318-93-0) and 40% dimethyl dialkyl (C14–18) ammonium organic modifier (CAS no. 61789-80-8).

The preparation of PP/clay nanocomposites containing 5 wt% of NANOMER®-I.44P was carried out by melt blending in a Brabender at a speed of 40 rpm at 190 °C for 5 min. In order to obtain samples of 1 wt% and 0.5 wt% MAPP, the pure PP (PP 31KK01) was blended with Polybond X5140 at required ratio.

2.2. Annealing experiments

About 5 g of samples were transferred into a mold (4 mm × 10 mm × 40 mm), and then the samples together with the mold were suppressed into a test bar at 190 °C by using a Carver Press (Model #33500-328). The obtained bar was transferred to an aluminum foil holder (bottom and side surfaces of the sample are in contact with the Al foil, whereas the top surface is directly exposed to atmosphere) and then positioned into a syringe. The syringe was sealed with a silicone rubber. The syringe was then heated in a thermostated isotemp furnace (Fisher Scientific Company) for a specified temperature and time. The actual temperature during annealing was monitored by a thermocouple. These samples were annealed under N_2 atmosphere containing the required ratio of air controlled by two calibrated flowmeters. The flow rate of the purging gas was 800 ml/min. The volume percentages of air used in the experiment are 6.25%, 12.5%, and 25%.

2.3. ATR measurements

The attenuated total reflectance Fourier transform infra red (ATR-FTIR) spectrometry was performed using a Thermo Nicolet Avatar 360 FT-IR equipped with an Attenuated Total Reflectance device. The spectra were collected on different spots of the top surface of each sample. The provided data are an average of at least five different measurements. The surface concentrations of clay in the samples were monitored by ATR-FTIR. The intensities of the peaks in ATR-FTIR spectra were normalized by dividing by the intensities of the CH_3 symmetric deformation peak at 1375 cm^{-1} [12]. The normalized intensities of the clay peak $-Si-O-$ at 1043 cm^{-1} (R_1) were measured in the nanocomposite formulations before (I^0_{Si} – the control sample) and after (I^A_{Si}) annealing. The ratio $R_2 = I^A_{Si}/I^0_{Si}$ – the control sample is used to quantify the change of clay concentration on the surface of the samples after annealing. The normalized intensity of the carbonyl peak (R_3) at 1714 cm^{-1} was measured in some samples, which were annealed under N_2 only and N_2 containing 25% air (Table 4).

2.4. XRD measurements and HREM measurements

X-ray diffraction (XRD) analysis was carried out on samples at room temperature by a Japan Rigaku D/max-rA X diffractometer (30 kV, 10 mA) with Cu ($\lambda = 1.54178$ Å)