Micro-hardness of Carbon Nanotubes Reinforced Epoxy Resin Nanocomposites

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4 authors:

Dr. Bahjat B. Kadhim
Mustansiriyah University

Haider O Muhsen

Ali Obies Muhsen Almayyali
University of Babylon

Mohammed Almajidi
University of Babylon

Micro-hardness of Carbon Nanotubes Reinforced Epoxy Resin Nanocomposites

Bahjat B. Kadhim[1], Haider O. Muhsen[1] and Ali O.Muhsen[2] , ALMAJIDI Mohammed,

Fatin –F- ALkhafajy[4] .

1- *Department of Physics, College of Sciences, University of Al- Mustansiriya, Iraq.*
2- *Department of physics ,College of Education Ibn Hayan ., University of Babylon , Iraq.*
3- *Department of chemistry , college of scoenice for woman . University of Babylon , Iraq*
4- *Department of physics ,College of Education Ibn Hayan . University of Babylon , Iraq .*

aliobies_1983@yahoo.com

ABSTRACT

The effects of reinforcement of multi-wall carbon nanotubes (MWCNTs) on Vickers hardness of epoxy resin based composites were studied. Epoxy resin was reinforced with CNTs type multi-walls (MWCNTs) to prepare nanocomposites with different volume fractions which were (0.1%, 0.2%, 0.3%, and 0.4%). Ultrasonic dispersion and magnetic stirring techniques were used to prepare the nanocomposites specimens using flash molds at standard conditions. Microhardness Vickers technique was used to determine the hardness according to ASTM- E92-82. Hardness Vickers results show that VHs values increase progressively by succession of volume fraction of fillers (MWCNTs). Atomic force microscopy was used as an indirect method for morphological analysis of the sample to help the interpretation of results.

Keywords: carbon nanotubes, nanocomposites, hardness properties

Nanocomposites can be defined as a composite material in which at least one of the phases (mostly the filler) shows dimensions in the nanometer range. As the fillers size reaches the nanometer level, the interactions at the interfaces become considerable large with respect to the size of the inclusion and thus the final properties show significant changes [1].

A nanocomposite, like a traditional composite has two parts, filler and the matrix. A traditional composite typically uses a fiber such as carbon fiber or fiberglass as the filler, in a nanocomposite the filler is a nano material. Nano material ranges in size from 1-100 nm .Some examples of nano material are CNTs, carbon nano fiber, and nano particles such as gold, silver, diamond, copper, and silicon. Of particular interest are CNT nanocomposites because of their high strength and stiffness composites they produce at relatively low CNT concentrations [2, 3].

The fillers used in polymer nanocomposites are usually inorganic fillers, although carbon nanotubes and carbon black (extensively used in rubbers) are exceptions. Nanofillers can have different shapes [4]: Spherical (silica, carbon black), Rod / fiber (synthetic whiskers and carbon nanotubes) and Sheet / platelet (layered silicates such as montmorillonite and similar synthetic structures such as synthetic mica).

The classes of nanocomposites that will be used in this work are the carbon nanotubes nanocomposites with a thermosets polymer (epoxy) as a matrix. Iijima.S, first observed carbon nanotubes while studying another class of macromolecules called fullerenes in 1991. Carbon nanotubes are made up of graphene molecules. They are composed only of four carbon atoms arranged in a three- dimensional cage like structure. Carbon nanotubes are fullerenes, which are extended in one dimension with a high aspect ratio, acquiring a cylindrical structure [5]. Nanotubes composed of a single layer of graphene are called single-wall carbon nanotupes (SWCNTs), where as those that have concentric multiple layers of graphene are called multi-wall carbon nano tubes (MWCNTs). Typically SWNTs have diameters of order 1 nm, and lengths of order 100 nm to several µm. MWNT have much larger diameters of tens to hundreds of nanometers. Intermediate to these are the so-called few-walled carbon nanotubes (FWNT) that have only a few layers, such as double-wall carbon nanotubes (DWNT) [6] as show in figure (1).

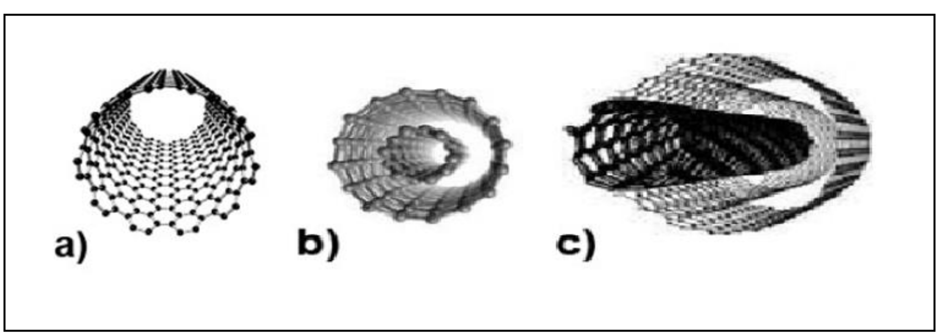

Fig. 1: Schematic of: (a) SWCNT, (b) DWCNT, and (c) MWCNT [1, 6].

