

Polyamide- and polycarbonate-based nanocomposites prepared from thermally stable imidazolium organoclay

Lili Cui^a, Jason E. Bara^b, Yefim Brun^c, Youngjae Yoo^a, P.J. Yoon^d, D.R. Paul^{a,*}

^a Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, USA

^b Department of Chemical & Biological Engineering, The University of Colorado at Boulder, Boulder, CO 80309, USA

^c E.I. DuPont Company, Central Research and Development, Wilmington, DE 19880, USA

^d Southern Clay Products, 1212 Church Street, Gonzales, TX 78629, USA

ARTICLE INFO

Article history:

Received 20 January 2009

Received in revised form

7 March 2009

Accepted 9 March 2009

Available online 28 March 2009

Keywords:

Nanocomposites

Organoclays

Thermal stability

ABSTRACT

This paper explores the possible advantages of the more thermally stable imidazolium-based organoclay over a more conventional ammonium-based organoclay for facilitating exfoliation and minimizing polymer matrix degradation in melt blended polyamide 6 (PA-6) and polycarbonate (PC) nanocomposites. The thermal stability of the two organoclays was evaluated by TGA analyses. The extent of clay exfoliation was judged by analysis of the morphology and tensile modulus of these nanocomposites formed using a DSM Microcompounder, while the extent of color formation and molecular weight change were used to evaluate polymer matrix degradation. For PA-6 and PC nanocomposites, the use of the imidazolium organoclay only produced slight differences in both exfoliation and molecular weight change, although the imidazolium organoclay is remarkably more thermally stable than the ammonium organoclay.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Melt processing is an attractive approach for forming polymer nanocomposites due to its advantages for commercial production. In this process, the polymer and organoclay are heated to temperatures well above the melting or softening point of the polymer, typically above 200 °C. Thus, for polymers that require high melt processing temperatures, e.g., polyamides and polycarbonates, the thermal stability of the organic component of the modified clay and its impact on the ability to exfoliate the clay platelets plus any consequent effect on the polymer matrix are issues that must be considered. As reported previously [1–3], the traditional ammonium-based organic surfactants used to modify commercial organoclays begin to show measurable thermal degradation at temperatures as low as 180 °C. Prior studies in this laboratory have suggested that the byproducts formed from the breakdown of the organic surfactant might lead to degradation of the polymer during melt processing [2,4]. Imidazolium-type cations have been reported to be much more thermally stable than ammonium-based cations [5–9]. Davis et al. [8] reported some fairly well-exfoliated poly(ethylene terephthalate) nanocomposites

with less intensive color formation using an imidazolium surfactant modified organoclay compared to that shown by nanocomposites formed from an ammonium surfactant modified organoclay. The syndiotactic polystyrene (s-PS)/Imidazolium organoclay nanocomposites formed by Manias et al. [10] using a static melt-intercalation method at 290 °C show intercalated morphology and slightly improved thermal stability compared to that of the neat s-PS.

In this study, two organoclays with remarkable differences in thermal stability, based on an imidazolium cation and an ammonium cation where each contains one long alkyl tail, were used to form nanocomposites. Polyamide 6 (PA-6) and polycarbonate (PC) were chosen as the polymer matrices. PA-6 is well known for its capability to form well-exfoliated nanocomposites from organoclays [11–14], while PC is susceptible to a variety of degradation reactions [15–18] during melt blending with commercial organoclays [4]. This paper explores the possible advantages of the more thermally stable imidazolium-based organoclay over a more conventional ammonium-based organoclay for facilitating exfoliation and minimizing polymer matrix degradation and color formation. The extent of clay exfoliation is judged by analysis of the morphology and tensile modulus of the nanocomposites formed using a DSM Microcompounder, while the extent of polymer matrix degradation and color formation experienced during the melt processing of the

* Corresponding author. Tel.: +1 512 471 5392; fax: +1 512 471 0542.

E-mail address: drp@che.utexas.edu (D.R. Paul).

