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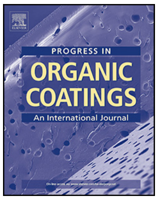

Highly stable polyimide composite films based on 1,2,4-triazole ring reinforced with multi-walled carbon nanotubes: Study on thermal, mechanical, and morphological properties

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ABSTRACT

A novel diamine bearing aromatic pendant triazole ring, namely, 3,5-diamino-N-(1H-[1,2,4]triazol-3-yl)-benzamide, was successfully synthesized. The prepared diamine and a commercial dianhydride were reacted in situ in the presence of carboxylated multi-walled carbon nanotubes (MWCNTs) with stirring to give a homogeneous MWCNT/poly(amic acid) mixture which was then heated under a heating program to give a series of MWCNT/polyimide (PI) composites with different proportions of MWCNT (5, 10, and 15 wt%). The composite films were tested for different properties including spectral, morphological, thermal, and mechanical properties. Scanning and transmission electron microscopy revealed the modified MWCNTs were well dispersed in the PI matrix while the structure of the polymer and the MWCNTs structure were stable in the preparation process. The thermal stability of the films containing MWCNTs was improved as the MWCNT content increased from 5 to 15 wt% due to the improved interfacial interaction between the PI matrix and surface-modified MWCNTs. Tensile tests on the composites showed an increase in the elastic modulus and the yield strength, and decrease in the failure strain.

1. Introduction

The engineering materials provide continuous research opportunities for the current industrial applications. Among all the nano functional materials, carbon nanotubes (CNTs) are the frontiers of these researches because of significantly improved and unusual properties. CNTs have exceptional mechanical, electrical, and thermal properties, which are strongly anisotropic [1]. In order to fully utilize these properties, numerous CNT/polymer composites have been produced and investigated [2]. These nanocomposites exhibit the superior physical properties such as enhanced tensile strength [3] and improved electrical conductivity [4]. Many polymers such as epoxy [5], polycarbonate [6], polyamide [7], polyimide (PI) [8], polystyrene [9], and polypropylene [10] have been used to prepare CNT/polymer composites. These materials have potentially superior thermal, electrical, and mechanical properties than the pristine polymers. In polymer-matrix composites made with non-continuous fillers, dispersion of the filler influences nearly all relevant properties of the composite. Unfortunately, pure CNTs are insoluble in the organic solvents and tend to form aggregates due to the extremely high surface energy, which leads to a heterogeneous dispersion in the polymer matrix and has negative effects on the properties of the resulting composites [11]. The degree of dispersion of CNTs and the consequent macroscopic behavior is strongly dictated by the choice of the matrix, the type of CNT, modification of their surface, and the processing method and associated parameters [12,13]. Several methods have already been developed over the last years to achieve an efficient dispersion of individual CNTs in a polymer matrix. The simplest method consists of directly mixing the polymer and the CNTs [14–17]. Stirring in a solvent, polymer solution, or a polymer melt is usually not sufficient to achieve this goal. For this purpose, ultrasound (bath ultrasonication) is frequently applied [18–21]. Like any sound wave, ultrasound propagates via a series of compression and rarefaction waves induced in the molecules of the medium through which it passes. One can also either modify the polymer in such a way that it can interact with the π-system of the CNT wall, or modify the walls of the CNTs by functionalization and so improve the wetting of the filler, as well as the dispersion in the medium [22,23].

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In this contribution in order to achieve fine dispersion of carboxyl-functionalized multi-walled CNTs (MWCNTs), we attempted to prepare MWCNT/PI composites using in situ polymerization approach (i.e., solution-casting followed by subsequent imidization). Thermal property, mechanical property and morphology of MWCNT/PI composites were then investigated. The introduction of several functional groups as well as triazole bulky units resulted in increased chain packing distances and decreased intermolecular interactions, leading to better interaction of the PI chains with MWCNTs and better dispersion of MWCNTs in the PI matrix.

