Influence of functionalized single-walled carbon nanotubes on morphology, conducting and oxygen barrier properties of poly (acrylonitrile-co-starch)

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ABSTRACT

Functionalized single-walled carbon nanotubes (f-SWCNTs) reinforced polyacrylonitrile-co-starch (PAN-co-starch) nanocomposites were prepared by in situ polymerization technique. X-ray diffraction pattern of synthesized PAN-co-starch/f-SWCNT nanocomposites was established. The morphology of nanocomposites was investigated by field emission scanning electron microscopy, high resolution transmission electron microscopy and atomic force microscopy. The electrical conductivity, tensile strength of nanocomposites was studied as function of f-SWCNTs concentration. Oxygen barrier property of PAN-co-starch/f-SWCNT nanocomposites was calculated and it was found that, the property was reduced by six times with increase of f-SWCNTs proportion. The thermal and chemical resistances of PAN-co-starch/f-SWCNT nanocomposites were increased with increasing concentration of f-SWCNTs.

1. Introduction

Polymer based nanocomposites represent a radical alternative to conventionally filled polymers because of the dispersion of nanometer sized sheets or tubes and these nanocomposites have improved properties when compared with conventional polymers and their microcomposites. The characteristic properties of nanocomposites are usually observed with nanofiller contents as low as 1–5% [1]. These improvements include increased electrical conductivity, high mechanical strength and decrease in oxygen permeability. So polymer nanocomposites based on carbon nanotubes are of current interest due to their potential application in various fields [2–5]. Carbon nanotubes (CNTs) were first discovered by Iijima [6] in 1991 and the first polymer nanocomposites using carbon nanotubes as reinforcement were reported by Ajayan et al. [7]. CNTs have attracted great interest because of their unique physical and chemical properties, such as high mechanical strength, electrical, thermal stability and chemical stability [8–12] as compared to the virgin matrix. As a result of their large aspect ratio and superior electrical conductivity and mechanical strength, CNTs have been widely considered as one of the most promising filler for making of novel composite materials. They have also attracted enormous interest for their use in a wide variety of application in

nanoelectronic devices [13], probe tips for scanning electron microscopes [14] or in the automotive and aerospace industries for the dissipation of electrostatic charges [15].

Single-walled carbon nanotubes (SWCNTs) are crystalline graphitic rods characterized by an average diameter in the range of 1–2 nm and a typical length of microns resulting an aspect ratio of significantly more than 1000. Excellent mechanical and electrical properties of SWCNTs have raised high expectations regarding their utilization in different fields including molecular electronics and advanced materials [16]. SWCNTs are expected to serve as active components in electronic nano-switches and nanotransistors and act as molecular wires connecting components in nanodevices [17].

Presently, polymer/CNT nanocomposites are prepared by three methods [18,19]: solution blending, melt mixing and in situ polymerization. Melt mixing cannot achieve homogeneous dispersion of CNTs in polymer or copolymer matrices. Solution blending does not form strong chemical bonding between CNTs and polymers. In this method, large amounts of solvent and the associated environmental pollution due to the removal of the solvent have prevented the adoption of this technique on a mass scale for the fabrication of composites [20]. The main disadvantage of emulsion polymerization is that the surfactants and other polymerization byproducts present are difficult to remove. But in situ polymerization technique confers stronger interactions between the reinforcing filler and the polymeric phase. In situ polymerization is considered to

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be an effective method for preparing polymer/CNT nanocomposites. Thus, composites fabricated by this technique exhibit better electrical and mechanical properties and lower percolation threshold [21].

Zhao et al. [22] obtained homogeneous dispersions of CNTs in polyamide 6 through *in situ* polymerization under sonication. Guo et al. [23] and Liang et al. [24] reported that poly(methyl methacrylate) (PMMA) could efficiently join on to the surface of single-walled carbon nanotubes by *in situ* free radical polymerization in a poor solvent for PMMA. Dai et al. [25] studied the effect of SWCNTs on PMMA matrix. They have investigated the surface morphology by SEM and TEM and studied the electrical conductivity and mechanical properties and found that both are increased with the increase of SWCNT concentration.

Although number of papers have been reported regarding polymer based nanocomposites reinforced by multi-walled and single-walled carbon nanotubes. However, the reports of copolymer based nanocomposites with reinforcement of functionalized single-walled carbon nanotubes are very scanty in the literature. In present study, a series of functionalized single-walled carbon nanotubes reinforced PAN-co-starch nanocomposites were prepared by nonconventional emulsifier free emulsion technique, i.e., in green technique. The interactions of f-SWCNTs with copolymer matrix along with structural and surface morphology of synthesized nanocomposites were investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM). Further, the nanocomposites exhibited an appreciable enhancement of electrical, mechanical, thermal, gas barrier and chemical resistant properties as compared to virgin copolymer.

