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Full Length Article

Optical, thermal and combustion properties of self-colored polyamide nanocomposites reinforced with azo dye surface modified ZnO nanoparticles

Mohsen Hajibeygi[a,*], Meisam Shabanian[b], Mehrdad Omidi-Ghallemohamadi[a], Hossein Ali Khonakdar[c]

[a] Faculty of Chemistry, Kharazmi University, 15719-14911 Tehran, Iran
[b] Faculty of Chemistry and Petrochemical Engineering, Standard Research Institute (SRI), Karaj, P.O. Box 31745-139, Iran
[c] Department of Polymer Engineering, Faculty of Engineering, South Tehran Branch, Islamic Azad University, P.O. Box 19585-466, Tehran, Iran

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ABSTRACT

New self-colored aromatic-polyamide (PA) nanocomposites containing azo and naphthalene chromophores were prepared with azo-dye surface-modified ZnO nanoparticles (SMZnO) using solution method in dimethylformamide. The X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) results showed the uniform distribution for ZnO nanoparticles in the PA matrix. The UV–vis spectra of PA/ZnO nanocomposites (PANC) showed a blue shift as well as reduction in absorbance intensities and the photoluminescence studies revealed that the increasing intensities of the violet emission in SMZnO loading. From thermo gravimetric analysis (TGA), the temperature at 10% mass loss (T_{10}) increased from 291.8 °C to 387.6 °C for PANC containing 8 mass% of SMZnO, as well as the char yield enhanced significantly, which was about 23.5% higher than the neat PA. The peak heat release rate resulted from microscale combustion calorimeter (MCC), by 8 mass% loading of SMZnO, decreased about 56.9% lower than the neat PA.

1. Introduction

Polymer composite containing inorganic nanomaterials have recently attracted in both academic and industrial interests due to their significant and enhanced properties such as thermal [1], mechanical [2], optical [3], electrical [4], magnetical [5], high flexible processability and homogeneity [6] as compared to unfilled polymers. These materials have exhibited the combined properties of polymer (such as flexibility and ductility) and inorganic materials (such as high thermal stability, rigidity, strength, hardness and high refractive index) [7–9]. They also have shown wide potential applications in various areas such as coatings [10], plastics and rubber reinforcement [11,12], catalysis [13,14], electronics [15], lithography [16] and biotechnology [17,18].

Metal oxide nanoparticles due to their unique chemical and physical properties have been widely used as filler in the preparation of polymer nanocomposites [9,19–22]. Zinc oxide (ZnO), iron oxide (Fe_3O_4), copper oxide (CuO), zirconium dioxide (ZrO_2), Aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), manganese dioxide (MnO_2), titanium dioxide (TiO_2) and nickel oxide (NiO) are the most important metal oxides that have been reported recently [23–26]. Zinc oxide, as the inorganic filler, due to its numerous significant properties, such as chemical [27] and thermal stability [28], catalytic [29], electrical and electronic [30] properties, low dielectric constant [31], optical and effective antimicrobial, antibacterial and bactericide properties [32] and also long-term environmental stability, non-toxicity, biocompatibility and low cost [28] has been used for preparation of inorganic polymer nanocomposites.

The main disadvantages of polymers reinforced with ZnO nanoparticles have been agglomeration and incompatibilities of ZnO nanoparticles in the polymer matrix, due to its hydrophilic surface and having high surface energy [33]. Therefore, the enhancement of the ZnO nanoparticles dispersion in the polymer matrix has been a significant characteristic for preparation of polymer nanocomposites [9]. Organic compound with the ability to form chemical bonding as coupling agent can be used for surface modification of metal oxide nanoparticles such as ZnO [34]. Modification of nanoparticles can be led to offer better compatibility of nanoparticles with dispersing to the polymer matrix, to prevent nanoparticles from aggregation, as well as increase the chemical

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* Corresponding author.
E-mail addresses: mhajibeygi@khu.ac.ir, mhajibeygi@gmail.com (M. Hajibeygi).

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reactivity of nanoparticles. This has also led to a better compatibility and homogeneity between the two phases and thus to design the materials with well properties [35].

Polymers containing azo-dye groups have been called azo-polymers. Optical properties of these materials have been very unique due to the presence of the —N═N— as a photochromic group [36]. The *trans*-cis isomerization of azo group has led to the changes of dipole moment, spatial volume at the molecular structure, and the color at the macroscopic level [37,38]. Therefore, azo-polymers have been used in variety of applications [39], such as non-linear properties [40], liquid-crystal materials [41] and also can be utilized in optical information storage or optical data recording and switches [42–44].

Aromatic polyamides (aramide) have already been noted for their favorable properties such as high temperature resistance and excellent mechanical properties. Polyamides have been one of the most versatile classes of high performance polymers and as a good candidate for matrix nanocomposites, which are used in wide range of applications [45]. But, they have been noted as difficult processable materials because of their poor solubility in organic common solvents, too high glass transition temperatures and high softening or melting temperatures [46]. Many approaches have been investigated for improve the solubility of aromatic polyamides include the addition of bulky pendant groups to the polymer backbone, incorporation of polar and flexible groups within the parent chain [47,48].

The aim of the present work was preparation of new nanocomposites based on the self-colored aromatic PA reinforced with azo-dye surface modified ZnO nanoparticles. From the presence of the azo and naphthalene ring in the polyamide structure, it was expected to provide acceptable optical properties. Also a good thermal stability due to fully aromatic structures was expected for PA and its nanocomposites. In this work, the effect of SMZnO on the optical properties, thermal stability and combustion properties of the developed PA was described.

