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Research paper

Zn–AL LDH reinforced nanocomposites based on new polyamide containing imide group: From synthesis to properties

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A B S T R A C T

A new series of polyamide/Zn–Al layered double hydroxide (LDH) nanocomposites (PANC) was prepared by solution intercalation technique under ambient condition in dimethylformamide as solvent. The polyamide (PA) containing pyridine ring and imide group was synthesized using direct polycondensation reaction with good solubility and desired molar mass. Organo-modified Zn–Al LDH (OLDH) was produced by one-step method and used to improve mechanical, thermal and flame properties of PA. The extent of dispersion of OLDH sheets was quantified by X-ray diffraction (XRD) and transmission electron microscopy (TEM) and the results showed a good dispersion for OLDH in the PA matrix. According to the results of mechanical tests, the tensile strength and the Young's modulus of PANC enhanced with increasing OLDH content. Thermal properties of PANC were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal property results in both nitrogen and air atmospheres showed that the addition of OLDH resulted in a substantial increase in the thermal stability and char yields of PANC as compared to the neat PA. Significant improvements in flame retardancy performance were observed for PANC from microscale combustion calorimeter (MCC) (reducing both the heat release rate and the total heat released).

1. Introduction

Polymeric nanocomposite materials have attracted increasing attention because of their potential in terms of improving thermal stability, flame retardancy, mechanical properties and film barrier characteristics with small nanoparticles loading in organic polymers. In recent years, many studies were reported about layered nanostructure materials as one of the potential candidates for polymeric nanocomposite preparation because of their large value of aspect ratio, diameter in nanometer range, thermal stability and other good properties even at low concentrations (Sinha Ray and Okamoto, 2003; Wang et al., 2007; Katiyar et al., 2010; Shabanian et al., 2014a).

Layered double hydroxides (LDHs), also called anionic clays, were considered as a class of clays which have a promising future in the field of nanocomposites due to their various unique properties. LDH can be prepared from a wide range of various metallic compositions (Kutlu et al., 2014). Chemical structure of LDH was found to be a stack of positively charged metal hydroxide layers with intercalated counteranions and water molecules (Wang et al., 2011b). LDH was used in various fields such as catalysts (Lopez et al., 2010; Wang and O'Hare, 2012), ion exchange hosts (Millange et al., 2000), drug delivery (Alcantara et al., 2010), hydrothermal reactor (Wang et al., 2013) and fire retardant additives (Nyambo et al., 2008; Manzi-Nshuti et al., 2009a). Recently many researches have been focused on polymer nanocomposites containing LDH (Lv et al., 2009; Wang et al., 2011a, 2011b; Purohit et al., 2012) and significant synergistic effects were observed in both thermal stability and flame retardancy for formulations containing polymer matrices with modified Mg–Al and Zn–Al LDH as nanofillers (Nyambo et al., 2008; Manzi-Nshuti et al., 2009a; Wang et al., 2012).

Due to the increasing demand for high-performance polymers as a good candidate for matrix nanocomposites, thermally stable polymers such as polyamides have attracted increasing interest over the past decade (Díez-Pascual et al., 2012; Shabanian et al., 2013b). Polyamides are one of the most versatile classes of high performance polymers which are used in wide range of applications and display unique properties, but they suffer from disadvantages such as low solubility in organic solvents and having high melting and/or glass transition temperatures, which cause some restrictions in their processing. However, these problems can be solved or reduced by introducing some flexible bonds such as aliphatic chains (Shabanian and Basaki, 2013), pendant bulky group (Hajipour et al., 2008; Ghaemy and Nasab, 2011) and heteroaromatic rings in the polyamide backbone (Liu et al., 2013).

Among these approaches, introduction of heteroaromatic rings into the backbone of polyamides has been considered in some reports

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(Mehdipour-Ataei and Heidari, 2003; Faghihi and Mozaffari, 2008; Kausar et al., 2010; Shabbir et al., 2010; Shabanian et al., 2014b). Pyridine is a heteroaromatic molecule with polarizability and rigidity. Some kinds of heteroaromatic structures containing pyridine unit have been designed and synthesized, and the heteroaromatic polymers have been synthesized from those monomers containing pyridine nucleus structures at the same time (Liu et al., 2004; Ma et al., 2010). In general, the heteroaromatic rings in the polymer backbone would impart certain properties to it, while pyridine with heteroaromatic structure would have excellent stabilities derived from its structural symmetry and aromaticity of pyridine ring (Madhra et al., 2002). Also polarizability resulting from nitrogen of pyridine ring could be suitable to improve solubility of polymer in organic solvents (Kurita and Williams, 1974; Butuc and Gherasim, 1984).

The aim of present work was the preparation of new reinforced nanocomposites based on OLDH and a polyamide containing pyridine and imide heterocyclic rings through solution intercalation technique. From the presence of the heterocyclic derivatives and the aliphatic groups in the polyamide structure it was expected to provide acceptable glass transition and good solubility in organic solvents. In this work, the effect of OLDH on the mechanical properties, thermal stability and flame retardancy of the developed nanocomposites was also described.

2. Experimental

2.1. Materials

Glutamic acid, phthalic anhydride, 4-hydroxy-3-methoxy-benzaldehyde (vanillin), 4-nitroacetophenone, N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), palladium charcoal (Pd/C), hydrazine monohydrate, pyridine (Py) and triphenyl phosphite (TPP) from Merck were used without further purification. Commercially available calcium chloride ($CaCl_2$, Merck) was dried under vacuum at 150 °C for 6 h. Zinc nitrate, aluminum nitrate, sodium hydroxide, and sodium dodecylbenzene sulfonate (SDBS) used for synthesis of OLDH by one-step route were also obtained from Merck.

