Applied Clay Science 52 (2011) 171–178

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research Paper

Montmorillonite/polypropylene nanocomposites: Mechanical properties, crystallization and rheological behaviors☆

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ARTICLE INFO

Article history:
Received 19 May 2010
Received in revised form 19 February 2011
Accepted 21 February 2011
Available online 5 March 2011

Keywords:
Montmorillonite
Polypropylene
Polyether
Mechanical properties
Rheological behaviors

ABSTRACT

In this work, montmorillonite (Mt) was modified by octadecyl amine ethoxylate ether (A) which has two poly (ethylene oxide) segments. Montmorillonite/polypropylene (Mt/PP) nanocomposites were prepared by a melt blending technique using different contents of modified Mt with and without maleic anhydride grafted polypropylene (PPg). The intercalated and exfoliated structures of Mt/PP nanocomposites were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Because of the typical intercalated and exfoliated structures, the mechanical properties of Mt/PP nanocomposites were improved significantly. The modified Mt in a PP matrix led to a significant reduction of melt viscosity and enhancement in Izod-notched impact strength and elongation at break. The Izod-notched impact strength and elongation at break of Mt/PP nanocomposites were 1.95 and 2.77 times as high as those of pure PP. The tensile strength of Mt/PP nanocomposites was also improved in the presence of PPg.

1. Introduction

During the last twenty years, not only in the academia but also in the industry clay polymer nanocomposites (CPN) have attracted significant interest (Okada et al., 1995; Vaia et al., 1995; Giannelis, 1996; Krishnamoorti et al., 1996; Krishnamoorti and Giannelis, 1997; Ke et al., 1999; Ray and Okamoto, 2003; Wang et al., 2006; Pavlidou and Papaspyrides, 2008; Zhu et al., 2009). They represent a new class of composite materials containing nanometric size (<100 nm) particles dispersed in a polymer matrix. Nanocomposites provide a significant improvement in polymer properties such as modulus, strength, and heat resistance, when compared to conventional composites. The structure of montmorillonite (Mt) consists of an octahedral sheet of alumina or magnesia that is surrounded by two tetrahedral sheets of silica. The thickness of each individual layer is about 1 nm and its width is around 500 nm. Mt has a great potential specific area, a high aspect ratio, a good swelling property and a low cost. It can significantly improve thermal stability and mechanical properties when dispersed in a polymer matrix with a low content. In general, there are two nanostructures in Mt/PP nanocomposites. Intercalated structures are well-ordered multilayered structures where the extended PP chains are inserted into the interlayer space of Mt. This leads to an expansion of the interlayer space. Exfoliated structures are formed when the silicate layers are individually dispersed as nanoscale particles in PP matrix. Generally, the morphology of Mt/PP nanocomposite is a mixed intercalated/exfoliated structure. The intercalated or exfoliated structure can improve many properties of polymers such as modulus, strength, and heat resistance.

However, the surface of the Mt layers is hydrophilic, and therefore has to be modified when used to fill hydrophobic commercial polymers. The most common method of Mt modification is cation exchange with organic ammonium salts containing different numbers, length and structure of organic chains. Cation exchange has been used for several decades (Beall and Goss, 2004). This modification is generally achieved by ion exchange reactions of organophilic ammonium salts and sodium ions which produce organophilic montmorillonite (OMt). In some cases, other kinds of organic compounds have been used (Brown et al., 2000; Fu and Qutubuddin, 2001; Moon et al., 2004; Monvisade and Siriphannon, 2009; Fu and Heinz, 2010). However, organic ammonium salts are characterized by low thermal stability and most of them are thermally degraded at the temperature not higher than 220–250 °C, which limit their applicability to certain polymeric materials.