2. Experimental

2.1. Materials

All materials and solvents were purchased either from Aldrich Chemical Co. (Milwaukee, WI), Merck or Fluka (Germany). 3-Amino-1H-1,2,4-triazole, 3,5-dinitrobenzoylchloride, hydrazine monohydrate, propylene oxide, pyromellitic dianhydride (PMDA), dimethyl sulfoxide (DMSO), and 10% palladium on activated carbon were used as received without further purification. N,N′-dimethylacetamide (DMAc) ($d = 0.94\,\mathrm{g\,cm^{-3}}$ at 20 °C) and N,N′-dimethylformamide (DMF) ($d = 0.94\,\mathrm{g\,cm^{-3}}$ at 20 °C) were purified by distillation under the reduced pressure over barium oxide. Carboxylated MWCNTs synthesized by chemical vapor deposition (CVD) (the outer-diameter 8–15 nm, the inner-diameter 3–5 nm, length ~50 μm, carboxyl content 2.56 wt% and purity >95 wt%), were achieved from Neutrino Co. (Iran). All other reagents were used as received from commercial sources.

2.2. Methods

Proton nuclear magnetic resonance (^{1}HNMR) spectra were recorded on a Bruker (Rheinstetten, Germany) Avance 500 instrument at room temperature in DMSO-d_6. Multiplicities were given as s (singlet). Chemical shifts ^{1}HNMR spectra are reported as δ in units of parts per million (ppm) and relative to the signal of DMSO-d_6 ($\delta = 2.50$, singlet). The number of protons (n) for a given resonance was indicated by nH. Carbon nuclear magnetic resonance (^{13}CNMR) spectra were reported as δ in units of ppm downfield and relative to the signal of DMSO-d_6 ($\delta = 39.50$). Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Bomem MB-Series 1998 FT-IR spectrophotometer (Quebec, Canada) at a resolution of 4 cm^{-1}. The samples were examined as a disc, grinded together with potassium bromide (KBr) salt. They were scanned at wavenumber (cm^{-1}) range of 400–4000 cm^{-1}. Band intensities were assigned as weak (w), medium (m), strong (s), and broad (br). Melting points were determined in capillary tubes using a melting-point apparatus (Barnstead Electrothermal 9200, Iowa, USA) without correction. Elemental analysis was run on an Elementar Analysensysteme GmbH (Hanau, Germany). Monitoring of the reactions was accomplished by thin layer chromatography (TLC) on silica gel polygram SILG/UV 254 plates (0.2 mm thickness). Inherent viscosity (η_{inh}) (at a concentration of 0.5 g/dL) was measured with an Ubbelohde suspended-level viscometer at 25 °C using DMF as solvent. Thermogravimetric analysis (TGA) was performed with the DuPont Instruments (TGA 951, 2805 West Frye Road Chandler 85224 AZ, USA) analyzer at a heating rate of 10 °C/min^{-1} under nitrogen (20 cm^3/min) in temperature range of 25–800 °C. Measurements were carried out on 10 ± 2 mg film samples. The mechanical properties of PI and the composite films were measured at room temperature on a universal testing machine (SANTAM, model STM-20, Iran), according to ASTM D 882 (standards). Tests were carried out with a cross-head speed of 12.5 mm/min until reaching a deformation of 20% and then, at a speed of 50 mm/min at break. The dimensions of the test specimens were $35 \times 2 \times 0.04\,\mathrm{mm^3}$. Property values reported here represented an average of the results for tests run on at least five specimens. Tensile strength, tensile modulus, and strain were obtained from these measurements. The X-ray diffraction (XRD) was used to characterize the crystalline structure of the samples. XRD patterns were collected using a Bruker, D8AVANCE (Rheinstetten, Germany) diffractometer with a copper target at the wavelength of λ CuKα = 1.54 Å, a tube voltage of 40 kV, and tube current of 35 mA. The samples were scanned at a rate of 0.05 °/min from 10° to 80° of 2θ. For XRD studies, rectangular pellets prepared by compression molding were used. The morphology of the MWCNTs and the dispersion morphology of the MWCNTs on the PI matrix were observed using field emission scanning electron microscopy (FE-SEM). The images were taken at 15 KV using a HITACHI S-4160 instrument (Tokyo, Japan). Transmission electron microscopy (TEM) images were obtained using a Philips CM 120 microscope (Netherlands) with an accelerating voltage of 100 kV. For TEM studies, ultra-thin sections (30–80 nm) of the composites were prepared using Leica Ultramicrotome. Branson S3200 (50 kHz, 150 W) ultrasonic bath (Americas Headquarters 41 Eagle Road, Danbury CT 06810, USA) was used for better dispersion of MWCNTs.