The polymer matrix is epoxy resin,The structure of epoxy resin is characterized by the epoxy group, also, known as epoxide or oxirane group as shown in figure (2). Epoxy resins of several families are now available ranging from viscous liquids to high melting solid. Among them, the conventional epoxy resins manufactured from epichlorohydrin and bisphenol. There are varieties of hardeners or curing agents generally used for epoxy resins. The amine type compounds are often used in structural application. The hardening effect is achieved through the formation of cross-links between the resin polymer chain and the hardener, or by direct linkage among the epoxy groups [7, 8]. Epoxy has been widely used in commercial applications with fiberglass, graphite, and aromatic fibers. Applications include: Aircraft components, pressure vessels, rocket motor cases, and car bodies [9].

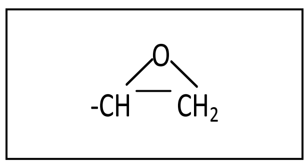

Fig.2: Structure of Epoxy group [7, 8]

Advantages of the use of epoxy resin include: excellent adhesion, excellent mechanical properties (strength and stiffness), excellent chemical resistance, excellent weather resistance, low shrinkage and good corrosion protection [9, 10 and 11]. In the past few years, a few researches related to the nanotube-polymer composites have emerged in the studies on their mechanical, geometrical and electrical properties. Kin-Tak et al, (2003) reports the micro-hardness and flexural properties of nanotube composites with different amounts of nanotubes content. The results show that the hardness of the nanotube composites varied with different nanotube weight fractions [12].

Subhranshu Sekhar Samal & Smrutisikha Bal (2008) added Randomly oriented multi-wall carbon nanotubes (RCNTs) and Aligned carbon nanotubes (ACNTs) into the epoxy resin were mixed by sonication and then cured to obtain nanocomposite samples. The mechanical properties of the composites were characterized in terms of flexural tests and hardness tests.

Scanning electron microscopy studies were employed to investigate the deformation mechanisms and crack propagation of the nanocomposites. Compared to random carbon nanotube-based composites, a significant increase in modulus and hardness was obtained with aligned carbon nanotube composites due to good load transfer from matrix to CNTs and effective bridging of cracks [13].

Smrutisikha Bal (2009) has fabricated epoxy nanocomposites of different content of carbon nanofibers upto 1 wt% under room temperature and refrigerated curing conditions. The composites were studied in terms of mechanical properties. Flexural modulus and hardness were found to increase significantly in refrigerated samples due to prevention of aggregates of nanofibers during cure condition [14].

Applications of polymer nanocomposites depend on matrix and nanofillers : automobile (gasoline tanks, bumpers, interior and exterior panels, etc.), Construction (shaped extrusions, panels), Electronics and electrical (printed circuits, electric components), Food packaging (containers, films), Cosmetics (controlled release of “active ingredients”), Dentistry (filling materials), Environment (biodegradable materials), Gas barrier (tennis balls, food and beverage packaging), flame retardant, military, aerospace and commercial applications [15].

The extraordinary characteristics of carbon nanotubes have attracted intense attention over the last decade. So, the aim of this work is studying the effect of volume fraction of carbon nanotubes (equivalent to volume percentage 0.1%, 0.2%, 0.3% and 0.4%) on the Vickers hardness of epoxy-matrix nanocomposites to produce good composites which used in military and aerospace applications such as space craft heat shield.

HARDNESS OF NANOCOMPOSITES

Fillers are added to the resins to improve mechanical properties such as compressive and flexural strength and hardness. Improved physical properties include a reduction of polymerization shrinkage and an increase in the modulus of elasticity [16]. The physical and mechanical properties of composite resins are also influenced by the characteristics of the fillers themselves, for example their size, distribution and content per volume of the filler particles [17]. The carbon-carbon chemical bond in a graphene layer is probably the strongest chemical bond in an extended system known in nature. Since CNTs are nothing but seamlessly rolled-up graphene layers, from the time of their discovery it has been speculated that these nanostructures have exceptional mechanical properties, and to quantify these properties has become a topic of great interest in the field of nanotechnology [18]. The mechanical selection for a variety of application is quite often based on mechanical tests such as hardness [19].

