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Simple and effective synthesis method of Polyethylenimine/ (MWCNTs) Nanocomposites by single step pyrolysis technique and its electrical properties

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were synthesized by one step pyrolysis technique using ferroceneFe(C₅H₅)₂ as a catalyst and xylene (C₈H₁₀) as carbon source. Novel polyethylenimine/CNT nanocomposites with weight percentages of 0.5, 1, 1.5, 4 and 8 have been fabricated by spin coating method. The synthesized MWCNTs and polyethylenimine/CNT nanocomposites were characterized by XRD and SEM. The yield of MWCNTs was estimated to be 55% by gas phase oxidation purification process. The polyethylenimine/CNT composite material obtained was found to possess significant electrical properties.

Keywords: MWCNTs; XRD; polyethylenimine; SEM; I-V characteristics.

INTRODUCTION

Carbon nanotubes (CNTs) are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio as large as 28,000,000: 1, which is unequalled by any other material [1, 2]. It has a quasi-one dimensional structure that can be metallic or semiconductor depending on their structural parameters. This makes the CNT as central elements in composite materials for many electronic applications. CNTs are generally classified as 2 types: Single Walled CNTs (SWCNT) and Multi walled CNTs (MWCNT). Among these MWCNTs is a promising nanomaterial for the commercial applications such as nanomechanical systems [3], sensors [4], biological applications [5, 6] etc. MWCNTs exhibit extraordinary strength and unique electrical properties and are efficient conductors of heat. It is used in composite materials to improve the electrical properties by controlling the orientation of MWCNT and polymers [7]. CNTs are synthesized in variety of methods such as laser ablation [8], arc discharge [9], pyrolysis methods [10], chemical vapor deposition [11, 12] etc. Although CNTs are very promising in a wide variety of fields, processing techniques such as purification and manipulation still remains as a bigger challenge. For potential application of CNTs, an effective simple method with low cost is essential for efficient and quality production in large scale [13].

Polymer composites containing carbon nanotubes are of great interest because they possess a novel combination of electrical, optical and mechanical properties [14, 15]. Initial experiment on CNTs containing polymer nanocomposites as filler was reported by Ajayan et al [16]. Every year there are numerous papers and patents on various polymer matrices used for composites/CNTs such as thermosetting resins [17], water soluble polymers [18], thermoplastics [19], liquid crystalline polymers [20], conjugate polymers [21] and so on. Polyethylenimine also known as polyaziridine is a polymer composed of amine group and carbon aliphatic spacer. It is an insulating polymer which is available in linear as well as in branched structures. The linear polyethylenimine are solids at room

temperature whereas branched ones are liquids and are known to effectively interact with carbon nanotubes[22]. It finds many applications in products like detergents, adhesives and cosmetics.

In this work, a single stage effective simple pyrolysis technique is used for the production of CNTs. The advantage of this system is that CNTs can be prepared in a single step and hence avoids complicated control parameters[23].Polyethylenimine/MWCNT nanocomposite films were synthesized using spin coating method. We have investigated the electrical transport properties with different wt% of CNTs in polymer composites. By adding conductive fillers in an insulating matrix, the composite film obeys the percolation theory which has been measured by two point probe method.The as-grown MWCNTs and polymer/CNTs were characterized by X-ray diffraction (XRD) analysis and scanning electron microscope (SEM).

MATERIALS AND METHODS

Analytical grade of Xylene (C_8H_{10}) and Ferrocene ($Fe(C_5H_5)_2$)were used as carbon source and catalyst, respectively. The detailed synthesis of polyethylenimine/MWCNTs is followed up in next sections.

2.1. Synthesis of multi-walled CNTs

Synthesis of CNTs has been carried out using a single step pyrolysis technique which consists of a single-stage furnace [24]. A mixture of 500 mg of ferrocene and 50 ml of Xylene were taken in a quartz tube of diameter 1.5 cm and length 56 cm, closed at one end. The whole assembly was placed inside the furnace and heated up to the desired pyrolysis temperature (750°C). The reaction was continued for 1hr 30 minutes, cooled down to room temperature. A crude product of CNT obtained as black material (75-85 mg) was collected from the quartz tube. The as-synthesized samples contain mostly CNTs along with some amorphous carbon and catalyst particles. Further purification was carried out by air oxidation, acid bath treatment method, ultra-sonication and finally centrifugation methods [25]. A net weight loss of the as-synthesized material was observed after purification and the yield of pure form of MWCNT was as high as 55%.

2.2. Synthesis of Polymer/CNTs Composite:

MWCNTs were purified by sonication in a mixture of sulphuric acid and nitric acid in the ratio 3:1 for 12 hrs. The temperature was maintained at 120°C[26]. The metal catalysts were removed and few numbers of carboxyl functional groups were formed at the edges of MWNTs. A range of polyethylenimine/MWCNT nanocomposite dispersions were prepared by mixing 2g of polyethylenimine with 10,20,30,80 and 160 mg of MWCNT to yield 0.5,1,1.5,4 and 8 weight % (wt%) proportions, respectively. The prepared dispersions were spin-coated onto a glass substrate to prepare nanocomposite films [27]. The electrical conductivity of these nanocomposite films were then measured with two point probe technique.

