A Study on the Role of Multi Wall Carbon Nanotubes on Tensile Properties of Epoxy Nanocomposites

M. Hoshyar Sadegian, S.M.Zebarjad[*], S.A.Sajjadi

Department of Material Science and Engineering, Ferdowsi University of Mashhad, Mashhad, Iran, P.O. Box: 91775-1111.
Email: Zebarjad@um.ac.ir

Abstract

The objective of the current research is focused on the producing of epoxy nanocomposites reinforced with different multi wall carbon nanotubes (MWCNTs) content and investigation of their tensile properties. For this purpose two series of epoxy matrix with different hardener were produced. Then the matrices were reinforced with different carbon nanotube content (0, 0.3, 0.6 and 1Wt%). Transition electron microscope (TEM) was used to evaluate the distribution of MWCNTs inside the matrix. The standard tensile specimens were made using casting method. Tensile test was done according to ASTM 638 at 1mm/min cross head speed using Zwick Z250 tensile machine. TEM micrographs showed carbon nanotubes were impregnated with the resin and proved that the interface was strong sufficiently. The results of tensile test showed that tensile properties of epoxy/MWCNTs varied as MWCNTs content added to it. In fact addition MWCNTs to epoxy caused to increase both yield stress and Young's modulus of epoxy. Also it illustrated that the role of MWCNTs reinforcing depends strongly on matrix stiffness. Indeed reinforcing effect of MWCNTs in soft matrix is much higher than that of hard ones.

I. INTRODUCTION

Multi-walled carbon nano tubes (MWNTs) have unique atomic structure, very high aspect ratio and extraordinary mechanical properties, making them ideal reinforcing materials in nanocomposites [1]. The recent researches have extensively focused on the epoxy resin-based carbon nanotube nanocomposites because of their wide applications in the electronics, aeronautics and astronautics industries. However, the reinforcement role of carbon nanotubes in epoxy-based nanocomposites seems divergent. Some early research results just showed barely stronger or weaker carbon nanotube–epoxy nanocomposites than the net epoxy [2-5]. Such low reinforcing ability of the nanotubes in epoxy nanocomposites, which is sometimes observed, can be explained by a number of reasons. One is the lack of interfacial adhesion, which is critical for load transfer in composites. Indeed, carbon nanotube surfaces are atomically smooth, which may limit the transfer of load from the matrix to nanotubes reinforcement [2, 3]. Another reason is the poor dispersion of nanotubes in the epoxy matrix, which is also significant for the fabrication of reinforced nanocomposites [4, 5]. In fact the dispersion of the CNTs in the matrix system is a further main problem to be solved for nanotube-reinforced polymers. Nano-scaled particles exhibit an enormous surface area ($1000m^2/g$ and more), which is several orders of magnitude larger than the surface of conventional fillers. This surface area acts as an interface for stress transfer, but is also responsible for the strong tendency of the CNTs to form agglomerations. An efficient exploitation of the CNT properties in polymers is therefore related to their homogeneous dispersion in the matrix or an exfoliation of the agglomeration and a good wetting with the polymer [6].Various dispersion methods (stirring, extrusion, kneading, etc) for the distribution of CNTs in polymers have been used. A common technique used in order to disperse CNTs is the sonication technique. A pulsed ultrasound exfoliates agglomerates and disperses CNTs in the matrix effectively.To take full advantage of these unique mechanical properties, optimization of nanotube-polymer interface properties such as wettability and adhesion is required. Carefully comparing these controversial results indicates that the stiffness of epoxy matrix seems to be a key point.

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[*] Corresponding Author

In summary material properties of epoxy are supposed to be improved by addition of carbon nanotubes. The focus on improving the mechanical properties led to two common key issues to be investigated: (a) dispersion and (b) interfacial adhesion. This paper describes the manufacturing process of MWCNT/epoxy matrix nanocomposites and the effect of the stiffness of epoxy matrix to the reinforcement role of carbon nanotubes by controlling the curing process.