2. Experimental

2.1. Materials

5-aminoisophthalic acid, 2-naphthol, sulfanilic acid, 1,5-naphthalenediamine, *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), pyridine (Py), triphenyl phosphite (TPP) and sodium nitrite from Merck were used without further purification. Commercially available calcium chloride ($CaCl_2$, Merck) was dried under vacuum at 150 °C for 6 h. ZnO nanoparticle powder with average particle size of 25–30 nm, 99.983% purity and density 5.6 g/mL was purchased from Tecnan-nanomat Co.

2.2. Measurements

^{1}H NMR spectra were recorded by a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded by a Perkin-Elmer RXI spectrometer. Vibration transition frequencies were reported in wave number (cm^{-1}). Band intensities were assigned (w) for weak, (m) for medium, (sh) for shoulder, (s) for strong and (br) for broad.

Inherent viscosity was measured at a concentration of 0.5 g/dL in DMF at 25 °C by a standard procedure using Ubbelohde viscometer.

Molar mass of the synthesized PA concluded mass-average ($-M_w$) and number-average ($-M_n$) molar mass, was performed in size exclusion chromatography (SEC) by Agilent Series (Agilent 1100, USA) system. The molar mass was calculated after calibration with poly(2-vinylpyrrolidone) standard.

X-ray diffraction (XRD) was described using 2-circle diffractometer XRD 3003 (Germany, Freiberg) by Cu-K_α radiation ($\lambda = 0.154$ nm) generated at 30 mA and 40 kV in the range of $2\theta = 2°–60°$. The surface morphology of the samples was analyzed by Field Emission-Scanning Electron Microscopy (FE-SEM) (Mira 3-XMU). The morphological analysis was carried out using transmission electron microscopy (TEM) with microscope LEO 912. The sample was analysis at room temperature, 120 kV acceleration voltage and bright field illumination.

Solid state UV–vis spectra were recorded at 25 °C in 190–790 nm spectral regions using a Cary 6000i UV–vis/Near-infrared spectrophotometer (Varian). Also solution state UV–vis spectrum was recorded at 25 °C in 190–790 nm using Perkin-Elmer UV–vis spectrometer Lambda 25. Photoluminescence (PL) emission spectra were investigated using Perkin-Elmer Florescence spectrometer LS 55.

The thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were recorded using a TA Instruments TGAQ5000 in the range between 25 °C to 800 °C at a heating rate of 10 °C/min in nitrogen atmospheres. The thermal events of PA and corresponding nanocomposites were measured by differential scanning calorimetry (DSC, TA instrument Q1000). Three cycles of heating-cooling-heating with rate of 10 °C/min and sample size of about 10 mg were performed. The combustion properties were investigated by microscale combustion colorimeter (MCC).

2.3. Monomer synthesis

2.3.1. Synthesis of diacid **3**

2-hydroxynaphthalen azo isophthalic acid **3** as diacid monomer containing azo group and naphthalene ring was synthesized according to Vogel textbook procedure [49] as following:

For preparation of diazonium salt, 0.50 g (2.7 mmol) of 5-aminoisophthalic acid, 15 mL distilled water and 0.3 g sodium carbonate were placed into a 100-mL beaker equipped with a magnetic stirrer. The reaction mixture was stirred at 15 °C. In another beaker, 0.3 g sodium nitrite was dissolved in 2 mL distilled water and was added to the first beaker. In the next step, the resulting solution was added to a mixture of 5 mL HCl 37% and 20 mL distilled water in an ice bath.

In another beaker, 0.397 g (2.7 mmol) 2-naphthol was dissolved in 10 mL of aqueous sodium hydroxide (10%) and stirred in ice bath and the solution of diazonium salt was added to 2-naphthol solution dropwise over a period of 20 min at 0 °C. After that, the reaction mixture was stirred at room temperature for 30 min. The red product was filtered and washed thoroughly with ethanol, and dried at 50 °C. Yield = 85%; mp: 223–225 °C. FT-IR (KBr): 2200–3500 (s, br, COOH, stretching), 1726 (s, C═O, stretching), 1621 (m, —C═C—, stretching), 1210 (m, C—O, stretching), 1508 (s, —N═N—, stretching), 1251 (s, C—O, stretching), 834 (m, ═C—H, bending), 746 (m, ═C—H, bending) cm^{-1}. ^{1}H NMR (DMSO-d_6, TMS) δ: 15.49 (s, 1H), 13.48 (s, br, 2H), 8.42 (s, 2H), 8.34 (dd, 1H), 8.31 (s, 1H), 7.89 (dd, 1H), 7.71 (dd, 1H), 7.62 (t, 1H), 7.43 (t, 1H), 6.81 (dd, 1H) ppm. ^{13}C NMR (DMSO-d_6) δ: 171.5, 166.0, 145.3, 141.2, 132.7, 132.6, 129.7, 129.5, 129.1, 128.0, 127.8, 126.4, 124.4, 122.5, 121.2 ppm.

2.4. Synthesis of polyamide (PA)

PA was synthesized according to Yamazaki method [50]. Briefly, 1.50 g (4.46 mmol) of diacid **3**, 0.70 g (4.46 mmol) of diamine **4**, calcium chloride (1.0 g), triphenyl phosphite (2.5 mL), pyridine (1.0 mL) and N-methyl-2-pyrrolidone (12 mL) were added into 100 mL round-bottomed flask equipped with a magnetic stirrer under N_2 atmosphere. The reaction mixture was heated in an oil bath at 70 °C for 1 h, 80 °C for 3 h and 115 °C for 6 h. Subsequently, the obtained viscose solution was poured into 100 mL