Hardness of nanocomposites is defined as the resistance to permanent indentation or penetration,

Hardness testing has been widely used in the study of optimum cure of composite resins and includes Vickers hardness testing. The Vickers tests are classified as microhardness tests in comparison with the Brinell and Rockwell macrohardness tests [16]. The hardness of all nanotube composites was measured by using micro-hardness tester [12]. The angle between the faces of pyramid is 136^0 as shown in figure (3); Vickers Hardness Number (VHS) of materials is obtained by dividing the applied force F, in Kgf, by the surface of the pyramidal depression yielding the relationship [20].

$$\mathbf{VHs=1.8544\times F/d^2}$$

Where d is the average length of diagonals in mm, Vickers hardness indentation is shown in figure (3).

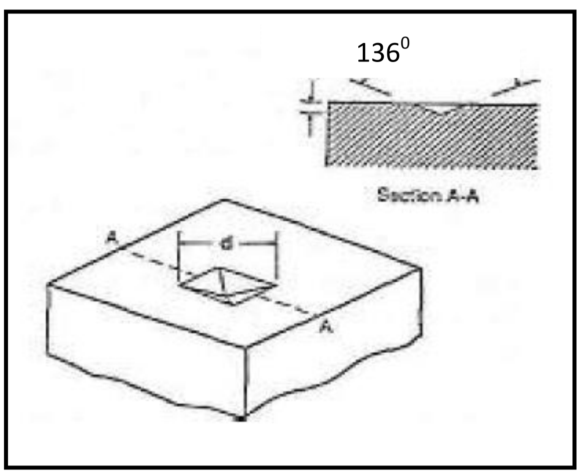

Fig.3: Vickers hardness indentation [20].

EXPERIMENTAL SECTION

Materials:

The polymer (Epoxy Resin), epoxy are supplied by Don Construction Products (DCP),Jordan, commercially known as Quickmast (105) in the form of liquid, low viscosity and good adhesion. The ratio between resin and hardener for this study was 2:1 by weight. Carbon nanotubes type multi-wall carbon nano tubes (MWCNTs) used in this study. The (MWCNTs) used were supplied by Material and Electrochemical Research (MER) Corporation, U.S.A. The nanotubes were produced by chemical vapor deposition (CVD). The diameter of (MWCNTs) was (140 +/- 30 nm) and a length of (7 +/- 2) microns.

Nanocomposites Preparation

To prepare the nanocomposite samples using a high-intensity ultrasonic processor and magnetic stirring technique. The MWCNTs were prepared with volume fraction which is (0.1%, 0.2%, 0.3%, and 0.4 %) to calculate the weight of resin and MWCNTs used sensitive electronic balance. The preparation of nanocomposites was divided into two steps.

They are as follows: The MWNTs were first dispersed in acetone solution under ultrasonic technique to achieve better state of dispersion and reduce the size of the MWNTs. The treated tubes were then added to the epoxy resin and sonicated for 2 h at room temperature. The second step: The hardener addition by using simultaneous magnetic stirring (100 rpm) for an hour to homogenization. This process was continued until weighted materials were finished. Then the mixture was cured under vacuum at (325K) for 4 h. The molds were smeared by wax before the mixture was poured into the molds after homogeneity. The samples were placed between two metal plates under pressure to reduce porosity forming during hardening. The prepared samples were treated at (325K) for 5 h in the oven to remove the moisture contents of the samples and in order to complete the chemical reactions and to reduce the internal stresses formed during the hardening process. Before measurements, the surfaces of the specimens were mechanically polished to minimize the influence of surface flaws, mainly the porosity.

Specimens were preparation according to standard methods for Vickers hardness test, ASTM E-92-82[21]. Figure (4) show the samples of hardness.

Fig.4: Samples of Hardness.

Vickers Hardness Test

The hardness of all specimens was obtained using a Vickers diamond indenter. Vickers indentation is a valid tool for evaluating the hardness of polymers. Both surfaces of the nanotube composites were polished by fine sand papers in order to produce a flat surface for the indentation test.

Vickers microhardness measuring machine is shown in figure (5), with a load of (0.4403 N). The load was applied for 20 seconds. In order to eliminate possible segregation effect a minimum of three hardness readings were taken for each specimen at different locations of the test samples. The operator of the test machine read the lengths of the diagonals immediately after each indentation, with a minimal (as short as 10 seconds) period of time elapsed between making and reading the indentations. It was assumed that, due to the short time elapsed between makings and reading the indentation, the viscoelastic recovery of the diagonals after indentation was minimal. The operator measured the diagonals, and the equipment automatically converted these measurements to Vickers hardness numbers VHN (Kg/mm^2) with a scale of 1 digit to the right of the decimal point in number. Three indentations were made on each specimen and the mean value was calculated.

