Carbon nanotubes based nanocomposite for electromagnetic wave absorption and dynamic structural strain sensing

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Carbon nanotubes (CNTs)-polymethyl methacrylate (PMMA) nanocomposites have been developed for electromagnetic wave absorption (EWA) and dynamic strain sensing in for structural health monitoring. For the purpose CVD synthesized CNTs were characterized for its structural and morphology using X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) before preparing nanocomposite. The CNTs obtained were of about 10 nm diameter and 0.5 µm length. The prepared CNT/PMMA nanocomposite films (CNT 5% loading) were characterized for their electrical properties, indicating metallic (resistive) behaviour and electromagnetic absorbance (EWA) behaviour in the X and Ku band showing absorption peaks of around 3.5 dB loss at 8.5 GHz and 20 dB loss at 14.5 GHz. The peppered CNT/PMMA nanocomposite films were used in strain sensor applications for structural health monitoring. The strain sensor results closely matched with standard strain gauge sensor under quasi static as well as dynamic conditions.

Keywords: Carbon nanotubes, Polymethyl methacrylate, Strain sensing, Nanocomposite, EMI shielding

1 Introduction

Carbon nanotubes (CNT)-based polymer composites are being considered in an increasing number of applications including aerospace, defense and infrastructure sectors. Exceptional features made CNTs ideal reinforcement for a variety of materials, including polymers, metals/alloys, and ceramics. CNT based composites are being considered as an alternative to conventional smart materials. CNTs thin-film (called bucky paper) has been reported as a multifunctional smart material which can serve as a structural and sensing (for eg. piezoresistive) function. However, due to slippage among CNTs (poor load transfer capability) limits its application as a strain sensor. Nanocomposites provide a method to improve load transfer capability by using CNTs as filler in a polymer matrix.

Recently, wide interest has been generated in building EMA materials and highly sensitive strain sensors with CNT based nanocomposites because of their light weight, resistance to corrosion, flexibility and processing advantages. EMA is a kind of functional material that can absorb or attenuate electromagnetic wave effectively and convert electromagnetic energy into heat or make electromagnetic wave disappear by interference for applications both for electronics industry and defense purpose. This attenuation results from the interplay of factors such as the electric conductivity, dielectric losses and depth of penetration, which needs to be less than the thickness of the material. The level of attenuation achieved varies from a few decibels to greater than 50 dB, reducing the reflected energy by as much as 99.99%. Strain induced change of electrical resistance (piezoresistivity) has been observed in CNT filled polymer films. In these studies, single-walled carbon nanotubes (SWNTs) or multi-walled nanotubes (MWNWs) have been used. The piezoresistive effect observed in the strain sensors made from polymer/CNT composites can be mainly attributed to the variation of conductive networks with strain, such as loss of contact between the fillers, tunneling effect in neighbouring fillers and conductivity change from deformed CNTs. Research on strain sensing using CNT based nanocomposite is in its early stage. For example, the piezoresistivity characteristic of these sensors under compression has not been well understood. In principle, a single tube of CNT can form a sensor and provide important intrinsic sensing properties. However, until the technology to form regular array of single wires is fully developed, it is an inappropriate device for mass production. Therefore, the realistic engineering sensor at present should be made of a thin film form of CNT/CNT nanocomposite. The method of pasting CNT nanocomposite is a direct and easy way, but
requires sequential processing of synthesis and collection of CNTs, as well as, dispersion in solutions or polymer and printing on substrates.

There are large numbers of techniques available to synthesize different types of carbon based nanostructures in the form of nanotubes, nanofibers etc., broadly classified as physical, chemical, hybrid and solvothermal/hydrothermal techniques. The technique used depends upon the application of interest, type of nanostructure CNT/CNF material, quantity (scale of production), cost etc. A majority of high quality CNT’s have been prepared using either the electric arc discharge or CVD.