II. MATERIALS AND EXPERIMENTAL TECHNIQUES

Materials

Epoxy resin was selected as the polymer matrix because it is know that the CNTs are dispersed well in the epoxy resin compared with other polymer resins. Epoxy polymer matrix was prepared by mixing 100 parts by volume of GY 6010 (Bisphenol A) epoxy resin (high viscosity) with 9 and 15 parts of triethylenetetramine (TETA) aromatic hardener.

MWCNTs used in this study as reinforcements were synthesized by the chemical vapor deposition (CVD) process and had the average diameter of about 10 nm and the length of 10-15 m with the nominal purity of 95%. For TEM studies, CNTs were dispersed in ethanol with an ultrasonic bath for several minutes and then were poured on the mili pore paper. Figures 1 and 2 show the SEM and TEM micrographs obtained from used MWCNTs respectively.
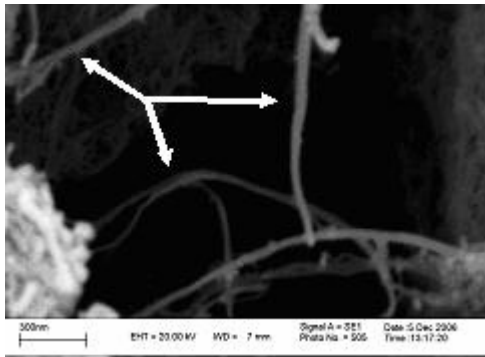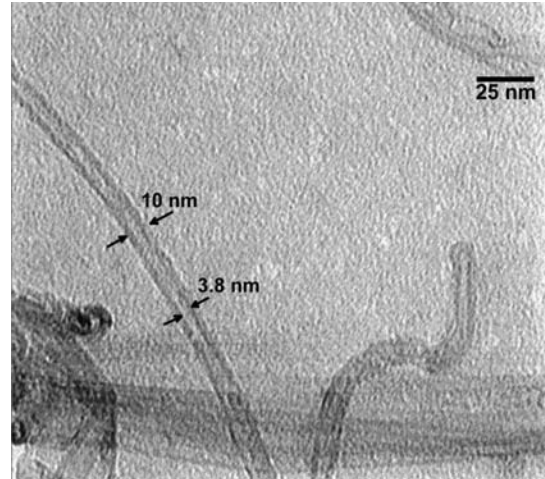

Figure 1. SEM micrograph of MWCNTs

Figure 2. TEM micrograph of MWCNTs

Experimental techniques

The CNTs of 0.3, 0.6 and 1 wt% were first dispersed in ethanol under sonication for 90 min and then stirred for 20 min by magnetic bar. The CNTs/ethanol solution with different CNTs weight fraction was then mixed with epoxy resin. The mixture was also stirred by using magnetic bar for 30 min at 100oC. The mixture was kept in a degasser for 45 min to remove air bubbles. Epoxy and TETA hardener were mixed by 100 parts of resin with 9 and 15 parts of hardener at 50oC. After adding the hardener, the mixture was stirred for 5 min and put under vacuum for 1-5 min to remove remained air bubbles. Finally the mixture was cast into a silicon rubber mold and was cured at room temperature for 24 h. All manufactured samples are listed in Table 1 were post cured at 80oC for 1h.

Table 1: List of produced nanocomposites in this study

No#	Symbol#	Parts of hardener in 100 parts of resin #	CNTs (wt %)#
1#	EP9	9	-#
2#	EP15#	15#	-#
3#	EP9/0.3CNT#	9#	0.3#
4#	EP9/0.6CNT#	9#	0.6#
5#	EP9/1CNT#	9#	1.0#
6#	EP15/0.3CNT#	15#	0.3#
7#	EP15/0.6CNT#	15#	0.6#
8#	EP15/1CNT#	15#	1.0#

Tensile test

Figure 3 shows dog-bone shaped specimen. The gauge length and the thickness of samples were 50±2.5 and 3 mm respectively. Tensile tests were carried out according to ASTM D638 using Zwick Z250 tensile frame at a cross-head speed of 1mm/min. Three samples per material were tested at room temperature.
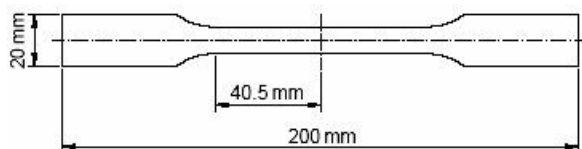

Figure. 3. Dimensions of dog-bone shaped specimen.

