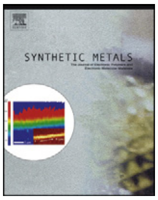
Synthetic Metals 162 (2012) 2010–2015

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Preparation of humidity-responsive antistatic carbon nanotube/PEI nanocomposites

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ARTICLE INFO

Article history:
Received 22 May 2012
Received in revised form
19 September 2012
Accepted 20 September 2012
Available online 9 November 2012

Keywords:
Carbon nanotubes
Polyetherimide
Poly(N,N-diethylacrylamide)
Antistatic
Humidity-response

ABSTRACT

A kind of polymer with antistatic property, poly(N,N-diethylacrylamide) (PDEAAm), was grafted onto the multi-walled carbon nanotubes (MWCNTs), and then such PDEAAm-g-MWCNTs was introduced into polyetherimide (PEI). The successful grafting was tested by FT-IR, XPS and TEM results, and the weight fraction of PDEAAm on the PDEAAm-g-MWCNTs was calculated according to the XPS and TGA. The PDEAAm-g-MWCNTs/PEI nanocomposites films were prepared by conventional solution processed method. The conductivity of nanocomposites increased by four orders of magnitude after absorbing moisture. The nanocomposites achieved the percolation threshold with the PDEAAm-g-MWCNTs loading of 0.25 wt.% and the volume conductivity reached 10^{-7} S/cm. Dynamic response and long-term stability test indicated good response sensitivity and stability property of this material. Thereby, such PDEAAm-g-MWCNTs/PEI nanocomposites had potential applications as passive humidity sensors.

1. Introduction

With the high performance polymer materials widely applied in the electronic and electrical devices, the damage caused by the static electricity, a build-up of static charge on the surface of objects, must be avoided [1]. Because of the high mechanical properties at elevated temperatures, heat resistance, solvent resistance and flame resistance, polyetherimide (PEI) is used in medical and chemical instrumentations. Unfortunately, the high electric resistance and low dielectric constant limit its applications in electronic devices, and become the necessary modification aspect before used [2,3]. Generally, two approaches are adopted for the antistatic modification of polymers. One is appending surfactant, such as quaternary ammonium, where water absorption plays a very important role for the antistatic property [4,5]. The other one is introducing the conductive fillers, such as carbon black, carbon fiber, carbon nanotubes (CNTs), and conductive polymer, which could improve the conductivity of the materials [6–8].

CNTs have been considered as a high performance conductive additive of polymer matrix, because of their unique aspect ratio, excellent electrical conductivity and excellent mechanical properties [9]. It is well accepted that the dispersion and the percolation of CNTs in polymer matrix constitute two key issues to obtain the better conductivity modification [10–12]. Li [13] synthesized a series of multi-walled carbon nanotubes (MWCNTs) ester/polysulfone composite films and researched the relationship between the conductivities of the films and the length of MWCNTs ester's alkyl chains. Our group enlarged the number of functional groups on the MWCNTs by the grafting of poly(acryloyl chloride) or poly(acrylic acid). Because of the high reactivity of acryl chloride or acrylic acid groups, many kinds of functional groups can be introduced onto the surface of MWCNTs. Therefore, the better dispersion of MWCNTs in corresponding polymer matrix could be achieved [14] and various functional MWCNTs could be obtained [15,16]. Vankayala [17] coated a layer of polyaniline on the surface of the CNTs and then such CNTs were added into nylon 6, the percolation threshold of the composite reached at 6 wt.%. Li dispersed the CNTs in the inner antistatic agent and prepared new polypropylene fibers. The antistatic property of them was improved by better hydrophilicity and conductivity [6].

