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## **INFLUENCE OF DISPERSION STATES OF CARBON NANOTUBES ON MECHANICAL PROPERTIES OF EPOXY NANOCOMPOSITES**

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### **ABSTRACT**

*Prior to the discovery of nanotubes, no other material known to mankind possessed such a unique combination of extraordinary properties. It is this fact that most of the research work in the field of nanotechnology has been concentrated in the past decade around CNTs and their applications. CNTs are proven to be the stiffest, strongest and the toughest fiber ever known. The values of tensile strength that have been reported are by far the highest for any material. Their outstanding electrical conductivity values make the polymer to exhibit metallic-type conductivity by incorporating them as filler. Continuing along this line of research, novel CNT-based composites have been fabricated using different methods, expecting that the resulting composites would possess enhanced or completely new set of physical properties due to the addition of CNTs. Effects of different dispersion states of carbon nanotubes (CNTs) on mechanical, properties of the epoxy nanocomposites were studied. The dispersion states were altered depending upon whether a solvent was employed or not. To characterize dispersion of the CNTs, optical microscope was used. It was found that the nanocomposites containing well dispersed CNTs exhibited higher flexural modulus than ones with poorly dispersed CNTs. From the morphological observation it was found that when the solvent was not used in the CNTs dispersion process, aggregates of pristine CNTs remained in the nanocomposites.*



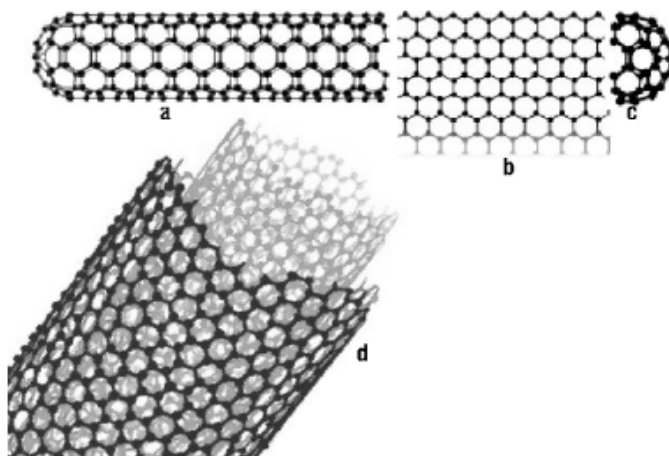
## 1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima (1), CNTs have been looked at extensively by researchers in various fields such as chemistry, physics, materials science and electrical engineering. CNTs are unique nanostructured materials with remarkable physical and mechanical properties (1- 5). These properties have inspired interest in using CNTs as a filler in polymer composite systems to obtain ultra-light structural materials with enhanced mechanical, electrical and thermal characteristics (6, 7). The prospect of obtaining advanced nanocomposites with multifunctional features, e.g., materials used for structures and electrical conductors, has attracted the efforts of researchers in both academia and industry (8-10). Industry in particular recognizes many potential applications such as electrostatically dissipative materials and aerospace structural materials (8-13). Currently, one of the major obstacles to using nanotubes as a polymer filler is cost; however, advances in the synthesis of CNTs continue to rapidly improve both their quantity and quality (14), though growing structurally perfect nanotubes at large scales is not yet at hand (15).

It is necessary to understand the effect of CNTs dispersion on various properties of the CNTs filled composites. Therefore, in this study, two different specimens with the well dispersed and the poorly dispersed CNTs were prepared depending upon whether a solvent was used during the CNTs dispersion process or not. Another nanocomposite was prepared using an over-aged hardener so that the epoxy matrix remains relatively soft and ductile even after polymerization. Mechanical properties of the nanocomposites were examined and differences in various properties between the respective cases were observed at the same weight content of the CNTs. Dispersion state of the CNTs in the epoxy nanocomposites were morphologically characterized by the optical microscope images.

## 2. Structure And Morphology Of CNT

A carbon nanotube is a hexagonal network of carbon atoms rolled up into a seamless, hollow cylinder, with each end capped with half of a fullerene molecule (3, 16, 17). Although similar in chemical composition to graphite, CNTs are highly isotropic, and it is this topology that distinguishes nanotubes from other carbon structures and gives them their unique properties. There are two main kinds of nanotubes: single-walled nanotubes (SWNTs), individual cylinders of 1-2 nm in diameter, which are actually a single molecule; and multi-walled nanotubes (MWNTs), which are a collection of several concentric graphene cylinders, a "Russian doll" structure, where weak Waals forces bind the tubes together (18). A schematic of these species is shown in Fig.1.