Microscopic evaluation

SEM micrographs were obtained with LEO 1450 VP operating at 20 kV to examine surfaces of the specimens fractured during tensile test. The samples were coated with Pt-Au for 4 min prior to the measurement to avoid charge build up. TEM observation was carried out with LEO 912AB at 100 kV for more exact characterization of the morphology. The TEM specimens were microtomed to an ultra thin section with the thickness of about 50 nm.

III. RESULTS AND DISCUSSION

The study of the cure reactions after introduction of carbon nanotubes into a polymer is very important for accessing their reinforcement role. Introduction of carbon nanotubes may have effect on the initial curing rate of the composites. The acceleration effect due to the nanotube introduction was reported for the epoxy system [7]. This acceleration effect was possibly attributed to the higher thermal conductivity of carbon nanotube, the physisorption of the hardener surrounding carbon nanotubes, and the surface groups attached on carbon nanotubes. In view of the SEM observations and the mechanical test results, a possible scenario of forming nanotube/epoxy composites with different hardener additions is proposed. For the lower concentration of hardener, the whole curing rate of epoxy is slower than higher hardener concentration, and because of the initial acceleration effect may be more significant in the earlier stage of curing, and thus the resulted composites have evidently increased mechanical properties.

Figure 4 shows the transmission electron microscopy (TEM) micrograph taken from produced Epoxy/MWCNTs nanocomposite (EP9/0.6CNT). As it can be seen the multi wall carbon nanotubes are dispersed inside the epoxy matrix implying the sufficient fabrication method.
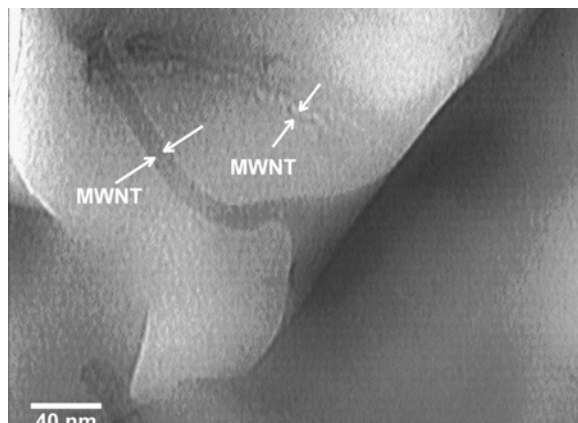

Figure 4. TEM micrograph of Epoxy/0.6%CNT nanocomposites (EP9/0.6CNT)

The stress-strain curves of pure epoxy and its nonaocomposites with different TETA are shown in Figures 5-a and 5-b. As seen tensile properties of pure epoxy depends strongly on TETA content. While TETA content increases from 9 to 15 parts both Young's modulus and tensile strength increase. This is because TETA leads the epoxy to be stiffer. Moreover the Young's modulus and the tensile strength of the nanocomposites are dictated by MWCNTs content for two composites with different stiffness. Figures 6-a and 6-b illustrate the variation of Young's modulus and tensile strength of both nanocomposite on carbon nanotube carbon content. The interesting result achieved in the current study is, the carbon nanotubes take a more significant role in the soft matrix nanocomposites than another (Soft or hard matrices define according to their Young's modulus).

