



Production and characterization of nanocomposites based on poly(amide-imide) containing 4,4'-methylenebis(3-chloro-2,6-diethylaniline) using nano-TiO₂ surface-coupled by 3-aminopropyltriethoxysilane

Shadpour Mallakpour^{a,b,*}, Elham Nikkhoo^a

^a Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran

^b Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran

ARTICLE INFO

Article history:

Received 20 May 2012

Received in revised form

10 September 2012

Accepted 17 September 2012

Available online 26 October 2012

Keywords:

Poly(amide-imide)

Nanocomposites

TiO₂ nanoparticles

Thermal properties

Ultrasonic irradiation

UV shielding

ABSTRACT

In this work, the poly(amide-imide) (PAI) was synthesized from the polymerization reaction of 4,4'-methylenebis(3-chloro-2,6-diethyl trimellitimidobenzene) as a diacid with 4,4'-methylenebis(3-chloro-2,6-diethylaniline) under green condition using molten tetra-*n*-butylammonium bromide and triphenylphosphite. Ultrasonic technique was used for preparation of PAI/TiO₂ nanocomposites (PAI/TiO₂ NCs). For the improvement of TiO₂ nanoparticles (NPs) dispersion and enhancing interactions between NPs and polymeric matrix the surface of TiO₂ was successfully modified by silane coupling agent (3-aminopropyltriethoxysilane). The resulting NCs were characterized by FT-IR, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The TGA of the obtained NCs proves the enhancement in the thermal stability with an increase in the percentage of titania NPs. TEM and FE-SEM images showed that the NPs were uniformly dispersed in the polymer matrix. The shielding effect of nano TiO₂ under UV radiation was examined by UV-vis.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Polymer nanocomposites (NCs) represent a novel class of material alternative to formal filled polymers. In this category of material, inorganic nanomaterials are dispersed in polymer matrix offering enormous improvement in performance properties of the polymer. In the recent years, the preparation of polymer NC materials has been extremely considered due to their comparatively remarkable diverse properties including mechanical, thermal, optical properties, and extremely decreased flammability [1–4].

Nanomaterials are classified into three divisions: (1) Nanoparticles (NPs): when the three dimensions of particulates are about nanometers, they are named isodimensional nanoparticles. (2) Nanotubes: when two dimensions are in the nanometers. (3) Nanolayers: when only one dimension is in the nanometers [5–11]. The addition of NPs to the polymer matrix has been the most usually accepted technique for manufacturing polymer NCs [12].

Titanium is the ninth fullest element in the earth's crust and the fourth fullest element. The most famously applied titanium product is titanium dioxide (TiO₂) [13]. Three well-known crystalline structures for TiO₂ have been known as anatase, rutile and brookite. The rutile shape is usually achieved when pure TiO₂ crystal is produced. Anatase structure is less stable and forms at lower temperatures and is most appropriate in catalysis and photocatalysis because of its higher surface area. Brookite form occurs only in extreme conditions [14]. TiO₂ is a chemically stable, nontoxic, biocompatible, inexpensive material, shown antibacterial activity, safe, high refractive index, low cost, posing little risk to human health [12,15–18]. TiO₂ used as porcelains and ceramics industries, inks [17], nutrients, toothpaste, cosmetic sunscreens, photocatalytic activities [19], that this makes TiO₂ NPs applicable in many fields such as self-cleaning, anti-bacterial agent, UV protecting agent, environmental purification, water and air purifier [14,20,21], gas sensors [22], and high efficient solar cell [13,23–25].

Because of their chemical structure, composed of carbon and hydrogen, polymers are very flammable [26]. Flame-retardant additives are mixed with polymers to progress their fire retardance and heat resistance by decreasing the rate of burning, flame spread, and smoke production. Flame retardant systems can act physically or chemically. Flame retardancy through chemical modification of the fire procedure can take place in gaseous or the condensed phase [27]. Halogenated polymers act mainly in the gaseous phase by a

* Corresponding author at: Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran. Tel.: +98 311 391 3267; fax: +98 311 391 2350.

E-mail addresses: mallakpour84@alumni.ufl.edu, mallak@cc.iut.ac.ir, mallak777@yahoo.com (S. Mallakpour).

radical mechanism to stop the exothermic processes and to repress combustion because they can give hydrogen halides that reduced the concentration of $\cdot\text{H}$ and $\cdot\text{OH}$ radicals [28,29].

Ionic liquids (IL)s are used widely because they are safe, can dissolve a large range of compounds, little toxicity and have negligible vapor pressure. Additionally, ILs are recyclable, a factor that could reduce the price of their use. IL technology has some utility for the polymer synthesis [30,31].

Polyimides are significant high-performance materials due to their excellent properties. But, their applications are limited due to their high melting temperatures and their very low solubility in most usual organic solvents. Copolycondensation is one of the possible methods for modification of polymer properties. In this sense, poly(amide-imide)s (PAIs) suggests the advantages of polyimides and polyamides, high thermal stability and good mechanical properties. In this work, at first, the thermally stable PAI was synthesized by direct polycondensation of 4,4'-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA) and diacid under green condition using molten tetra-*n*-butylammonium bromide (TBAB) and triphenylphosphite (TPP). Then PAI/TiO₂ NCs were synthesized under ultrasonic irradiation. The resulting NCs were characterized by a number of miscellaneous techniques.