2.3. Synthesis of 3,5-dinitro-N-(1H-[1,2,4]triazol-3-yl)-benzamide (3)

The synthetic pathway leading to the synthesis of target diamine is outlined in Scheme 1. Into a 50 mL round-bottomed flask equipped with a condenser, a magnetic stirring bar and a nitrogen gas inlet tube, 3.45 g (15.0 mmol) of 3,5-dinitrobenzoyl chloride and 1.26 g (15.0 mmol) of 3-amino-1H-1,2,4-triazole were dissolved in 15.0 mL of DMAc at 0 °C. After 30 min, 1.00 mL of propylene oxide was dropped into the stirring was continued at 0 °C for 6 h. The reaction mixture was slowly warmed to room temperature, stirred for additional 6 h, and poured into 150 mL of distilled water. The resulting yellowish powder was collected by filtration and washed with boiling ethanol and distilled water several times. The crude product was dried under reduced pressure at 70 °C. The yield of the crude product was 3.67 g (88%) with the melting point of 270–272 °C.

FT-IR (KBr; cm^{-1}): 3431, 3382 (s, N—H stretching), 3073 (w, C—H aromatic), 1656 (s, C=O amide stretching), 1546, 1332 (s, N—O stretching), 1189 (w, C—O stretching), 774 (w, N—H out of plane bending). ^{1}HNMR [dimethylsulphoxide-d_6 (DMSO-d_6), δ, ppm]: 7.92 (s, 1H, Ar—H, triazole ring), 8.47 (s, 2H, Ar—H), 8.69 (s, 1H, Ar-H), 10.12 (s, 1H, NH, amide), 12.72 (s, 1H, NH, triazole ring). ^{13}CNMR (DMSO-d_6; δ, ppm): 181.5 (C, C=O), 168.4 (C, triazole ring), 157.2 (C, triazole ring), 149.4 (C, Ar), 137.3 (CH, Ar), 128.5 (CH, Ar), 123.2 (CH, Ar). Elemental analysis: calculated for $C_9H_6N_6O_5$: C, 38.86%; H, 2.17%; N, 30.21%; found: C, 38.84%; H, 2.15%; N, 30.17%.

2.4. Synthesis of 3,5-diamino-N-(1H-[1,2,4]triazol-3-yl)-benzamide (4)

To a 100 mL round-bottomed three-necked flask equipped with a dropping funnel, a reflux condenser and a magnetic stirring bar, 3.34 g (12.0 mmol) 3,5-dinitro-N-(1H-[1,2,4]triazol-3-yl)-benzamide (3) and 0.05 g palladium on activated carbon (Pd/C, 10%), were dispersed in 40 mL of ethanol. The suspension solution was heated to reflux, and 5 mL of hydrazine monohydrate was added slowly to the mixture. After a further 18 h of refluxing, the solution was filtered hot to remove Pd/C, and the filtrate was cooled to give yellow crystals. The product was collected by filtration and dried in vacuum oven at 80 °C. The yield of the reaction was 78% (2.04 g), and the melting point was 255–257 °C.