For example addition 1 wt% MWCNTs to epoxy make an increase in Young's modulus and tensile strength of EP9 matrix up to 99% and 24% respectively. But the nanotube composite with the matrix of high stiffness shows only a slight increase in the modulus and tensile strength. It proves that the interface interaction between MWCNTs and the surrounding epoxy is poor in the stiff matrix composite. On the other hand, with increasing the hardener (TETA), physical contact at the molecular scale was believed as the main factor that attributes to the carbon nanotube-polymer interfacial decreases. Therefore, carbon nanotubes in a stiff epoxy matrix may have a little contribution on the mechanical properties under the tensile stress, as the results shown.
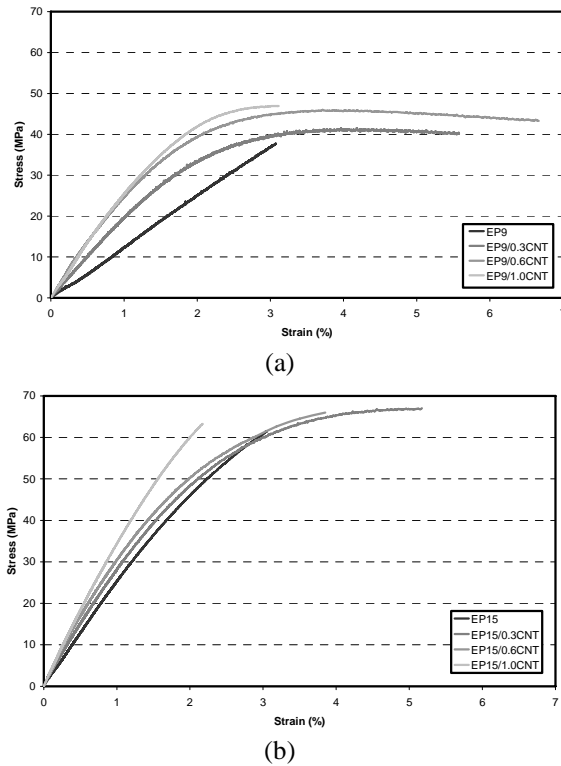
(a)

(b)

Figure 5. Stress-strain curves of epoxy nanocomposites a) EP9, b) EP15
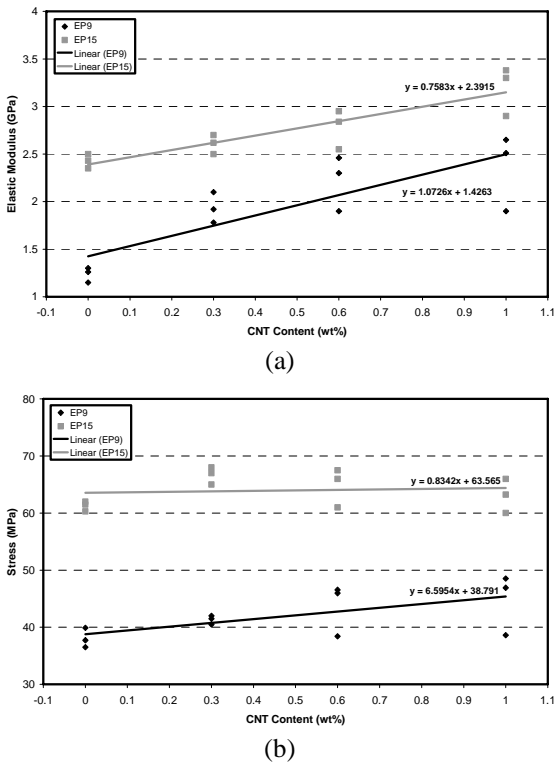

(a)

(b)

Figure 6. Tensile properties of epoxy nanocomposites a) Elastic modulus and b) Tensile strength

