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Effect of mechanical properties on fracture surfaces of carbon nanotube composites pre-treated at different temperatures

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Abstract- CNT-based composites have been fabricated through different novel methods and were subjected to different environmental conditions. Flexural moduli of all samples were determined. The resulting composites possess enhanced or completely new set of physical properties due to the addition of CNTs because of their high mechanical strength. Effect of mechanical testing on composites has been examined microscopically by SEM through fracture surface. Results confirmed that nanocomposites pretreated with hot water are tough and those treated in liquid nitrogen are brittle. An improvement of the physical properties of polymer nanocomposites, based on carbon nanotubes (CNTs), is addicted to a good dispersion and strong interactions between the matrix and the filler.

1. INTRODUCTION

The discoveries of carbon nanotubes (CNT) have initiated researches in many different areas; one of the most intriguing applications of CNT is the polymer/CNT nanocomposites [1,2,3,4,5]. The high mechanical, electrical and thermal property of CNT makes them ideal candidate as fillers in lightweight polymer composite [6]. Due to their high specific strength and specific stiffness, nanotube-reinforced polymer composites have become attractive structural materials not only in the weight-sensitive aerospace industry, but also in the marine, armor, automobile, railway, civil engineering structures, and sporting goods industries. Epoxy resin is the polymer matrix used most often with reinforcing nanotubes for advanced composite applications. The resins of this class have good stiffness, specific strength, dimensional stability, and chemical resistance, and show considerable adhesion to the embedded fiber [7]. Because micro-scale fillers have successfully been synthesized with epoxy resin [8–11], nanoparticles, nanotubes, and nanofibers are now being tested as filler material to produce high performance composite structures with enhanced properties [12–14].

Since nanotubes have been appreciated as strong reinforcements for advanced materials for aerospace applications, these materials must be able to survive in an extremely low temperature without apparently generating any structural degradation to structures. Besides, increasing the temperature of the nanotube composites may catalytically enhance the chemical reaction between the nanotubes and polymer based materials. Therefore, the in-depth studies on these issues are important. Different polymer/CNT nanocomposites have been synthesized by incorporating carbon nanotubes (CNTs) into various polymer matrices, such as polyamides [15], polyimides [16–18], epoxy [19], polyurethane [20–21] and polypropylene [22–24]. The purpose of this paper is to show the effect of carbon nanotubes on the mechanical properties of epoxy composite. Flexural tests were performed to evaluate mechanical performances. Again analysis of the flexural properties of the composites has been done under ambient, sub ambient (cryogenic) and intermediate temperatures. Microscopic approaches were used to investigate the material's fracture behavior and mechanisms.

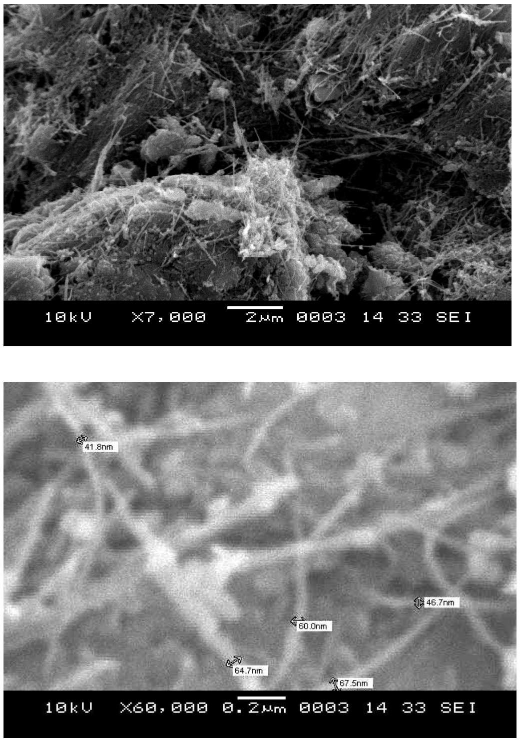


Figure 1: SEM of Multiwall carbon nanotubes (MWCNTs) showing diameter

II. EXPERIMENTS

A. Materials

Multiwall carbon nanotubes (MWCNTs) used for the preparation of nanocomposites were obtained from MER corporation, USA. They are produced by arc plasma method (purity 95%, length 10-50 µm and diameters 20-70 nm). SEM morphology of the products (Fig. 1) was carried out with a "JEOL JSM-6480 LV Scanning Microscope". Epoxy polymer matrix was prepared by mixing epoxy resin (Ciba-Geigy, araldite LY-556 based on Bisphenol A) and hardener HY-951 (aliphatic primary amine) in wt. ratio 100/12. Epoxy resin (5.3-5.4 equiv/kg) was of low processing viscosity and good overall mechanical properties.