Recently, intercalation of poly(ethylene oxide) (PEO) and low molar mass poly(ethylene glycol) into the interlayer space of Mt led to the formation of hybrid structures with a wide range of interesting properties and important uses (Ruizhitzky et al., 1996; Ogata et al., 1997; Chen and Chang, 2001; Loyens et al., 2005). For example, Mt/PEO nanocomposites have yielded a new class of ionic conductors. It can be used in some possible electronic applications, such as solid-state batteries, electrochemic devices, sensors, etc. Most of research in this field have focused on the conformation and crystallinity of PEO in the interlayer space of Mt

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☆ Contract grant sponsors: the National Basic Research Program of China (2005CB623800) and the Program for New Century Excellent Talents in University (NCET-10-0562).

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0169-1317/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2011.02.021

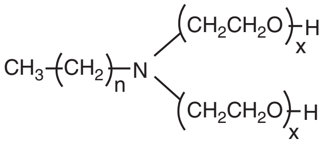
related to ionic conductivity (Chaiko, 2003; Homminga et al., 2005; Ratna et al., 2007; Miwa et al., 2008; Lorthioir et al., 2009). It is reported that oxyethylene units of PEO can act as ligands of interlayer cations, giving rise to stable complexes (Aranda and Ruiz-Hitzky, 1992). Thus, it is possible to improve compatibility between polymer and Mt by preparing polyether containing a terminal functional group (OH, NH_2, COOH, anhydride, etc.).

In this study, modified Mt polyether was used as filler for preparation of commercial Mt/PP nanocomposites. We intercalated octadecyl amine ethoxylate ether (A), which has two poly(ethylene oxide) segments as shown in the chemical structure below, into the interlayer space of Mt, and the modified Mt was used to prepare Mt/PP nanocomposites by a melt blending technique with and without maleic anhydride grafted polypropylene (PPg). The mechanical properties, crystallization and rheological behaviors of Mt/PP nanocomposites were investigated.

2. Experimental part

2.1. Materials

A commercially available isotactic polypropylene (F401) was supplied from Lanzhou Chemical Industry Factory (Lanzhou, China), with a melt flow index of 2.5 g/10 min (190 °C, 2.16 kg). Ca^{2+}-montmorillonite (Ca^{2+}-Mt) with a cation exchange capacity (CEC) of 90 m mol/100 g and OMt was supplied by Zhejiang Fenghong Clay Chemicals Co. (Zhejiang, China). OMt was sodium montmorillonite modified with octadecyl trimethylammonium chloride. Octadecyl amine ethoxylate ether (A) was purchased from Haian Petroleum Chemical Co. (Jiangshu, China), which was used as surfactant and the molecular structure (n = 17, x = 30) showed as follows:



2.2. Modification of montmorillonite

The surfactant A (50 g) was first dissolved in water till a limpid solution was obtained and then Ca^{2+}-Mt (50 g) were added to this surfactant solution. The AMt dispersion was heated at 60 °C under vigorous stirring. The A/Ca^{2+}-Mt (AMt) hybrids were dried in a 60 °C oven for several days and then pulverized. The power was sieved by passing though a 200-mesh stainless steel sifter. A/OMt (AOMt) hybrids were prepared in the same way.

2.3. Sample preparation

AMt or AOMt hybrids were added with 1–5 parts per hundred parts of PP (phr) by weight, then extruded by a general three-section twin-screw extruder (D = 20 mm, L/D = 40). Screw speed was set at 200 rpm and the temperatures were 175 °C, 190 °C, and 190 °C for each section of the barrel and 185 °C for the die. An injection-molding machine (K-TEC400, Klarke international Co., Ltd.) was used to prepare the specimens for the mechanical tests.

2.4. Characterization methods

Fourier transform infrared spectroscopy (FTIR) was performed in the transmission mode with a Nicolet-560 spectrometer. The spectra were collected at 2 cm^{-1} resolution between 400 and 4000 cm^{-1} with collection times of approximately 1 min. In order to remove the physical adsorption of A, the samples were extracted by boiling xylene for 72 h before scanning, respectively.