The results of current study show that by increasing carbon nanotube content, the agglomeration size increase. It is clear that the reinforcing effect of the MWCNTs reduces because of agglomeration. This is because they act as a concentrator inside the resin. This is why the poorly dispersed CNT/epoxy composites have lower mechanical properties than the well dispersed ones. SEM micrograph of the fracture surface of epoxy nanocomposite after tensile tests of EP9/1CNT is shown in Figure 7. A cluster of MWCNTs inside the epoxy composite can be observed in EP9/1CNT sample. Generally, most of carbon nanotubes in both the soft composites and the stiff ones are shown as the bridging, pull-out and broken failure mode. Figures 8 and 9 can be the examples for role of MWCNTs on bridging mechanism in epoxy nanocomposites.
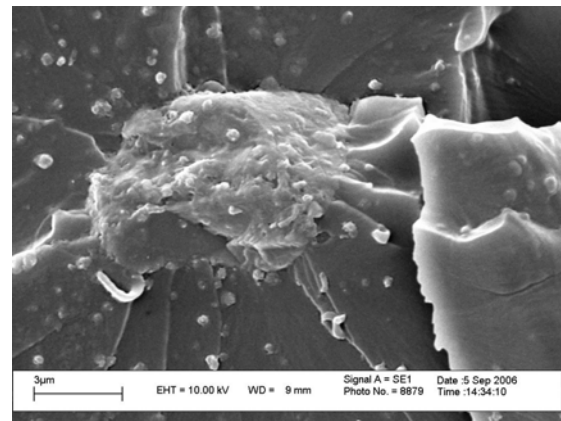

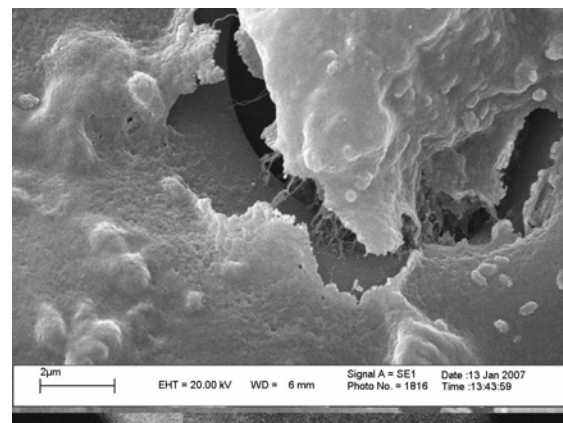**Figure 7.** Agglomeration of MWCNTs dispersed in epoxy composite (EP9/1CNT)

Figure 8. Fracture surface of epoxy reinforced with 0.6Wt% MWCNTs (EP9/0.6CNT)
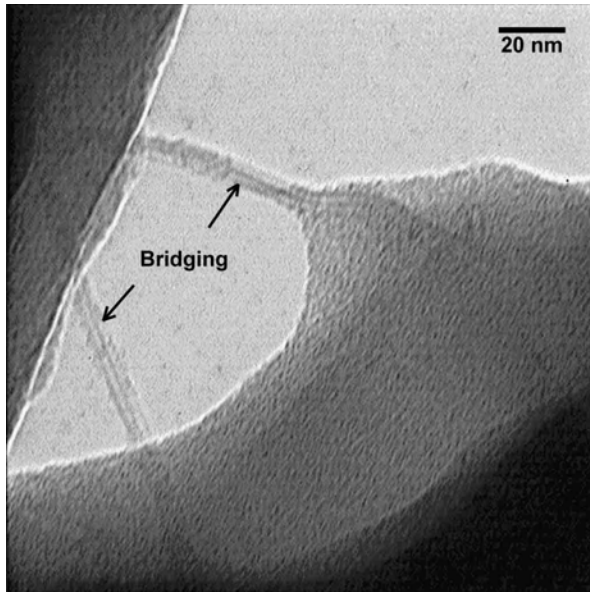
Figure 9. TEM micrograph showing bridging phenomenon in EP9/0.6CNT due to presence of MWCNTs

IV. CONCLUSION

Two series of epoxy matrix with different hardener (TETA) were produced. The matrices were reinforced with different multi wall carbon nanotubes content (0, 0., 0.6 and 1 Wt%). The produced nanocomposites were investigated using tensile test and microscopic evalauation. The results are summarized as follows.
- Tensile properties of epoxy/MWCNTs varied as MWCNTs content added to it.
- addition MWCNTs to epoxy caused to increase both yield stress and Young's modulus of epoxy.
- The role of MWCNTs reinforcing depends strongly on matrix stiffness.
- Role of MWCNTs on bridging mechanism in epoxy nanocomposites was observed.

V. REFERENCES

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