B. MWNT/epoxy composite preparation

Nanocomposites were prepared by the method of sonication. To achieve better state of dispersion first the nanotubes were treated with alcoholic medium for the deagglomeration of the tube bundles. The treated tubes were then added to the epoxy resin and sonicated for 2hrs at room temperature. Then the mixture was cured under vacuum at 90^0 C for 10 hrs and another set of samples were cured under refrigeration condition to get ductile samples. The prepared samples were treated at 80^0 c for 6 hrs in the oven to remove the moisture contents of the samples. The finally prepared samples were treated at different environmental conditions for 24 hrs before the mechanical tests were performed. Few samples were treated by hot water at 80^0 C and some are treated in the cryofreezer at liquid nitrogen temperature (-180^0 C).

C. Flexural strength test

Four types of flexural test samples were fabricated: they were, pure epoxy beam & its ductile one and the nanotube composite beam & its ductile one. The beams were placed into different temperature environments for 24 hours prior the test, these were: (a) room temperature (20 ^{0}C), (b) warm water (80 ^{0}C) and (c) liquid nitrogen (-180 ^{0}C). The pure resin sample be named as R_0 and the nanocomposite sample as R_1. Respective ductile samples those settled in refrigerator were named as DR_0 and DR_1. The corresponding samples treated in hot water are designated as H_0, H_1, DH_0, DH_1 and in cryofreezer are C_0, C_1, DC_0, DC_1. The test was conducted immediately once the beams were picked up from the specified environments. From each sample, five rectangular specimens were taken for three-point bend test as per ASTM D790 (width=2.7cm, thickness=0.7cm, span=11.2cm, length=12cm). Flexural tests were carried out at ambient temperature using Instron 1195 keeping the cross-head speed 2 mm/min. Flexural modulus of each sample was determined from the average value of five specimens.

D. Fracture surface Topography Characterisation

Scanning electron microscope (Jeol JSM-6480 LV) was used to conduct the fracture surface topography characterization. The cured samples were fractured and the fracture surfaces were coated with a thin platinum layer.

III. Results and Discussion

A. Flexural measurements

Flexural modulus of pure resin & its CNT composite and ductile resin & its nanocomposite samples are found to be R_0, 24.52; R_1, 136.86; D_0, 44.15; D_1, 176.38. Increase in flexural modulus is more pronounced in samples treated in hot water (H_0, 49; H_1, 148.8; DH_0, 64; DH_1, 210) in comparison to samples treated in cryofreezer (C_0, 33; C_1, 140.2; DC_0, 36; DC_1, 159.3). Because at high temperature the filler can constrain the mobility of polymer chains as well as their relaxation spectra [25], which can change the glass transition