Significant advances have been made in using CNT filled polymer films for EWA and strain sensing. Independently, CNTs have been explored for variety of applications. Combined application for electromagnetic shielding and dynamic structural strain sensing for aerospace applications is particularly significant for defense applications. In the present paper, the results on the use of CNTs based nanocomposite for EWA and strain sensor having potential application for radar absorption and structural health monitoring in defense, are reported. For the purpose CVD obtained CNT’s were first characterized, functionalized followed by the development of CNT-based composites and its use as radar absorption material (RAM) and structural strain sensing applications.

2 Experimental Details

2.1 Preparation of nano-composite film for strain sensor

The obtained CNTs, synthesized using chemical vapour deposition (CVD), were purified before use. Typically, 0.8 g of as grown nanotubes were refluxed in 60 mL of mixed concentrated nitric and sulphuric acid (1:3 volume ratio) at 130°C for two hours. The oxidized tubes were then washed many times to pH 7, giving yield of about 50 wt%.

For preparation of CNT composite, polymethyl methacrylate (PMMA) have been used. PMMA requires only simple laboratory instrumentation for the production of composite, and it is easier to uniformly combine CNTs with it. There are three main steps involved in the preparation of composite:

Dispersing CNT in a solvent — Dispersion during composite processing was required to produce a suspension of independently separated nanotubes that can be manipulated into preferred orientations for large scale applications. Mechanical dispersion using ultrasonication was used for dispersing the CNT’s DMF solvent, 2.5 mg ml⁻¹ and put in a sonicator bath for one hour, resulting fully dispersed CNT solution.

Mixing PMMA and CNT — After the dispersion processing, the PMMA was added to a suspension of CNT’s in DMF and mixed using shear force with hand and magnetic stirrer at 70°C for 1 hr.

Casting of the CNT polymer composite in a mould — After dispersion and mixing process, the resulting polymer nanocomposite was cast in a self-fabricated teflon mould to form a film and it was initially cured in a vacuum oven at room temperature for 30 min to remove air. It was then fully cured in a vacuum at 120°C for 12 h to evaporate the solvent and anneal the CNTs in the binding material. Then, the freestanding film was peeled off from the teflon mould. Same process was followed to prepare CNT-PMMA nanocomposites of different CNT loadings. The results presented in this paper are for 5% of CNT loading in PMMA.

2.2 Characterization

The morphology of different samples was examined using JOEL, JSM-6360A Scanning electron microscope(SEM). The crystal structure of different CNT nanostructure samples was analyzed using Xpert PRO Panalytical Powder X-ray diffractometer (XRD) in the scanning range 20-80° (2θ) using Cu Kα radiations with wavelength 1.5045 Å. Electrical characterization of CNT-PMMA composite film was done by fixing film on a glass substrate of approximate size 35 mm × 15 mm and by painting two 2-3 mm narrow conducting silver strips at approximate gap of 5-6 mm on top of the composite film. For electrical characterization a controlled temperature laboratory set up and DT-80 De-Logger data acquisition system were used.

2.3 Electromagnetic wave absorption (EWA)

EWA properties of CNT based composite samples were measured using a R & H Vector Network Analyzer calibrated in the frequency range 40 MHz-20 GHz with waveguides. Single port parameters were measured with inserting the sample at the end of a matched terminated waveguide. The corresponding reflectivity was obtained as the reflection coefficient (S11) measured at input port of the long waveguide short-circuited at its output port.

2.4 Experimental set-up for strain sensing

A flexible strain sensor was fabricated by cutting it with a proper length and that was connected to electrodes as shown in Fig. 1. The prepared CNT
based composite was tested for strain sensing by fixing it to an Al beam. An Al cantilever beam was used as it was a simple structure for modelling and testing the response of the sensor. One end of the beam was rigidly clamped to a iron cuboids block as shown in Fig. 1. Each strain sensor was tightly bonded using epoxy adhesive to ensure that the superglue makes a stiff bond to transfer the strain across the sensor without any slippage. The sensors were connected to Cu lead wires with silver conducting paint to reduce the contact resistance. The change of resistance of each strain sensor was measured by Data Acquisition System (DT 80 De Logger) with respect to the displacement due to bending of the cantilever beam. Full bridge circuit was used to measure change in resistance to minimise the errors due to temperature variations.