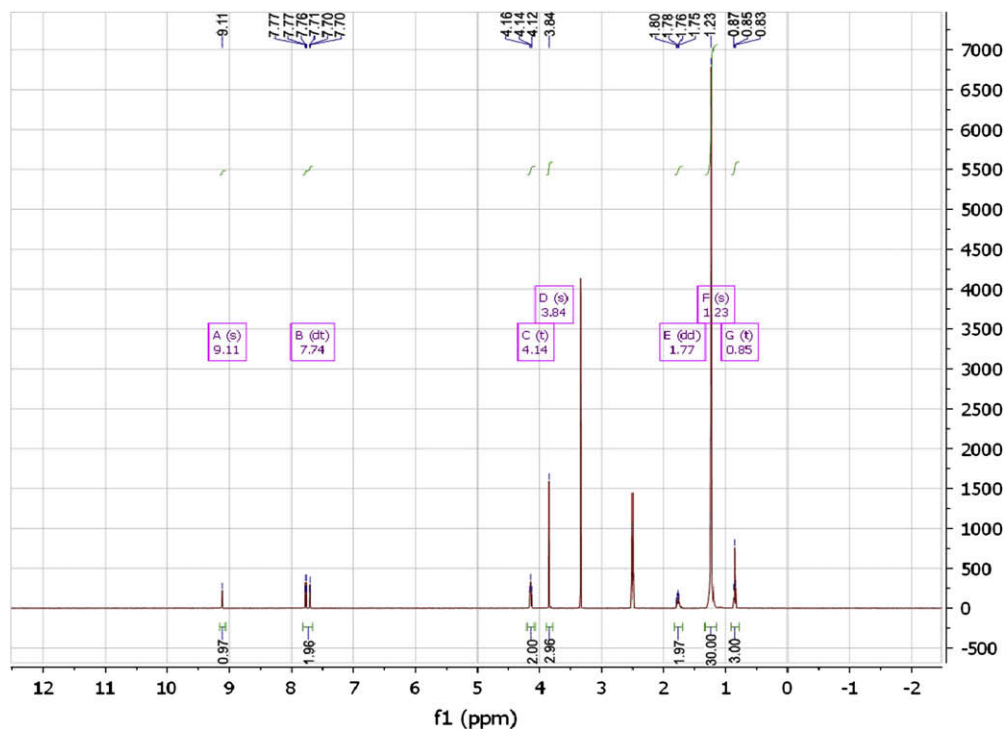


Fig. 1. ^1H NMR spectrum of 1-octadecyl-3-methylimidazolium bromide.

nanocomposites are characterized through the determination of the polymer molecular weight and colorimeter measurements.

2. Experimental

2.1. Materials

Two commercial polymers, i.e., Capron B135WP (PA-6) from Honeywell and Lupilon E2000FN (PC) supplied by Mitsubishi Engineering Plastic Corporation, were used in this study to form the two series of melt compounded nanocomposites.

The octadecyl-trimethyl ammonium chloride surfactant used was supplied by Akzo Nobel. The 1-octadecyl-3-methyl imidazolium bromide surfactant was synthesized using chemicals purchased from Sigma–Aldrich (Milwaukee, WI, USA). The chemicals were used as-received with the exception of 1-bromooctadecane, which was received as a dark brown solid. This material was dissolved in *n*-hexane and the solution was passed through a plug of silica. The clear, colorless filtrate was reduced via rotary evaporation and the remaining product was dried under vacuum at 65 °C for several hours. Subsequent cooling to ambient temperature produced

a colorless solid. 90.00 g (269.9 mmol) purified 1-bromooctadecane was dissolved in 200 mL toluene, and 19.95 g (243.0 mmol) 1-methylimidazole was added. The reaction was heated at reflux (110 °C) overnight. After this, cooling of the reaction mixture produced a white solid, which was collected and washed with 500 mL Et_2O . 1-Octadecyl-3-methylimidazolium bromide was recrystallized from 700 mL hot EtOAc followed by being dried under vacuum as a fine white powder (Yield = 97.52 g (96.6%)). The imidazolium bromide salt formed is quite pure, as evidenced by the ^1H NMR spectrum (400 MHz, DMSO) in Fig. 1. The primary chemical shifts are described as follows: $\delta = 9.11$ (s, 1H), 7.74 (dt, $J = 1.8, 26.8$, 2H), 4.14 (t, $J = 7.2$, 2H), 3.84 (s, 3H), 1.77 (dd, $J = 7.3, 14.3$, 2H), 1.23 (s, 30H), and 0.85 (t, $J = 6.9$, 3H). The peak at 2.50 ppm is DMSO in d_6 -DMSO, and the peak at about 3.35 ppm is water in the d_6 -DMSO.

The two experimental organoclays based on montmorillonite (see Table 1) were formed at Southern Clay Products, Inc. using a cationic exchange procedure. The aqueous suspension of sodium montmorillonite (CEC = 92 milliequivalent per 100 g) containing ~3% dry clay was heated to 65 °C to promote the cationic exchange reaction, and then was reacted in a stirred tank by pouring 95 milliequivalent of the surfactant based on 100 g of the sodium montmorillonite for 30 min. Then, the flocculated organoclay was transferred to a homogenizer to finish the reaction followed by washing with water and vacuum filtering. The excess water was removed in a convection oven. The dry organoclay was milled to a fine powder which passed through a 0.12 mm screen and subsequently a 0.08 mm screen. Neither of the organoclays formed was subjected to the frequently reported [18,19–21] exhaustive purification protocol to remove the excess unreacted surfactant and the byproduct sodium halide of the ion-exchange process. The presence of the residual nucleophilic halide anions usually impair the thermal stability of organoclays [1,5,22], which may consequently contribute to the degradation of the matrix polymer; however, the major difference in the thermal stability of the two organoclays originates from their cation types, and the purity of these organoclays is not the key issue for this investigation.

Table 1
Organoclays used in this study.

Organoclay designation	Surfactant cation structure
$\text{M}_3(\text{C18})_1$	$\begin{array}{c} \text{M} \\ \\ \text{M}-\text{N}^+-\text{M} \\ \\ \text{C}_{18}\text{H}_{37} \end{array}$ Octadecyl–trimethyl ammonium
Imidazolium (C18) $_1$	$\begin{array}{c} \text{M}-\text{N} \quad \text{N}-\text{C}_{18}\text{H}_{37} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{N}^+ \end{array}$ 1-Octadecyl-3-methyl imidazolium

Download English Version:

<https://daneshyari.com/en/article/5184917>

Download Persian Version:

<https://daneshyari.com/article/5184917>

[Daneshyari.com](https://daneshyari.com)