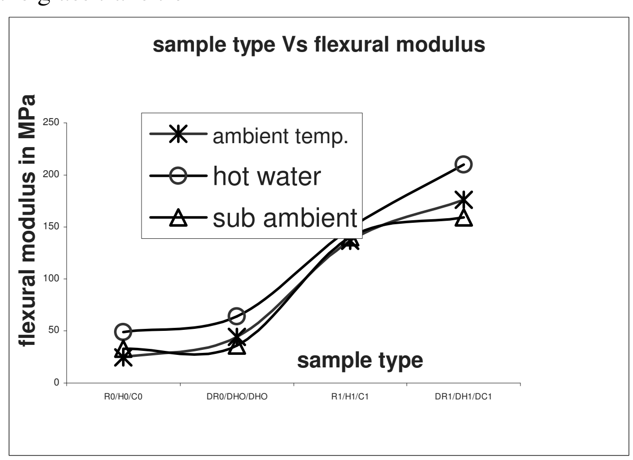
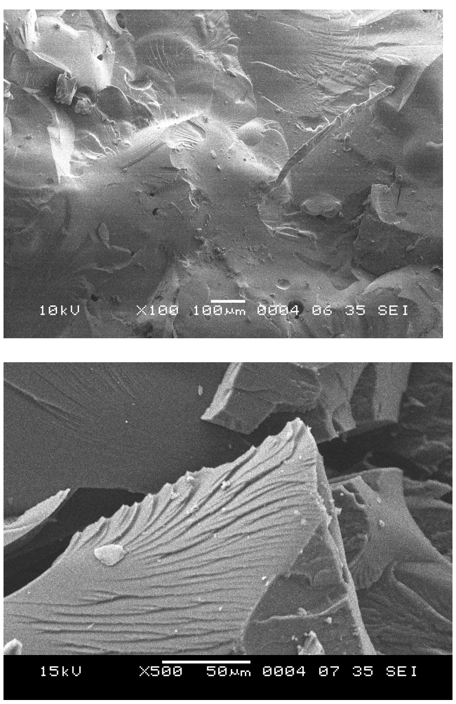


Figure 2: Flexural moduli of resin as well as composite samples placed in different environment

temperature [25, 26] and modulus of the matrix. All the composite samples are showing greater modulus than pure resin samples. This may be due to the high mechanical strength of CNT. The ductile composite samples after submerged into liquid nitrogen (DC_0 and DC_1) revealed reduction in flexural modulus in comparison to room temperature treated samples (D_0 and D_1). The cause of reduction is may be due to the structural non-homogeneity and/or existence of a weak bonding interface between the nanotubes and surrounding matrix. The results of the refrigerated samples are showing variable behaviour. Ductile samples, which were, treated in hot water showed the best result. And those kept in cryofreezer became more brittle and hence less modulus. This may be due to contraction of the matrix, which increased the clamping stress to the nanotube surface, and thus increased the frictional force between the nanotubes and the matrix.

B. Fracture surface

Neat epoxy resin (Fig. 3a) exhibits a relatively smooth fracture surface and the higher magnification SEM picture in Fig. 3 indicates a typical fractography feature of brittle fracture behavior, thus accounting for the low fracture toughness of the unfilled epoxy.

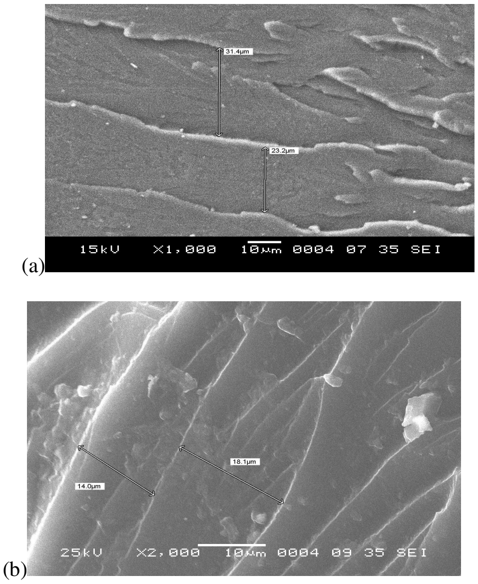


(a)

(b)

Figure 3 (a&b): Fracture surface of Epoxy resin at different magnifications

The distance between two cleavage steps (Fig.4a) is about 23-32 μm and the cleavage plane between them is flat and featureless. The fracture surfaces of the nanocomposites show considerably different fractographic features. For example, the failure surface of the nanocomposite are rougher with the CNTs added into the epoxy matrix (Fig. 4b). The higher magnification SEM picture shows that the size of the cleavage plane decreased to 14-18 μm after the infusion of the CNTs. The decreased cleavage plane and the increased surface roughness imply that the path of the crack tip is distorted because of the carbon nanotubes, making crack propagation more difficult.