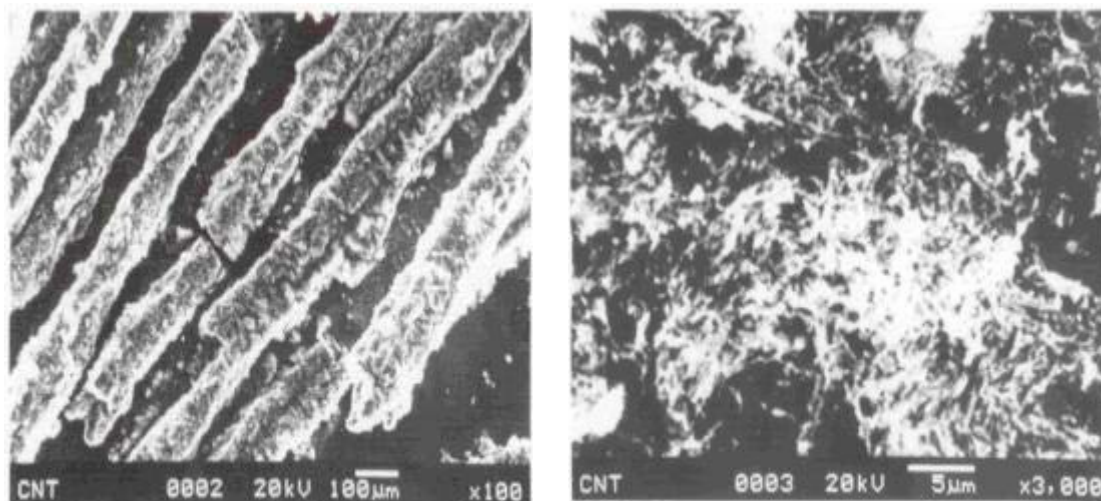
**Fig.1. Schematics of a single-walled carbon nanotube (a 5,5 armchair tube is shown) (a), a graphite sheet (b), a hemispherical end cap (c) and a multiwalled carbon nanotube (d). The solid circles in each figure represent the carbon atoms.**

The diameter, chirality and form of the nanotube determine its properties (19). Since carbon-carbon covalent bonds are among the strongest bonds in nature, a structure based on a perfect arrangement of these bonds oriented along the axis of the nanotubes produces a very strong material with an extremely high strength-to-weight ratio. This qualifies CNTs as the "ultimate" carbon fiber (20, 21). The mechanical properties of various types of nanotubes have been extensively studied both by experimental and computational means (22, 23).

## 2.1. MWNT

**2.1.1. Synthesis.** CNTs used in this study were synthesized by (CVD) thermal decomposition of hydrocarbon gas. Benzene was used as carbon source, thiophene as growth promoter, ferrocene as catalyst and hydrogen as carrier gas. The relative ratio of different components in the reaction system was controlled by adjusting the carrier gas flow rate. Through controlling the reaction time and relative components of benzene, thiophene and ferrocene, carbon nanotubes and carbon nanofibers of different diameter and structure can be obtained.

**2.1.2. CNTs morphology.** SEM observations were carried out with a "JEOL JSM-5800 Scanning Microscope, OXFORD" to examine the morphology of the CVD products. The CNTs are MWNTs, with diameters in the range of 1-20 nm and average length a few hundreds microns (Fig. 2). They are highly entangled and randomly organized. There are some catalyst particles, amorphous carbon and onions as impurities.



**Fig. 2. SEM micrographs of CNT at different resolutions**

### 3. Composite preparation

Epoxy polymer matrix was prepared by mixing 15 parts by volume of epoxy resin (Bisphenol A-epichlorhydrine) with 2 parts of aromatic hardener (triethylenetetramine). Epoxy resin contains one or more epoxide groups that serve as cross-linking points when the resin reacts with the hardener to form longchains, the polymerization.