3 Results and Discussion

Figure 2 shows the SEM of used CNT samples. SEM confirms the formation of CNT which is of about 10nm in diameter and 0.5 μm in length. The EDAX spectra of sample are shown in Fig. 3 which show dominance of carbon component as compared to very less atomic percentage of Mg and Fe impurities used as catalyst as well as oxygen content.

XRD of CNT sample is shown in Fig. 4. The diffraction peaks were observed at 26.3°, 43.7° and 53.8° which correspond to CNT (101), CNT (102) and CNT (110) plane. Obtained CNTs were MWNTs in nature and most prominent peak observed at 43.7° indicates good crystalline quality of the CNTs.

The change of resistance of the CNT/PMMA nanocomposite at room temperature under applied voltage of 0 to 10 V is shown in Fig. 5. I-V characteristics of nanocomposite are linear between 0 and 10 V. The corresponding I-V behaviour indicates that the films have metallic (resistive) behaviour close to room temperature. As reported, CNTs can be either metallic or semiconducting depending on the chirality of the tube, the nanocomposite film has metallic (resistive) properties.

3.1 Electromagnetic wave absorption

Figures 6 and 7 show the EMA loss coefficient of PMMA, CNT-PMMA nanocomposite films of 1mm
thickness for X band (8-12 Ghz) and Ku band (12-18 Ghz). The graphs of PMMA show good absorption of around 3.5 dB loss at 8.5 GHz in X band and about 20 dB loss at 14.5 GHz in Ku band. The absorption properties are also seen improving with the addition of CNTs. In X band, CNT PMMA nanocomposite has shown significantly different behaviour than PMMA whereas in Ku band absorption coefficient has improved at 14.5 GHz. The primary mechanism of EMI shielding is usually a reflection of the electromagnetic radiation incident on the shield, which is a consequence of the interaction of EMI radiation with the free electrons on the surface of the shield. As a result, the shield has to be electrically conducting although a high conductivity is not required. Earlier researchers have reported a maximum absorption loss of 2 dB at 0.5 vol. % to about 13 dB at 10 vol. % loading for CNT-PMMA nanocomposite film of about 2 mm in the X band.

3.2 Strain sensor response

Static response — Figure 8 shows the change in electrical resistance with strain. The change of the resistance of the strain sensor was converted to normalized change of resistance ($R_s$)

$$R_n = \frac{R_s - R_o}{R_o}$$
Dynamic response — Figure 9 shows the change in resistance of nanocomposite strain sensor with respect to strain measured when the beam was deflected and allowed to oscillate freely. The sensor response in Fig. 9 is almost identical to the output of the standard strain sensor, Type NK-7B having Gauge Factor 2.82 (M/s Rohits & Co.), which means that the composite sensor measures the strain signal from the structure in real time and without much distortion. It showed consistent piezoresistive behaviour under repetitive straining and unloading and good resistance stability.

4 Conclusions

CNT-PMMA nanocomposite films have been successfully prepared. The prepared films were investigated for EMA and dynamic structural strain sensing applications. The developed CNT nanocomposite strain sensor followed the free vibration pattern similar to pattern of standard reference strain sensor demonstrating good static and dynamic response. It showed consistent piezoresistive behaviour under repetitive loading and unloading and good resistance stability. The piezoresistance effect is promising for strain sensor. CNT composite material not only showed flexibility and electrical conductivity, but also directional sensitivity that makes it possible to measure strain under dynamic conditions in aerospace applications for structural health monitoring. Besides, CNT based nanocomposites being light weight, high load bearing have dual advantage acting as smart and EMA material for active applications in defense.

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