2. Experimental

2.1. Materials

Single-walled carbon nanotubes (SWCNTs) were purchased from SRL (Mumbai, India) with diameter of 1.5 nm and length 2 μm (aspect ratio ≈1333). Starch was purchased from Fischer scientific (Mumbai, India) of extra pure and used as such. Acrylonitrile (AN) was obtained from Merck (Germany) which was purified by phosphoric acid and sodium hydroxide followed by treatment with double distilled water before use. Concentrated sulfuric acid, concentrated nitric acid, potassium persulfate and ammonium ferrous sulfate were of analytical grade and were directly used without any special treatment.

2.2. Functionalization of single-walled carbon nanotubes

SWCNTs were functionalized by treatment with a mixture of concentrated H_2SO_4 and HNO_3 in a volume ratio of 3:1 followed by sonication (120 W/60 KHz) for 24 h at about 40 °C in a flask. The solution was then diluted with double distilled water and filtered. The residue was washed repeatedly with distilled water. Further the open ended tubes were treated with hydrogen peroxide and H_2SO_4 in a volume ratio of 1:4 with stirring at 70 °C for 30 min. The resultant solution was diluted with distilled water and centrifuged to get the functionalized SWCNTs (f-SWCNTs).

2.3. Preparation of PAN-co-starch/f-SWCNT nanocomposite

PAN-co-starch/f-SWCNT nanocomposites were synthesized by *in situ* polymerization technique. The f-SWCNTs were dispersed in deionised water and sonicated (120 W/80 KHz) for 30 min to form delaminated suspension and then acrylonitrile and starch
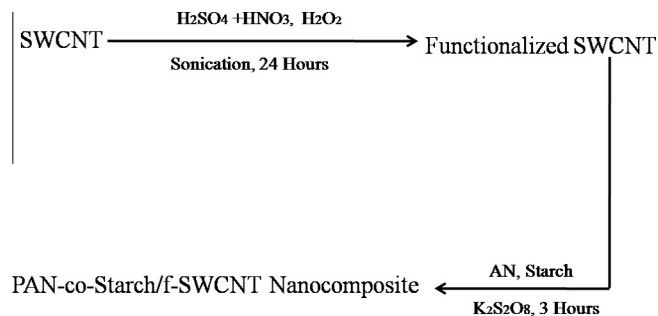

Fig. 1. Synthetic route for the preparation of PAN-co-starch/f-SWCNT nanocomposites.

were added to the suspension via stirring and again the mixture was sonicated for 30 min. The polymerization process was carried out by addition of potassium persulfate and the mixture was allowed to stir for 3 h. The polymerization process was terminated by the addition of ammonium ferrous sulfate. The product was filtered and washed with deionised water and dried in a hot air oven at 50 °C for 48 h. The schematic representation of synthesis of PAN-co-starch/f-SWCNT nanocomposites is illustrated as Fig. 1.

2.4. Characterization

XRD measurements were carried out using a Rigaku X-ray diffractometer using Cu Kα radiation (model no. DD966). The morphology of samples was obtained by using FESEM (JEOL-JSM-5800) and HRTEM (Tec-nai 12, Philips) operating at 120 kV. For AFM measurement, a thin film of purified sample was deposited on a mica surface and the AFM measurement was performed using a pico plus 5500 ILM AFM, with a piezoscanner maximum range of 100 μm.

Conductivity was measured with a two probe conductivity test meter (LCR-Hi-Tester, HOIKI, 3532-50) after the samples being pressed into pellet form. The pellets were coated with silver paints to ensure a good electrical contact. The measurements were performed at ambient temperature. The mechanical properties of nanocomposites were measured by ASTM (American Society for Testing and Materials) D-638-00 using an Instron testing machine (model 5567). Tests were carried out at a crosshead speed of 50 mm/min. The five specimens for each composition were used for measurement and average values were reported. Nanocomposite films were made with a thickness of 0.5 mm and these films were used to measure the oxygen permeability with ASTM F 316-86 by using gas permeameter (PMI, GP-201-A, USA). The average permeability of five similar samples was reported for comparison.

3. Results and discussion

3.1. Structural analysis

The XRD patterns of f-SWCNT, PAN-co-starch and PAN-co-starch/f-SWCNT nanocomposite are shown in Fig. 2. The f-SWCNT shows a diffraction peak at 2θ value of 24.6° whereas PAN-co-starch and PAN-co-starch/f-SWCNT nanocomposite both show a diffraction peak at 2θ value of 16.7° is due to PAN-co-starch. It is found that, the intensity of peak at 2θ value of 16.7° in PAN-co-starch/f-SWCNT nanocomposite is less than that of virgin PAN-co-starch. From qualitative observation, it is due to the change in crystallinity by dispersion of f-SWCNTs in PAN-co-starch matrix [26]. The morphology of PAN-co-starch and PAN-co-starch/f-SWCNT nanocomposite is observed by FESEM