The as-prepared CNTs material consists of aggregates of different sizes. The bigger ones are millimetric or even centimetric. This would be an obstacle to the uniform dispersion of MWNT into the epoxy matrix. A procedure of two steps was followed. Epoxy composites containing well dispersed CNTs were prepared by the following procedures. The CNTs of 0.5 wt.% were first dispersed in ethanol, under sonication for 2 h. The CNTs/ethanol solutions were then mixed with the epoxy resin. The mixture was also sonicated for 1 h at 80°C. After adding the hardener, the mixture was stirred by using a magnetic bar for 15 min under sonication. For mechanical tests, the epoxy resin loaded with the CNTs was injected into a mold and cured in the oven for 5 hours. On the other hand, the poorly dispersed CNTs/epoxy composites were prepared under sonication for 3 h without using the solvent. It was expected that when the solvent was employed in the CNTs dispersion process relatively well dispersed CNTs nanocomposites could be obtained. But, without using the solvent, the aggregates of pristine CNTs could remain in the polymer matrix. The poorly and well dispersed samples are denoted as sample-1 and sample-2 respectively. The corresponding ductile samples are named as sample-D1 and sample-D2. The neat epoxy and the ductile epoxy are designated as sample-0 and sample-D0.

### 4. Mechanical measurements

Mechanical properties of neat as well as CNTs/epoxy composites were measured by Instron 1195. Flexural tests were carried out at ambient temperature and at the constant cross-head speed of 2 mm/min. Rectangular specimens were made as per ASTM standard .



Fig.3 shows the mechanical responses of neat epoxy as well as MWNTs-based composites prepared with and without using solvent. Each graph is the average of five tests. Fig. 4 shows variation in mechanical parameters of ductile neat and composite samples. For each, the first graph corresponds to the unloaded epoxy resin. So it results that filling epoxy with multiwall nanotubes leads to brittle materials. The comparison between sample-0, sample-1 and sample-2 shows an increase in flexural modulus for all composites. Fig. 3 shows that the flexural modulus increase is more pronounced for sample-2 (4 times) than for sample-1 (57%). In case of ductile samples the poorly dispersed sample-D1 is showing 25% increase in flexural modulus while the well dispersed sample-D2 is showing almost 3 times the flexural modulus of neat sample-D0 (Fig.4). This is due to the fact that these MWNTs are easier to disperse and/or to be impregnated. Further it is worth noticing that the ductile sample-D2 has 24% more flexural modulus value than sample-2.

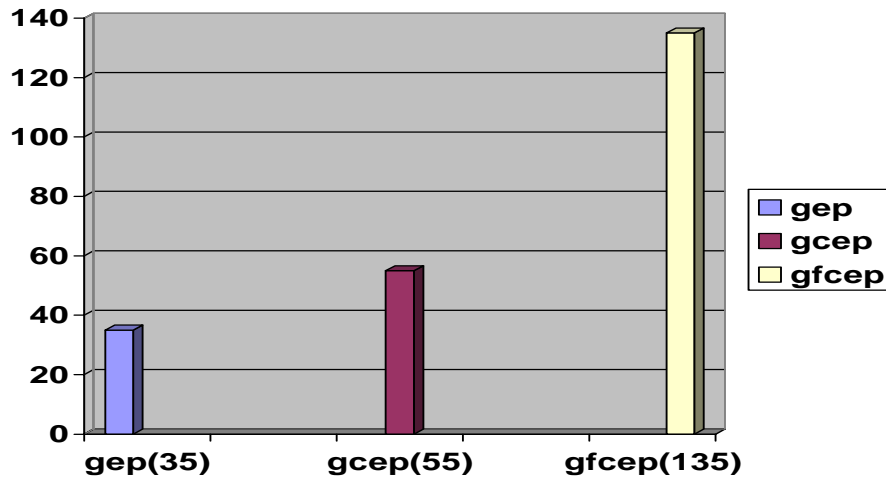


Fig.3. Flexural tests of sample-0, 1 & 2.