2.3. Techniques used:

X-ray diffractograms were recorded using X'pertpro operating at 40 k and 25 mA $CuK\alpha$ radiation with a wavelength of 1.54 was used with a step size of 0.02 in the 2θ range. The SEM measurements were performed on a SEM instrument with an AMETEK operated at an accelerating voltage of 30 KV. Electrical conductivity measurements were done by using two probe of Model 6487 Picoammeter/Voltage Source.

RESULTS AND DISCUSSION

X-ray diffraction pattern of MWCNTs and polyethylenimine/CNTs composites is shown in the Fig.2 a & b. The powder XRD pattern($CuK\alpha \lambda=1.5406^{\circ}A$) confirms that the CNTs have crystalline nature and the peaks are indexed to the (002), (100), (101) reflections of hexagonal phase. A prominent peak is observed at 26.4 °C which is attributed to MWCNTs. In the XRD pattern of polyethylenimine/CNTs composite, (002) peak characteristic for CNT is reduced in intensity which is indicative of the % additions of the polymer. Further, there was also a broadening and reduction in intensity of peaks (100),(101) in polyethylenimine/CNTs observed, with increasing MWCNT concentration. Such a reduction in intensity and broadenings of the characteristic CNT peaks are indicative of the difference in phase compositions as already reported by [28]. Thus, here in our case, such alterations in peak nature are suggestive of the altered amorphous and crystalline phases of the polymer nanocomposite prepared.

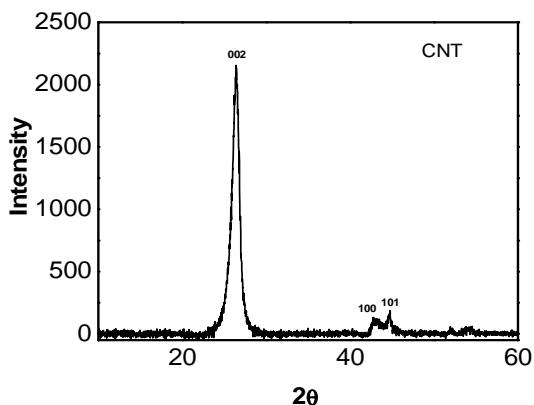


Fig. 2aXRD pattern of purified MWCNTs

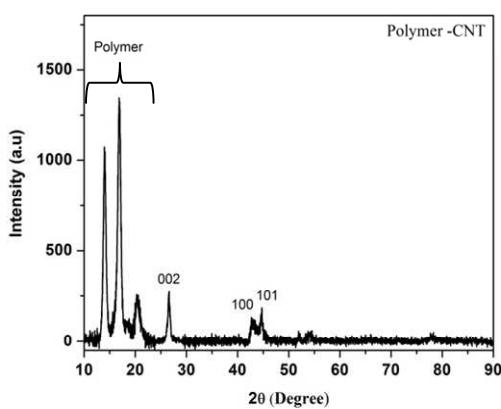


Fig. 2bXRD pattern of Polymer/MWCNTs

SEM images of (Fig. 3a) as-prepared CNTs (Fig. 3b) purified CNTs (Fig. 3c) aligned CNTs and Polymer/CNTs (Fig. 3d) are as shown. It is clear that the MWCNTs are seen along with small amount of amorphous carbon and catalytic particles (Fig. 3a). The purified nanotubes are free of catalytic particles and amorphous carbon (Fig. 3b). SEM images revealed the better dispersion of CNTs in polymer matrices (Fig. 3d).

Depending on the concentration of CNTs, the conductivity of composite is found to vary over many orders of magnitude[29]. The high aspect ratio of CNTs is an advantage in making a percolation network with different weight percentages (0.5wt%, 1wt%, 1.5 wt%, 4 wt% and 8 wt%) of polymers. This was established with a graphical plot in which variation of conductance with increasing weight percentage of CNTs was studied at room temperature.(Fig. 4a) and the data are collected in Table 1. It confirmed that the conductance of nanocomposite increased rapidly with increasing CNT weight percentage and was found to be the maximum at 8 wt% of CNT. Hence, the current–voltage relation was also studied which proved to be almost linear. Figure 4b shows the I/V Characteristics of 8 wt% polymer/CNT composite at room temperature which is evident of a linear increase in current with respect to changes in voltage.

