ELECTRICAL PROPERTY OF MULTIWALLED CARBON NANOTUBES/EPOXY COMPOSITES

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Abstract: In this paper, an experimental investigation of electrical property of multiwalled carbon nanotubes (MWCNTs)/epoxy composites were conducted. Surface modification has been successful applied to improve the homogeneous dispersion of MWCNTs in epoxy. Dispersion and structural integrity of MWCNTs before and after surface modification were compared. The electrical property of MWCNTs/epoxy composites were evaluated by the four-point probe method, as well as the percolation concentration of MWCNTs/epoxy was calculated through classical percolation theory. The results of electrical property will lay a foundation for establishing the relationship between electrical resistance and strain of MWCNTs/epoxy.

1 Introduction

Carbon Nanotubes (CNTs) are one of the fillers with great potential in tailoring composites because of its remarkable electrical, thermal and mechanical properties since it were discovered in 1991 by Iijima in Japan [1-6]. Electrical and mechanical properties of carbon nanotubes have been extensively investigated in the past. However, carbon nanotubes tend to agglomerate when dispersed into epoxy composites, which restricts seriously its application in the improvement of nanocomposites. To achieve homogeneous dispersion of carbon nanotubes into polymer matrixes, raw carbon nanotubes must be with enough dispersive initially. There are a lot of literatures about the dispersion methods of carbon nanotubes into polymer nanocomposites, such as, surface chemical modification, dispersion by dispersant, ultrasonic sonication, mechanical stirring and dissolution in solution [7-9]. The modified CNTs can be applied to various fields, such as capacitance, gas sensor, strain sensor, etc. Preliminary studies on single walled carbon nanotubes (SWCNTs) sensors were based on detecting changes in conductance in CNT-FETs due to adsorption of gases to the sidewall of CNTs. Nitrogen dioxide (NO₂) and ammonia (NH₃) were the first gases detected by Dai’s research group at Stanford University [10,11]. Further research has found that modifying the nanotube with a polymer coating or target/receptor pair can greatly increase sensitivity and selectivity of these nanosensors. The small diameter of nanotubes has also been exploited in biosensors since sizes of 10-100 nm are on the order of the sizes of biological macromolecules. Moreover, it has been confirmed that the electrical conductivity of SWCNTs could be dramatically changed by introduction of strain using atomic force microscopy (AFM), as a consequence of the band gap and structural changes under the effect of mechanical strain [12-14]. It was predicted that integrating CNTs into polymers would open up a whole range of smart structure applications [15-18]. In particular, great interest has recently been aroused in building strain sensors with CNTs [19-23]. Recently, Gao et al. introduced pressure and strain sensors on transparent elastic films of CNTs [24]. Hata et al. successfully realized a CNTs strain sensor for human-motion detection [25]. Other carbon nanostructures/polymer composites such as carbon blacks and carbon nanofibers (CNFs) have been explored as multifunctional strain sensors [26-33]. Even though these carbon nanostructures have different responses against microscopic deformation, their macroscopic deformation causes common percolation network changes, and they can therefore be utilized as strain sensors. Zhu et al. recently fabricated an electrically conductive elastomeric nanocomposites reinforced with CNFs for sensing large mechanical
deformations [34]. Hu et al. put forward a tunneling effect on the base of a large amount number of experiments and numerical simulations [35-37]. In this work, we investigated the electrical property of nanocomposites made of commercial MWCNTs Baytubes® and epoxy experimentally. The MWCNTs were chemically treated to facilitate a homogeneous dispersion in epoxy. The electrical conductivity of the nanocomposites was measured by a four-point probe method.

2 Experimental Investigation

2.1 Materials

The polymer matrix used for the composite was an epoxy system consisting of a Bisphenol-A (PT-2712) and an aromatic amine hardener (Part B3). Epoxy polymer matrix was prepared by mixing 28 parts by volume of epoxy resin (Bisphenol-A) with 1 part of aromatic amine hardener.

The MWCNTs were a commercial product (Baytubes®) from Bayer and Co. Ltd (Fig. 1), by a chemical vapor deposition method (CVD). The MWCNTs have a purity of >95 wt% with several tens nanometers of diameter and lengths up to 1 micrometer long.

2.2 Methodologies

2.2.1 Chemical modification of MWCNTs

One gram of the MWCNTs were suspended in a mixture of HNO₃(68%)/H₂SO₄(98%) (1:3, V/V) solution with a volume of 100ml and refluxed at 120 °C for 4 hours. Then, the carboxylated MWCNTs were filtered and washed with distilled water until PH value was 7 and dried in vacuum oven for 3 hours (Fig.2).