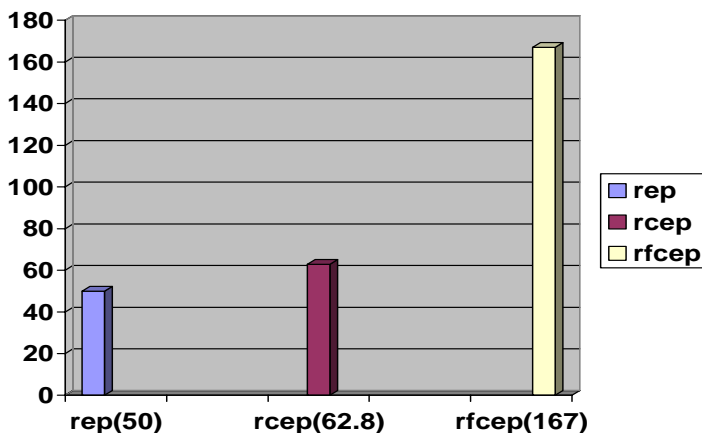
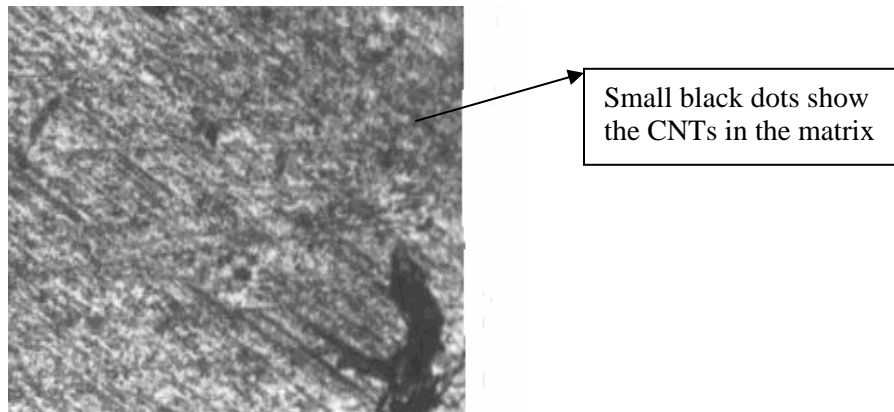


Fig.4. Flexural tests of ductile samples-D0, D1 & D2.

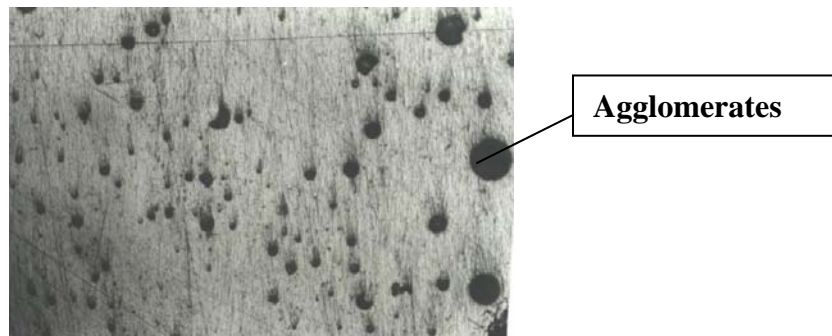


## 5. Morphological characterization

Nanotube dispersion in polymers can affect the final nanocomposite properties. To optimize nanotube dispersion, we need to investigate and quantify the dispersion. This can be done by visualizing the nanotubes themselves, the interface, and the effect of the CNTs on the surrounding matrix. It is not surprising that at the nanolength scale, characterization, testing and modeling are much more difficult (8). Optical techniques, typically used for characterizing dispersion, cannot discern between single CNTs. Electron microscopy techniques are used but are not always easy to implement due to issues with sample preparation and a lack of contrast between the polymer and the CNT.



**Fig.5: Optical micrograph of well dispersed MWNT in epoxy matrix**



**Fig.6 : Optical micrograph of epoxy cnt composites with agglomerates**

Morphology of poorly dispersed (without solvent) and well-dispersed (in ethanol) CNTs/epoxy composites have been analyzed. Optical microstructures were obtained using "optical microscope(Verasmet-II, Union 7685)". Fig.5 & Fig.6 show the image of the dispersion states of well dispersed (sample-D2) and poorly dispersed (sample-D1). It is obvious from the micrographs that some agglomerates were remaining in sample-D1. Compared to that in sample-D2, where MWNTs were mixed in ethanol, better dispersion state was obtained.



## Conclusions

In order to investigate the influence of CNTs dispersion on the nanocomposites, mechanical properties of the epoxy composites were experimentally examined. Morphology of the nanocomposite was characterized by optical microscope images. As a result, variations in the properties are caused by different dispersion state of the CNTs. The nanocomposites containing the well dispersed CNTs exhibited higher flexural modulus than ones with the poorly dispersed CNTs. It means that the well dispersed CNTs composites have, from a rheological point of view, a more solid-like behavior. The CNTs nanocomposites have poor interfacial bonding between the CNTs and the polymer matrix, which is identified in the optical images. The nanocomposites filled with a little wt% CNTs yield much higher mechanical properties than neat epoxy samples.

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