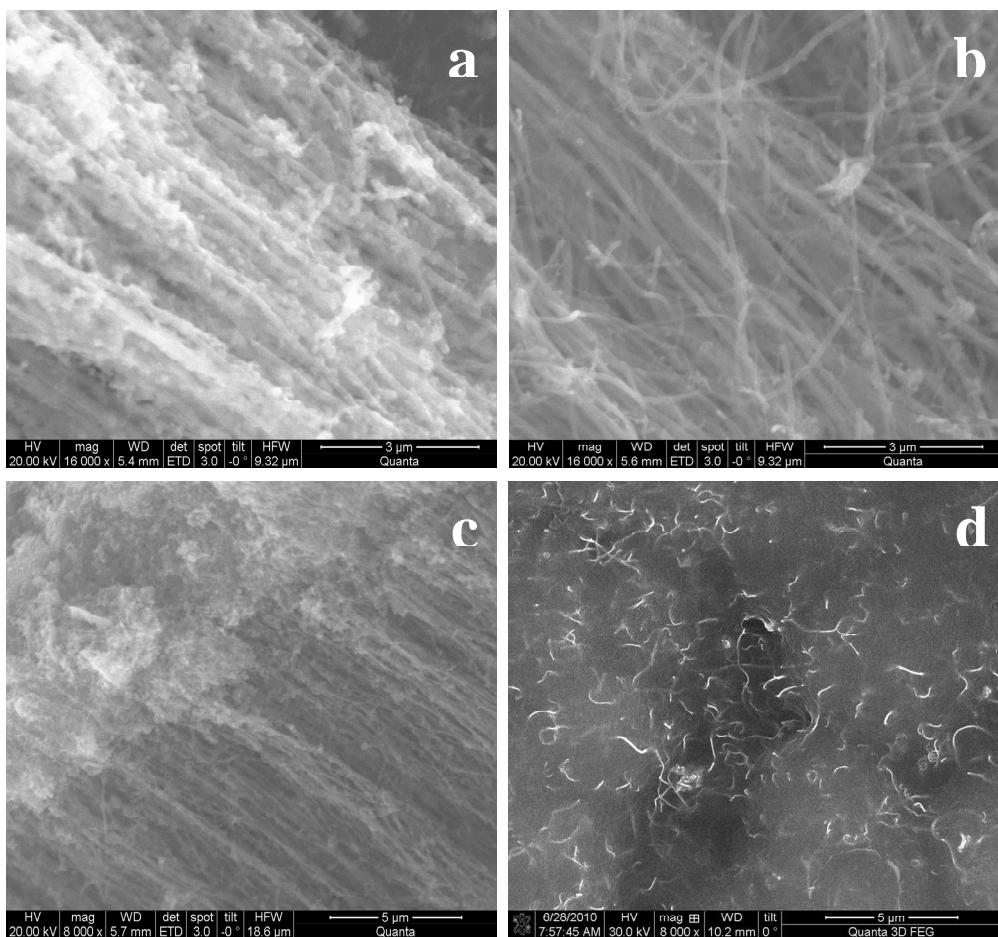


Fig. 3 (a) SEM images of as-prepared MWCNTs **(b)** purified MWCNTs **(c)** aligned MWCNTs **(d)** polyethelenimine /MWCNTs

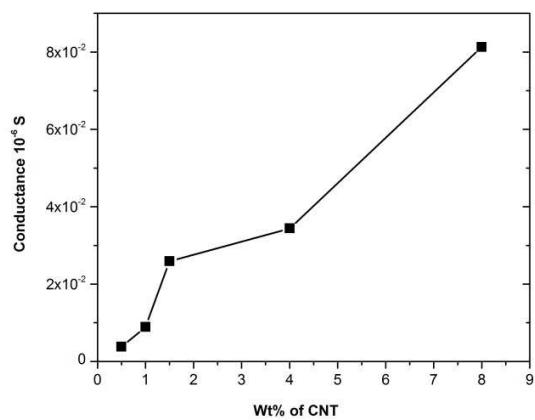


Fig. 4a Variation of conductance with increasing weight percentage of MWCNTs

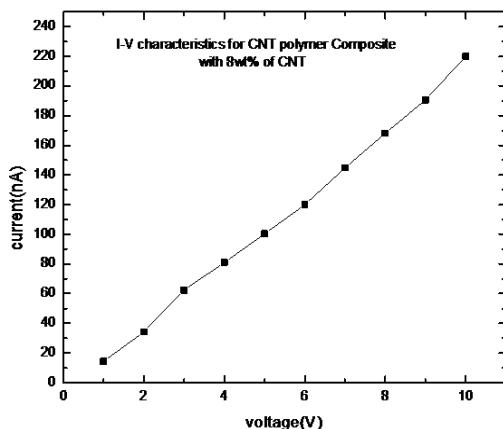


Fig. 4b I-V Characteristics of 8 wt%polyethylenimine/MWCNTs composite

CONCLUSION

A simple pyrolysis technique is used in synthesizing MWCNTs. Polymer/CNTs composite with CNTs weight percentages of 0.5, 1, 1.5, 4 and 8 in polyethylenimine have been synthesized. The powder XRD confirmed the crystallization of hexagonal phase of MWCNTs. SEM images confirmed good quality of MWCNTs with small quantity of amorphous carbon and catalytic particles and it confirmed the dispersion of polyethylenimine in MWCNTs. The conductance variation was studied and was found that the conductance increased with increase in the wt% of CNTs and I-V characteristics of polyethylenimine/CNT composite with 8 wt% of CNT showed a linear variation of current with applied voltage.

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