2. Experimental

2.1. Materials

All chemicals used were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. Nanosized TiO₂ powder was purchased from nanosabz Co. (Tehran, Iran) with average particle sized of 25–30 nm. The coupling agent (3-aminopropyltriethoxysilane) (KH550), obtained from Merck Chemical Co. *N,N'*-Dimethylformamide (DMF) were dried over BaO and then were distilled under reduced pressure. TBAB, trimellitic anhydride (TMA) and MCDEA were purchased from Merck Co.

2.2. Equipments

Proton nuclear magnetic resonance (¹H NMR, 400 MHz) spectrum was recorded in dimethyl sulfoxide (DMSO-*d*₆) solution using a Bruker (Germany) Avance-400 instrument. Proton resonances are designated as singlet (s), doublet (d), and multiplet (m). Fourier transform infrared (FT-IR) spectra were recorded on Jasco-680 spectrophotometer (Japan). The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm⁻¹). Band intensities are assigned as weak (w), medium (m), strong (s), and broad (br). Inherent viscosities were measured using a Cannon-Fenske routine viscometer (Germany) at concentration of 0.5 dL g⁻¹ at 25 °C. Specific rotations of polymer samples were measured by a Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on a STA503 win TA instrument in a nitrogen atmosphere at a rate of 20 °C/min. XRD patterns were recorded using a Philips Xpert MPD X-ray diffractometer with a copper target at 40 kV and 35 mA and Cu K α λ = 1.54 Å in the range 10–80° at the speed of 0.05°/min. The dispersion morphology of the NPs on PAI matrix was observed using transmission electron microscopy (TEM) analyses were performed using a Philips CM 120 operating at 100 kV and field emission scanning electron microscopy [FE-SEM, HITACHI (S-4160)]. The reaction was performed by MISONIX ultrasonic liquid processors, XL-2000 SERIES. Ultrasound was a wave of frequency 2.25×10^4 Hz and power 100 W.

2.3. Monomer and polymer synthesis

4,4'-Methylenebis(3-chloro-2,6-diethyl trimellitimidobenzene) diacid (1) and PAI were prepared according to our previous work [32].

2.4. Preparation of PAI/TiO₂ NC coatings

It is usually necessary for the NP surfaces to be modified that achieve good dispersion in the polymer. First, TiO₂ NPs were reacted with the KH550 as coupling agent molecules, resulting in the coupling agent being attached to the surface of the NPs (modified-TiO₂). Preparations of PAI/TiO₂ NCs were carried out through the following procedure: different amounts of surface modified TiO₂ NPs (5, 10, 15 and 20 wt.%) were mixed with 0.1 g of synthesized PAI. The mixture was dispersed in 20 mL of absolute ethanol and then irradiated under ultrasound waves for 4 h. After irradiation, the solvent was removed, and obtained NCs were dried in vacuum at 80 °C for 2 h [33].

3. Result and discussion

3.1. Monomer synthesis

The diacid compound (1) was synthesized by the condensation reaction of anhydride and diamine in DMF (Scheme 1). The ¹H NMR spectrum of diacid showed peaks between 0.94–1.02 ppm as two triplets that were assigned to the methyl groups. Diacid presented signals due to trimellitimide ring protons at 8.13–8.16 ppm as a doublet, 8.38 ppm as a singlet and also 8.46–8.48 ppm as a doublet. The FT-IR spectrum of diacid showed a broad and strong peak at 3650–2250 cm⁻¹, which was assigned to the COOH groups and two absorption bands at 1781 and 1725 cm⁻¹ are characteristic peaks for imide rings [32].

3.2. Polymer synthesis

PAI was synthesized by polycondensation reaction from mixture of diacid 1 with MCDEA using TBAB and TPP as green solvent and activating agent. As shown in Scheme 1 the FT-IR spectrum of pure PAI showed absorptions around 3360 cm⁻¹ (N–H) and carbonyl groups (amide and imide's C=O) absorptions at 1776, 1725, and 1663 cm⁻¹, respectively. Absorption at 1380 and 727 cm⁻¹ showed the presence of the imide heterocycle in this polymer. The resonance of aliphatic protons appeared in range of 0.96–1.11 ppm, 2.35–2.63 ppm, 4.24 and 4.34 ppm. The resonance of the amide protons appeared at 9.58 ppm and 10.30 ppm.

3.3. Solubility of PAI

The solubility behavior of the prepared PAI was tested qualitatively (5 mg of polymer in 1 mL of solvent) in various organic solvents. This polymer was readily soluble in polar aprotic solvents such as DMSO, DMF, *N*-methyl-2-pyrrolidone and protic solvents but it was not soluble in solvents like methylene chloride, chloroform, methanol and ethanol.

3.4. Manufacture of PAI/TiO₂ NC coatings

Due to exist of OH groups on the surface of NPs, it is easy for TiO₂ NPs to greatly agglomerate in polymer matrix. Several techniques can be used to modify NPs, such as, surface-active agent, coupling agent, fatty acid and alcohol [34–38]. Silane coupling agents are one of the generally used materials for enhancing the dispersion stability of the NPs in the polymers [39–41]. The silane coupling agents

Download English Version:

<https://daneshyari.com/en/article/692806>

Download Persian Version:

<https://daneshyari.com/article/692806>

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