It could be summarized that the organic materials coated on CNTs could not only improve dispersion of CNTs in the polymer matrix, but also play a role on the conductivity of composites. If we introduce an organic material whose conductivity could be changed according to the environment onto the surface of CNTs, and then add them into polymer matrix, the environmental sensitive nanocomposites could be obtained. Shashoua [18] reported the poly(N,N-diethylacrylamide) had high charge decay rate and was good antistatic agent at high relative humidity conditions, which might be caused by the dipolar resonance of the N-alkyl amide groups. In this work, MWCNTs were treated by acid and then grafted with poly(acryloyl

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http://dx.doi.org/10.1016/j.synthmet.2012.09.014

chloride). Poly(N,N-diethylacrylamide) (PDEAAm) could be generated from the reaction between diethylamine and poly(acryloyl chloride). Adding the PDEAAm functionalized MWCNTs into PEI, the conductivity of PEI nanocomposites would be improved obviously because the better dispersion of MWCNTs in PEI, which attributed to the similar structure and polarity of PDEAAm and PEI. Moreover, because the PEI resin and PDEAAm could absorb humidity, the electric resistance of the CNTs network would decrease dramatically with the presence of humidity-absorbed PDEAAm layer. Thus, a humidity-responsive antistatic MWCNTs/PEI nanocomposites was prepared, and then the structures and properties of the nanocomposites were studied.

2. Experimental

2.1. Materials

MWCNTs with an average outer diameter 10–30 nm and length 0.5–500 μm were supplied by Shenzhen Nanotech Port, China. Acryloyl chloride (>96%) was purchased from Acros Organic Co. Diethylamine (AR), triethylamine (TEA, AR), N-methyl-2-pyrrolidone (NMP, AR), 1,4-dioxane (AR), tetramethylene oxide (THF, AR), azobisisobutyronitrile (AIBN, AR), sulfuric acid (AR) and nitric acid (AR) were all purchased from XILONG Chemical Co., China. Polyetherimide (PEI, ULTEM 1000) were provided from SABIC. Silver paste (SCP-03B) was purchased from Electrolube Co.

2.2. Synthesis of PDEAAm grafted MWCNTs

The raw MWCNTs were first dispersed in the concentrated sulfuric acid for 24 h, then refluxed in the mixture of concentrated acids (HNO_3/H_2SO_4 = 1/1,volume concentration) at 140 °C for 30 min. The oxidized MWCNTs were washed with the de-ionized water until the filtrate was neutral.

1 g of acryloyl chloride, 18 mg of AIBN and 3 mL of dry dioxane were mixed and heated to 60 °C for 40 h. Then, 100 mg of oxidized MWCNTs dispersed in 100 mL of dry dioxane was added dropwise to the solution under ultrasonic. The reaction was kept at 60 °C for 10 h and the poly(acryloyl chloride) grafted MWCNTs (PACl-g-MWCNTs) were collected by high speed centrifugation.

1.6 g of diethylamine and 2.23 g of TEA were dissolved in dry dioxane and dropped into the PACl-g-MWCNTs solution, and then reacted at room temperature for 6 h. The product, named PDEAAm-g-MWCNTs, washed by de-ionized water and THF three times, respectively, and dried in the vacuum at 80 °C. The whole synthesis process was presented in Scheme 1.

2.3. Preparation of PDEAAm-g-MWCNTs/PEI nanocomposites

PDEAAm-g-MWCNTs were mixed with PEI in NMP at 120 °C for 1 h under ultrasonic. Then the solution was poured into a plane mould. NMP was vaporized at 140 °C under vacuum. A black PDEAAm-g-MWCNTs/PEI nanocomposites films were finally prepared.

