Polymer Degradation and Stability 95 (2010) 651–655

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Structural design of imidazolium and its application in PP/montmorillonite nanocomposites

Aihua He [a,*], Limei Wang [b], Wei Yao [a,*], Baochen Huang [a], Dujin Wang [c], Charles C. Han [d]

[a] Key Laboratory of Rubber-Plastics (Ministry of Education), School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China
[b] Department of Chemistry, Dezhou University, Shandong 253023, China
[c] CAS Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, No. 2, 1st North Street, Zhongguancun, Beijing 100080, China
[d] State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, No. 2, 1st North Street, Zhongguancun, Beijing 100080, China

ARTICLE INFO

Article history:
Received 4 November 2009
Accepted 5 December 2009
Available online 21 December 2009

Keywords:
Surfactants
Montmorillonite
Polypropylene
Nanocomposites

ABSTRACT

Four kinds of imidazolium surfactants with high thermal stability were designed and synthesized accordingly. The structures of these surfactants were characterized by ^{1}H NMR spectra. The TGA results indicated that the thermal stabilities of these surfactants with saturated alkyl groups were relatively high and the initial decomposition temperatures at 5% weight loss ($T_{0.05}$) were higher than 250 °C. Imidazolium(O) modified montmorillonite (MMT) was prepared by cation exchange. TGA results showed that the OMMT showed obviously higher thermal stability than the surfactants themselves and the $T_{0.05}$ values of OMMT were higher than 330 °C. The dihexadecane imidazolium (DHI) with two long tails has the ability to enlarge the interlayer spacing to a bigger degree compared with other imidazolium surfactants with only one long tail. Polypropylene(PP)/OMMT nanocomposites were prepared by solution blending and the effects of these surfactants with different structures on the silicate layer dispersion in PP matrix were measured.

1. Introduction

Since the Nylon-6/clay nanocomposites with some excellent properties, such as enhanced mechanical properties, increased heat distortion temperature and decreased gas/vapor permeability [1–8] were successfully prepared by Toyota researchers [1,2] in the late 1980s, many research interests from both academic and industrial labs have been focused on the polymer/clay nanocomposites [9–22]. Recently, more efforts focus on the creating of high-performance poly(propylene) (PP)/clay nanocomposites for potential applications in the field of packaging and the automotive industry as a substitute of high-performance engineering plastics.

PP, as one of the commodity plastics, is expected to have improved toughness, enhanced modulus and barrier properties, and could be used in automotive fields. PP nanocomposites filled with well dispersed silicate layers is thought to be an effective way to modify PP. However, it is difficult to prepare well dispersed PP/clay nanocomposites because of the incompatibility of hydrophobic PP and hydrophilic clay, and the strong self-agglomeration of silicate layers especially during PP processing process at high temperature. In order to improve the compatibility of clay and PP, alkyl-ammonium surfactants have been used to modify montmorillonite (AMMT) [10–17,23,24]. However, it was found that the alkyl-ammonium surfactant began to degrade at 104 °C [20] and the thermal degradation of alkyl-ammonium surfactants at the PP processing temperature (200 ± 10 °C) not only accelerated the aging and decomposition of PP, but also led to the re-stacking of the silicate layers. This behavior has been reported in PP/clay composites via both melt- blending method and in-situ polymerization method [20,25].

In our previous work, monoalkylimidazolium (Im) modified montmorillonite (IMMT) were used to prepare novel Ziegler–Natta /IMMT compound catalysts, and subsequently, the exfoliated PP/montmorillonite(MMT) nanocomposites with good thermal stability were successfully synthesized via intercalative polymerization method [20,21]. It has been accepted that the surfactants used in clay modification will play an important role on the processing stability of PP/clay nanocomposites. Therefore the design of surfactants with higher thermal stability, better compatibility for clay and PP, and enhanced clay exfoliation ability are becoming more and more crucial.

* Corresponding authors. Tel.: +86 532 84022951; fax: +86 532 84022951.
E-mail addresses: aihuahe@iccas.ac.cn (A. He), yaowei@qust.edu.cn (W. Yao).

0141-3910/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2009.12.003

In this paper, four kinds of imidazolium compounds with different chemical structures and relatively high thermal stability have been designed and synthesized as clay modification surfactants. The ^{1}H NMR spectra were used to characterize those synthesized surfactants. Basic physical properties including thermal stability of those surfactants were investigated in detail. Organic montmorillonite (OMMT) modified with those surfactants were prepared by ionic-exchange and PP/OMMT composites were prepared by solution blending accordingly. The effects of surfactants with different chemical structures on the physical properties of OMMT and PP/OMMT nanocomposites were studied.

2. Experimental

2.1. Materials and instruments

Na^+-MMT was supplied by Qinghe Chemical factory with about 80-100 mequiv. /100 g cationic exchange capacity (CEC). Pure polypropylene granule (PP) with melting index 44 was supplied kindly by the Institute of Chemistry, Chinese Academy of Sciences. 1-Methylimidazole (Analysis Purity, AP) and 1-iodohexadecane (AP) were purchased from Aldrich Co. Imidazole (AP) was purchased from Tianjin Fuchen chemical reagent Co. of China. 1-bromohexadecane (CP) was purchased from Beijing reagent Co. of China. 1-hexadecaneimidazolium was supplied kindly by our group member (the Institute of Chemistry, Chinese Academy of Sciences). 2-bromoethanol (CP) was purchased from Alfa Aesar Co. Allyl chloride (CP) was purchased from Shanghai Chemical reagent Co. of China. Other solvents such as acetonitrile, hexane, ether, ethanol, etc, were used after dried with 4A molecular sieves overnight.