Fig. 5: Vickers microhardness measuring machine (HVS-1000).

RESULTS AND DISCUSSION

Atomic Force Microscopy

Atomic Force Microscope Explorer Thermo Microscopes was used as an indirect method for morphological analysis of the sample. Maximum scanning size of the microscope probe was (*10x10* μm). Resolution of AFM was (*300x300 pixels*). The sample used in this work was measured in tapping mode. Nominal diameter of tip was (*10 nm*). The reason for the usage of AFM for nanotubes analysis is very simple. AFM is a powerful tool in manipulating and characterizing the properties of nanostructures due to these method atomic planes of nanoparticles can be observed. Figure (6) and figure (7) show structures and nanopartical size of CNTs in two and three dimensions. The surface analysis mode with tapping-mode AFM shows the smoothness surface.

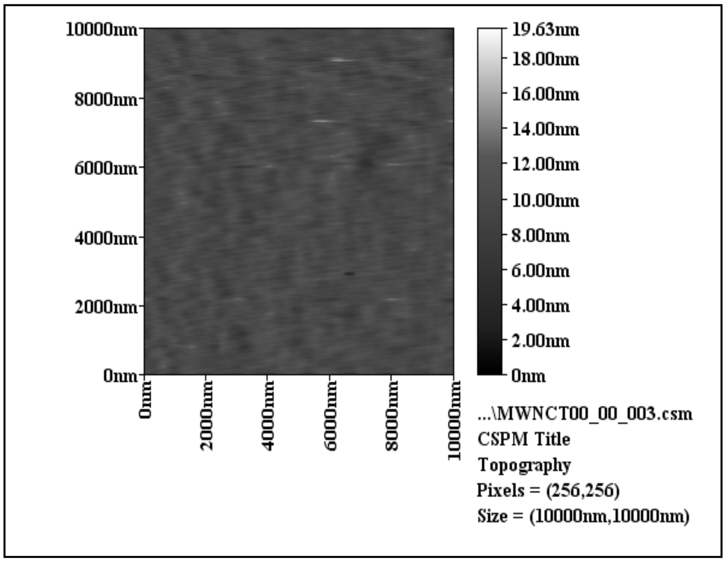

Fig.6: Atomic force microscopy of structures and nanopartical size of MWCNTs in two

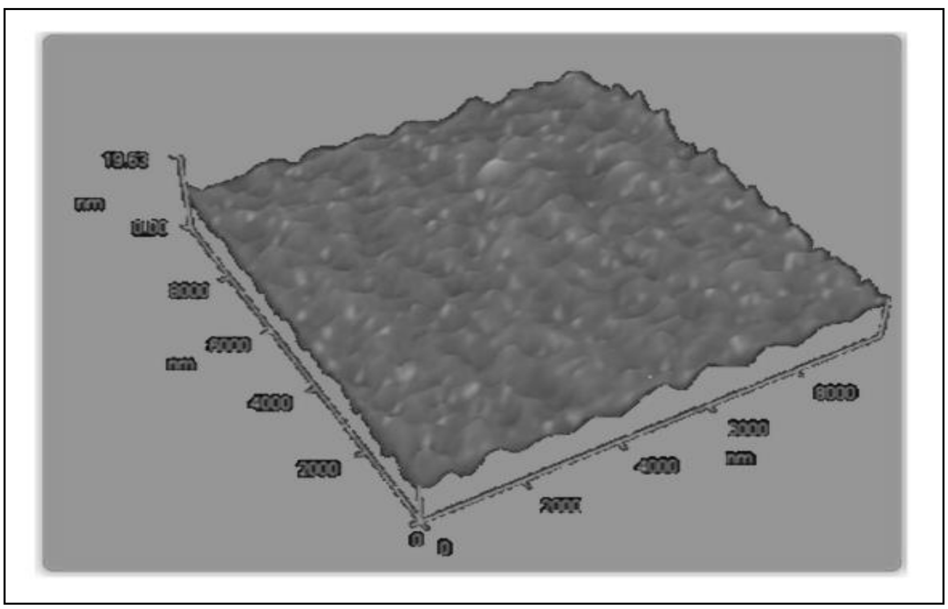

Fig.7: Atomic force microscopy of structures and nanopartical size of MWCNTs in three dimensions.