2.4. Characterization

The functional groups on the surface of various MWCNTs were investigated by Fourier transform infrared spectrometer (FT-IR, Nicolet-Nexus 670), which was measured as pellets with KBr. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB 250 spectrometer using monochromatised AlKα X-ray source at a constant analyzer. Thermogravimetric analysis (TGA, TASC 414/4) was conducted from 40 to 800 °C at 10 °C/min under nitrogen atmosphere. The morphologies of PDEAAm-g-MWCNTs and PDEAAm-g-MWCNTs/PEI nanocomposites were observed by transmission electron microscope (TEM, JEM100CX). Water contact angles (JC2000A, SHANGHAI GUANGDIAN Co.) were measured at 1 min after deionized water dropping on the sample surface. Electrical conductivity was measured by a two-probe method using a megger (ZC-90, Yuanzhong Electron) in AC current mode. Measured samples were clipped into 10 mm × 30 mm × 1 mm. Silver paste was coated onto two ends of samples in order to make sure good electrical contact between the electrodes and the samples. A static humidity chamber (BE-TH80, Bell Group) was adopted to create particular humidity.

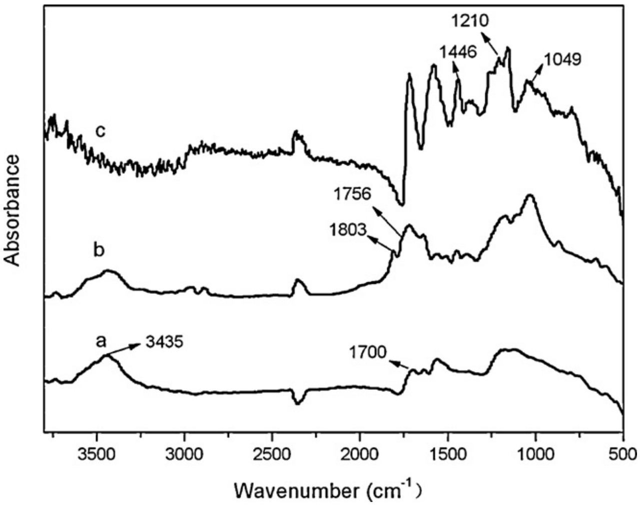

Fig. 1. FT-IR spectra of (a) oxidized MWCNTs, (b) PACl-g-MWCNTs and (c) PDEAAm-g-MWCNTs.

3. Results and discussion

3.1. FTIR analysis

Fig. 1 shows the FT-IR spectra of various MWCNTs. For oxidized MWCNTs (Fig. 1a), the peak at 1700 cm^{-1} is attributed to characteristic C═O stretching vibration of carboxyl. The broad absorption at 3435 cm^{-1} is attributed to the O─H stretching vibration of hydroxyl groups, which are the beginning of the next grafting. After reacted with PACl, two peaks at 1756 cm^{-1} and 1803 cm^{-1}, the characteristic peaks of C═O stretching vibration of acryl chloride, are observed in Fig. 1b. In Fig. 1c, the peak at 1446 cm^{-1} of the C─N stretching vibration of amide, and the peaks at 1210 cm^{-1} and 1049 cm^{-1}, representing the absorption of the $(C_2H_5)_2N$─C group, are detected. Meanwhile, the two peaks at 1756 cm^{-1} and 1803 cm^{-1} disappear. Therefore, it can be deduced that all PACl is reacted with the diethylamine and PDEAAm-g-MWCNTs are successfully synthesized.

3.2. XPS analysis

XPS tests the elements on the surface of the polymer-encapsulated MWCNTs. It indicates that there are C 1s and O 1s peaks at 284.79 eV and 532.92 eV, and there are 10.9 mol% oxygen and 89.1 mol% carbon in oxidized MWCNTs (Fig. 2a). Due to the grafting of PDEAAm on the MWCNTs, a peak of N 1s emerged at 400.83 eV in Fig. 2b. The relative molar concentrations of the carbon, nitrogen and oxygen were 80.77 mol%, 2.52 mol% and 16.17 mol%, respectively. In order to understand the quantity of the functional groups on the surface of the PDEAAm-g-MWCNTs, the high-resolution C 1s spectrum is resolved into several individual component peaks (Fig. 3). The molar ratio of each functional group is obtained according to the corresponding peak's area and is listed