^{1}H NMR spectra were recorded at 300 MHz on a Brucker DMX-300 NMR Spectrometer with $CDCl_3$ as the solvent and TMS as the internal reference. Thermogravimetric analysis was performed with Perkin-Elmer TGA at a heating rate of 20 °C/min under nitrogen atmosphere. Differential Scanning Calorimetry (DSC) was conducted using a Perkin–Elmer DSC-7 thermal analyzer under nitrogen atmosphere with a heating rate of 10 °C/min in a temperature range of 40–200 °C for dynamic scanning, and T_m was determined in the second scan. Wide-angle X-ray diffraction (XRD) analysis was performed on a Japan Rigaku D/max-2500 diffractometer with Cu Kα radiation ($\lambda = 0.1504$ nm) at a generator voltage of 40 kV and generator current of 100 mA. Scaning was performed in a step of 0.02° at a speed of 2°/min. The interlayer spacing (d_{001}) of MMT was calculated in accordance with Bragg equation: $2d \sin\theta = \lambda$.

2.2. Synthesis of the surfactants

2.2.1. Synthesis of the 1-hexadecane-3-methylimidazolium bromine (HMI)

Equimolar quantities of 1-methylimidazole and 1-bromohexadecane were placed into a 500 mL flask with reflux condenser under the argon atmosphere. Then the reactor was degassed and sealed under vacuum. The reactants were left stirring for approximately 7 days at 120 °C. The resulted solid was recrystallized from dry acetonitrile and washed by hexane for 3 times and then dried under vacuum overnight. The yield was 84 wt%.

2.2.2. Synthesis of the 1,3-dihexadecane imidazolium iodine (DHI)

A precise amount of imidazole and 1-iodohexadecane were placed into a 500 mL flask with reflux condenser under the argon atmosphere (the molar ratio of imidazole to 1-iodohexadecane was 1:2.2). Then the reactor was degassed and sealed under vacuum. The reactants were left stirring for approximately 6 days at 110 °C. The resulted solid was recrystallized from dry acetonitrile and washed by hexane for 3 times and then dried under vacuum overnight. The yield was 41 wt%.

2.2.3. Synthesis of the 1-hydroxyethyl-3-hexadecane imidazolium bromine (HHI)

1-hexadecaneimidazolium and 2-bromoethanol with the molar ratio of 1:1.2 were placed into a reactor with reflux condenser under the argon atmosphere. The reactants were left stirring for approximately 2 days at 80 °C. The resulted solid was washed by ether and then dried under vacuum overnight. The yield was 84 wt%.

2.2.4. Synthesis of the 1-allyl-3-hexadecane imidazolium chloride (AHI)

1-Hexadecaneimidazolium and 1-allyl chloride with the molar ratio of 1:1.25 were placed into a reactor with reflux condenser under the argon atmosphere. The reactants were left stirring for approximately 3 days at 60 °C. The resulted solid was washed by ether and then dried under vacuum overnight. The yield was 63 wt%.

2.3. Preparation of organically modified montmorillonite (OMMT)

The surfactant (twice the CEC of Na^+-MMT) was dissolved in ethanol at 50 °C and the surfactant solution was added to a 10 wt% aqueous suspension of montmorillonite under vigorous stirring. The mixture was stirred for 8 h at 60 °C, then the products were collected by filtration, washed with hot ethanol, and paper filtered until no halide anions were measured. OMMT was dried at 80 °C under vacuum for 24 h.

2.4. Preparation of PP/OMMT nanocomposites

The dried OMMT was dispersed in xylene, the pure PP was dissolved in xylene at 130 °C. Then the above mixtures were blended at 130 °C for 6 h at nitrogen atmosphere. The product was collected by precipitating in ethanol and dried at 80 °C under vacuum for 2 days.

3. Results and discussion

3.1. ^{1}H NMR characterization of the synthesized surfactants

Imidazolium compounds have been generally studied as the ionic liquids or anti-bacterial agents [26,27]. However, as compatibilizers for clay and PP, imidazolium were little studied. The advantageous features of the imidazolium compounds include the imidazole ring which will offer the compound high thermal stability compared to that of alkyl-ammonium compounds, and the various alkyl substitute groups which will improve the hydrophobility of clay and benefit the enlargement of the gallery of silicate layers. Therefore, in order to obtain the desire surfactant for PP and clay composites, four kinds of imidazolium compounds were designed and synthesized accordingly. The structures of the synthesized surfactants were characterized by the ^{1}H NMR measurements. The ^{1}H NMR spectra of those surfactants were shown in Fig. 1. The chemical structure of each surfactant was given and the assignment of each peak in Fig. 1(a–d) was also assigned according to the H sequence number of the formula, as shown in Fig. 1.

The results of the ^{1}H NMR spectra showed that 1-hexadecane-3-methylimidazolium bromine (HMI), 1,3-dihexadecane imidazolium iodine (DHI), 1-hydroxyethyl-3-hexadecane imidazolium bromine (HHI) and 1-allyl-3-hexadecane imidazolium chloride (AHI) could be synthesized according to the above mentioned synthesized routes.