Vickers Hardness

The results of Vickers Microhardness test in figure (8) show the influence of CNTs vol. % on the hardness of epoxy matrix at room temperature. From the figure the reinforcement by CNTs leads to increase hardness values with the increasing volume fraction. This increment was differentiated in epoxy nanocomposites depending on the CNTs type, as well as the interface effect between the matrix and the filler, also the high adhesion between them. Carbon nanotubes have excellent properties, such as a high aspect ratio depending on manufacturing process, and hence they can be considered as one-dimensional nanostructures and they are expected to have very good mechanical properties by analogy to graphite and diamond. Carbon-Carbon covalent bond is one of the strongest bonds and this bond oriented along the axis of nanotubes produces an extremely strong material. High strength and long nanotube reinforcements may result in forming a network structure that improves the hardness of the nano composites. This result was in a good agreement with that obtained by L. Kin-Tak et al [12], the continuous increase of the nanotube content resulted in increasing the number of high strength reinforcements inside the composites, and thus it increased their hardness property.

Another agreement was obtained by Smrutisikha Bal [14] and S.Sekhar Samal [22], which is the improvement of mechanical properties like hardness resulted from them.

Comparison of hardness values for Pure resin samples reached (9.47) MPa while resin reinforcement by 0.4 vol. % CNTs samples reached (20.74) This increment reached to more than 50% of pure resin sample, this means increasing volume fraction of CNTs leads to increase the hardness of nanocomposites.

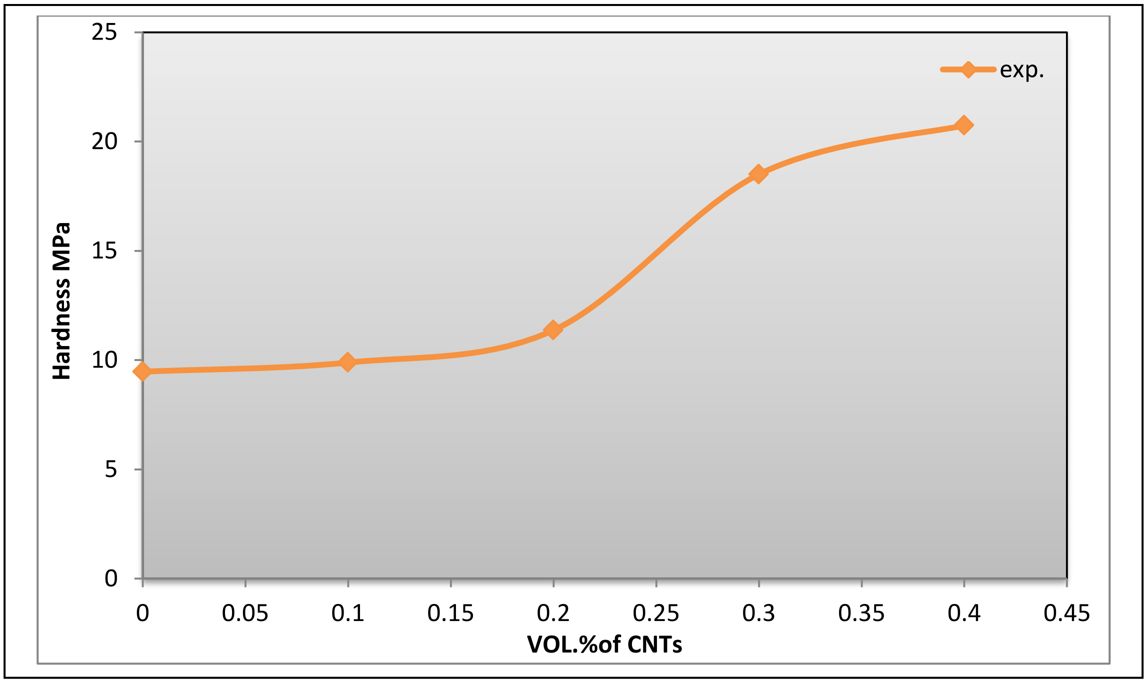

Fig.8: influence of CNTs volume fraction on the Hardness of epoxy resin.

CONCLUSIONS

The experimental results of our study indicate to the reinforcing of epoxy resin by multi-wall carbon nanotubes (MWCNTs), has improved the hardness of nanocomposites in different volume fraction, depending on the following factors; kind of additives, characteristic of its properties, and nature of interface between the matrix and reinforcement additives. Epoxy reinforcement by 0.4 vol. % CNTs showed an increase in the hardness more than 50% when compared to the pure epoxy.

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