2.2. Measurements

^{1}H-NMR spectra were recorded by a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer RXI spectrometer. The KBr pellet technique was applied for monitoring changes in the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}. Approximately 3 mg of the powdered components was mixed with 100 mg KBr and pressed into pellets and used for further characterization. Vibration transition frequencies were reported in wavenumber (cm^{-1}). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br).

Inherent viscosity was measured at a concentration of 0.5 g/dL in DMF at 25 °C by a standard procedure using a Technico Regd Trade Mark Viscometer.

Molar mass (mass-average ($\overline{M}_w$) and number-average ($\overline{M}_n$)) determination was performed in size exclusion chromatography (SEC) using Agilent Series 1100 (Agilent, USA) system consisting of a pump, degasser and differential refractive index (RI) detector. Two Zorbax PSM Trimodal-S 250 mm × 6.2 mm columns (Rockland Tech, USA) were used. The measurements were performed using a mixed eluent DMAc with 2 vol.% water and 3 g/L LiCl at a flow rate of 0.5 mL/min. The molar mass was calculated after calibration with poly(2-vinylpyrrolidone) standards.

Wide angle X-ray scattering (WAXS) was performed using 2-circle diffractometer XRD 3003 (GE Inspection Technologies/Seifert-FPM, Freiberg, Germany) using Cu–K_α radiation ($\lambda = 0.154$ nm) generated at 30 mA and 40 kV in the range of $2\theta = 2°–12°$ with a step length of 0.05° and slit aperture of 1°. XRD patterns of the samples were measured randomly in a continuous mode with a scan speed of 0.005°s^{-1}.

Elemental analyses were performed by Vario EL equipment.

The morphological analysis was carried out using a LEO 912 transmission electron microscopy (TEM) operated at room temperature with an acceleration voltage of 200 kV in a brightfield illumination.

Mechanical properties were performed at room temperature on a Testometric Universal Testing Machine M350/500 (Mainz, Germany); rate, 3 mm/min; according to ASTM D882 (standards). The mechanical properties were repeated five times. The average values along with standard deviations were reported.

Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA4000 System under N_2 and air atmosphere at rate of 10 °C/min. Differential scanning calorimeter (DSC) was conducted with DSC, Mettler 110 (Switzerland) at heating rate of 10 °C/min in nitrogen atmosphere.

The flame retardancy properties were analyzed by microscale combustion colorimeter (MCC) that is a convenient and relatively new technique. The average values along with standard deviations were reported. The detailed procedure was as follows: about 5 mg of samples was heated to 700 °C with a heating rate of 1°Cs^{-1} in a stream of nitrogen flowing at 80 cm^3/min. Then, the volatile anaerobic thermal degradation products were mixed with 20 cm^3/min gas stream containing 20% oxygen and 80% nitrogen, respectively, prior to entering to a 900 °C combustion furnace. All measurements were repeated at least in duplicate.

2.3. Monomer synthesis

2.3.1. Synthesis of diacid

2-(1,3-Dioxoisoindolin-2-yl)pentanedioic acid as a diacid monomer was synthesized by the condensation reaction of phthalic anhydride and glutamic acid in an acetic acid solution according to previous research (Faghihi et al., 2010).

2.3.2. Synthesis of diamine

4-(2,6-Bis(4-aminophenyl)pyridine-4-yl)-2-methoxyphenol as a new diamine compound containing pyridine ring was synthesized by two step reactions according to previous researches (Tamami and Yeganeh, 2001; Hajipour et al., 2008; Shabanian et al., 2014b) as follows;

Synthesis of 4-(2,6-bis(4-nitrophenyl)pyridin-4-yl)-2-methoxyphenol; 1.08 g (6.56 mmol) of 4-nitroacetophenone, 0.5 g (3.28 mmol) of vanillin, 6 g of ammonium acetate and 12 mL of glacial acetic acid were added into 100 mL round-bottom flask. The reaction mixture was heated in an oil bath at 120 °C for 18 h. Upon cooling, the precipitated yellow solid was collected by filtration and washed with ethanol. FTIR (KBr): 3531 (m), 1593 (s), 1547 (m), 1513 (s), 1439 (m), 1347 (s), 1271 (m), 1209 (m), 1031 (m, sh), 846 (s), 815 (m), 735 (m), and 691 (m) cm^{-1}. ^{1}H-NMR (DMSO-d_6, TMS) δ: 9.50 (s, 1H), 8.60 (d, 4H), 8.36 (d, 4H), 8.35 (s, 2H), 7.61 (s, 1H), 7.56 (d, 1H), 6.93 (d, 1H), and 3.94 (s, 3H) ppm.

Synthesis of 4-(2,6-bis(4-aminophenyl)pyridin-4-yl)-2-methoxyphenol; 1.62 g (3.67 mmol) of dinitro, 0.1 g of 10% Pd/C, 20 mL of ethanol, 5 mL of DMF and 3 mL of hydrazine monohydrate were added into a 100 mL round-bottomed flask. The reaction mixture was heated in an oil bath at 90 °C for 5 h. Then, the mixture was filtered to remove the Pd/C and the filtrate was poured into water and dried. FTIR (KBr): 3434 (m, sh), 3352 (m), 3212 (w), 3031 (w), 2934 (w), 1607 (s), 1596 (s), 1513 (s), 1437 (m), 1393 (m), 1269 (m), 1179 (m), 1126 (m), 831 (m), and 581 (m) cm^{-1}. ^{1}H-NMR (DMSO-d_6, TMS) δ: 9.30 (s, 1H), 7.97–8.00 (d, 4H), 7.72 (s, 2H), 7.43 (s, 1H), 7.35–7.38 (d, 1H), 6.88–6.91 (d, 1H), 6.65–6.68 (d, 4H), 5.39 (s, 4H), and 3.91