The thermogravimetric (TG) analysis was performed on TAQ-600 (TA Co., USA). The heating rate was 10 °C/min in a high purity flowing nitrogen atmosphere. An open platinum pan was used for holding the sample with the initial mass about 15 mg.

X-ray diffraction (XRD) patterns were recorded with a DX-1000 CSC diffractometer (China). The X-ray beam was nickel-filtered Cu Ka ($\lambda = 0.1542$ nm) radiation operated at 40 kV and 25 mA. Ca^{2+}-Mt, OMt, AMt and AOMt were studied as powders. Samples of Mt/PP nanocomposites were from the injection mold. The scanning range was varied from $2\theta = 1.5°$ to 40° with a rate of 1.8°/min.

Transmission electron microscopy (TEM) was carried out with an H-7100 (Tokyo, Japan) instrument with an accelerating voltage of 100 kV. The ultrathin sections of the samples from injection mold with a thickness of 50 nm were cut at 20 °C by a Reichert Ultracut cryoultramicrotome without staining.

Crystallization and melting behaviors were recorded on a DSC1 (Mettler Tolede Co., Switzerland) differential scanning calorimeter (DSC) under constant nitrogen flow. Sample weight was maintained at low level (5–6 mg) for all measurements. All samples were first heated to 200 °C, held at 200 °C for 5 min, and then cooled with a rate 10 °C/min to 50 °C, and held at 50 °C for 5 min. They were then scanned from 50 to 200 °C at a rate of 10 °C/min. The crystallinity (Xc) of the blends was calculated from the equation $X_c = \Delta H_m / \Delta H$, where ΔH_m was the enthalpy of fusion of Mt/PP nanocomposites, directly obtained by DSC. ΔH, the enthalpy of fusion of 100% crystalline polymer, was 209 J/g for PP (Avalos et al., 1996).

Tensile tests were carried out according to the GB/T 1040–92 standard on a CMT 4104 machine (Sans Material Testing Technical Co., Shenzhen, China). Elongation at break was measured at a cross-head speed of 50 mm/min. Izod-notched impact strength was measured with ZQK–20 (Dahua Material Testing Technical Co., China) according to the GB/T1043-93 standard.

The fracture surfaces of Izod-notched impact tested specimens of Mt/PP nanocomposites were examined under an acceleration voltage of 10 kV with a Philips scanning electron microscopy (SEM) equipment. Before being examined, the specimens of Mt/PP nanocomposites were coated with a thin layer of gold.

The rheological measurements were carried out on a Gottfert Rheograph 2002 (Gottfert Co., Germany). The capillary diameter and its length-to-diameter ratio were 1 mm and 30, respectively. The die had an entrance angle of 180°. Entrance pressure losses were assumed to be negligible for such a long capillary die, and therefore no Bagley correction was applied. The flow properties of these specimens were measured at 190 °C.

3. Results and discussion

3.1. FTIR and TG analysis of montmorillonite modified with A

FTIR was extensively used to probe the structure and conformation of surfactant in OMt (Vaia et al., 1994; Osman et al., 2004; Xi et al., 2005). Before analysis by FTIR and TG, all samples were extracted by boiling xylene for 72 h in order to get rid of free A component.

The characteristic peaks at 2923 and 2851 cm^{-1} in the FTIR spectra of AMt were ascribed to the stretch vibrations of methylene of A (Fig. 1 (b)). However, there were no bands at 2923 and 2851 cm^{-1} in the FTIR spectra of Ca^{2+}-Mt. It can be confirmed that A still existed in AMt though it was extracted by boiling xylene for 72 h. This indicated that there was a strong interaction between A and Ca^{2+}-Mt. In fact, the large number of cations in the interlayer space of Mt were coordinated by the ether type oxygen atoms of the polymer (Strawhecker and Manias, 2003). Because the characteristic peaks of alkyls in OMt may be similar to that of A in AOMt, it seemed that whether A existed in OMt could not be confirmed by characteristic peaks at 2923 and 2851 cm^{-1} of AOMt. The relative content