2.2.2 Nanocomposite Preparation

Firstly, the carboxylated MWCNTs were mixed into the epoxy resin Bisphenol-A, then sonicated (Sonicer SC-40) for 6 hours. Secondly, it was mixed with hardener and sonicated again for another 2 hours. All of the above processes were mixed at room temperature. Thirdly, the mixed samples were degassed in a vacuum oven (Fisher Scientific Model 281A) at 50 °C for 1 hour. Then, they were injected into sample molds (40mm × 4mm × 4mm). Finally, the nanocomposites were cured for 12 hours at room
temperature and followed by 5 hours at 120 °C in the oven for post curing (Fig. 3 and Fig. 4).

2.3 Measurements

2.3.1 Composites DC measurements procedure

DC conductivity of the MWCNTs/epoxy composites were measured by the four-point probe method (Fig. 5) according to the ASTM F1529-97 using a Keithley 6221 resistivity test fixture and a Fluke 16 multimeter at room temperature. According to the Ohm’s Law theory [11, 18], the resistivity \( \rho \) was calculated as

\[
\rho = 2\pi S \frac{V}{I}
\]

(1)

Where voltage \( V \) is measured between the two inner probes, \( I \) is current from current source, \( S \) is the distance between probes respectively. If the inter probe spaces are equal, then \( S = S_1 = S_2 = S_3 \).

The volume electrical conductivity \( \sigma \) was obtained by simply inverting the correspondence values of the resistivity as follows:

\[
\sigma = \rho^{-1}
\]

(2)

3 Results and discussion

3.1 Dispersion of MWCNTs

MWCNTs were observed by scanning electron microscope (SEM) in order to confirm that their structure integrity before and after the surface
modification. From Fig. 1 and Fig. 2, there is no obvious difference in diameter between pristine MWCNTs and carboxylated MWCNTs. There were lots of studies shown that the chemical treatments with a strong acid does not affect to MWCNT's structure [38-43]. However, the length of carboxylated MWCNTs was shorter than pristine sample from SEM of Fig. 1 and Fig. 2.

![Fig. 6 Dispersions stability of the same amount of pristine and carboxylated MWCNTs in water after dispersion.](image)

Comparing the stability of MWCNTs in water is one of the most direct methods to understand the effects of dispersion. The figures of dispersion states of MWCNTs in water shown that the pristine MWCNTs rapidly precipitate after few minutes (Fig.6). The stability of the chemically modified MWCNTs is better than the pristine sample in 48 hours. In fact, the modified MWCNTs showed excellent dispersion until now.

### 3.2 Microstructure analysis of MWCNTs/epoxy

![Fig. 7 SEM images of (a) 1.0 Vol. % MWCNTs, (b) 5.0 Vol. % MWCNTs](image)

The scanning electron microscope (SEM) micrographs of MWCNTs/epoxy nanocomposites are shown in Fig. 7. The dispersion of difference concentration of MWCNTs in epoxy was well done.

### 3.3 Electrical property
The DC conductivity results are shown in Fig. 8 as a function of MWCNTs volume concentration. The conductivity of epoxy was about $1 \times 10^{-14}$ S/cm [24, 39]. A sharp increase of the conductivity value was observed at 1 vol.%, where the conductivity changed from $1 \times 10^{-14}$ to $3 \times 10^{-4}$ S/cm. This behavior is indicative of a percolation transition. Percolation theory predicts that threshold at which a conductive path is formed in the composite causing the material to convert from an insulator to a conductor. In order to determine the critical volume concentration, the volume conductivity data was fitted to a power law in term of volume fraction of MWCNTs [43-49]. Fig. 9 shown that a good fit achieved between the experimental data and the fit function, with a correlation factor $R=99.7\%$. The conductivity is linear with ($V - V_c$) in a logarithmic scale and the relationship is described by the equation below:

$$\sigma_{dc} = \sigma_0 (V - V_c)^t$$  \hspace{1cm} (3)

Where $\sigma_{dc}$ is the conductivity of the MWCNTs/epoxy; $V$ is the volume fraction of the MWCNTs in the composite; $V_c$ is the critical volume fraction; $\sigma_0$ and $t$ are the fitted constants. A best fit to the data resulted when $V_c$ was assumed to be 0.05vol. %. In the percolation theory, the value of $\sigma_{dc}$ in Eq.(3) should approach the conductivity of the MWCNTs itself (theory conductivity of MWCNTs were $0.5 \times 10^1$ S/m to $2 \times 10^4$ S/m) [21, 35, 36]. However, there exists a contact resistance between the MWCNTs which decrease the effective conductivity of the MWCNTs themselves [50-54].

4 Summaries

In order to improve the dispersion of MWCNTs in epoxy, the MWCNTs were chemically modified using HNO$_3$ and H$_2$SO$_4$. The stability images of the carboxylated MWCNTs in water and SEM images of nanocomposites strongly support the fact that the chemically modified MWCNTs have been homogeneously dispersed in epoxy and water. Electrical conductivity of MWCNTs/epoxy nanocomposites was measured using the four-point probe method. The measured conductivity also be described by a percolation like power law equation with a percolation threshold of 0.05 Vol. % MWCNTs.

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References