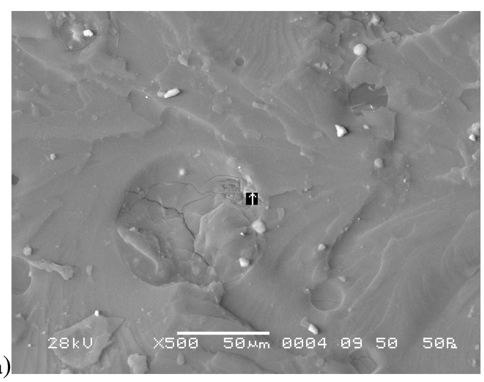


(a)

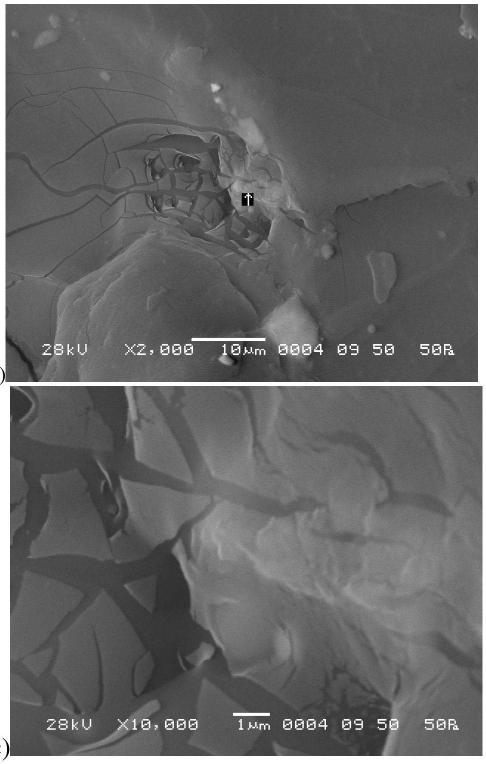
(b)

Figure 4: Cleavage plane of (a)pureepoxy and (b)composite sample

A large particle, an agglomeration of several carbon nanotubes (Fig. 5), was observed in the fracture surface. At a low stress level, the agglomerated particle increased the stiffness of the material, but at a high stress level, the stress concentration caused by the agglomerated particle initiated a crack, which made the sample fail quickly.



(a)

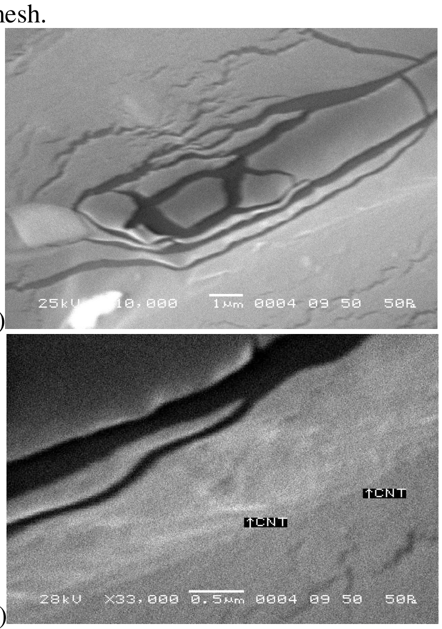


(b)

(c)

Figure 5(a,b&c): Agglomeration of several carbon nanotubes showing by arrow mark

Fig. 6a shows original traces of nanotubes in the composites. The fracture process did not follow the nanotube pullout pattern as in Fig. 6b, cracks propagated along the plane of the nanotube mesh.



(a)

(b)

Figure 6: Traces of nanotubes in the composites near crack

This agrees with Lau and Hui [27] that the all nanotubes, aligned close to the load direction in nanotube polymer composites were always pulled out at failure. This was a result of a poor interfacial bonding between the nanotubes and matrix. Therefore, the nanotubes inside the composites could not fully take up the load on the nanotube's longitudinal direction, which resulted in the decrease of flexural strength of the nanotube composite beams.

IV. CONCLUSION

Addition of nanotubes enhanced the flexural properties because all the composite samples are showing better result than pure resin samples. Flexural modulus is maximum in case of ductile composite samples treated in hot water at 80^0 C. These nanocomposites appeared tough while sub-ambient ductile samples are showing brittleness. The fracture surfaces of nanotube/polymer composites after flexural tests show different failure mechanisms for composites pre-treated under different conditions. The fracture process of composite beam appeared to indicate that failure was the result of agglomeration due to which crack initiation occurs.

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