The Effect of Multi Wall Carbon Nanotubes on Some Physical Properties of Epoxy Matrix

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Abstract. This research involves using epoxy resin as a matrix for making a composite material, while the multi wall carbon nanotubes (MWNCTs) is used as a reinforcing material with different fractions (0.0, 0.02 , 0.04 , 0.06 ) of the matrix weight.

The mechanical (hardness), electrical (dielectric constant, dielectric loss factor, dielectric strength, electrical conductivity), and thermal properties (thermal conductivity) were studied. The results showed the increase of hardness, thermal conductivity, electrical conductivity and breakdown strength with the increase of MWCNT concentration, but the behavior of dielectric loss factor and dielectric constant is opposite that.

Keywords: Epoxy resin, MWCNT, Electrical properties, Hardness, Thermal conductivity.

1. Introduction

Epoxy resin is one of the polymers has used as a matrix of fiber reinforced composites for advanced application [1]. Addition of MWCNTs results in significant improvement of epoxy resin [2,3]. The researchers in recent years have reported to use of CNTs in metals [4], ceramic [5] and polymers [6], so they have paid much attention to the unique properties of CNTs [7-11] has led to their use in development of the next generation of new composites [12].

CNTs owe to their attractive electrical, mechanical, and thermal properties with chemical stability, have found a wide range of applications consist of nanomodifier of both thermoplastic and thermostet [13,14]. That unique properties led to a variety of applications as sensors, energy conversation, energy storage devices, radiation sources, field emission displays, interconnects, coatings, hydrogen media[15-17], aerospace industry [18] and others.

The aim of this study was to investigate the structural, electrical, thermal and mechanical properties of epoxy / MWCNTs composite for different concentrations of MWCNTs.
2. Experimental

2.1. Matrix material
In this study (thortex) epoxy (EP) resin was used, because it has an excellent adhesion, low shrinkage and good dimensional stability.

The epoxy resin is formed by a reaction of peroxides with a hardener Metaphylenediamine (MPDA) used with epoxy by ratio (1 : 3).

2.2. Carbon nanotubes
The nanolabs based manufacturer of carbon nanotubes, which can be exact to customer specifications. Our criteria carbon nanotubes products, including multi wall (MWCNTs), nanotubes used in this work and single wall nanotube (SWNTs) and double nanotubes (DWCNTs). The MWCNTs were used in the research have purity about (95%), the tube diameter ranges (30 - 50) nm and the tube length ranges (3 to 1) µm.

2.3. Samples preparation
The hand lay-up technique has been used to prepare sheets of composites. The carbon nanotube in different weight fractions (0, 2, 4, 6) % by weight of the sample mixed with amount of epoxy. The dimension was made according to the shape and size of the samples are per ASTM involve the samples of tensile test, hardness, thermal conductivity and electrical conductivity.

2.4. Measurement

2.4.1. Hardness
The hardness was measured by instrument Shore (D) and the device used for this test kind (shore D hardness tester TH 210), that is a tool by stitches in needle the surface of the sample and then record the number which comes out the screen of the device.

2.4.2. Thermal conductivity
Thermal conductivity coefficient was measured by using lee’s disk (manufacture by Griffin and George /England), thermal conductivity coefficient can be calculated from the following equations [19]:

\[ K = \frac{(T_2 - T_1)}{d_s} = e \left[ T_1 + \frac{2}{\pi} \left( \frac{d_1 + d_2}{2} \right) T_1 + \frac{d_3 - T_2}{r} \right] \]

And the terms (e) can be evaluated from [10].

\[ IV = \pi r^2 e \left( T_1 + T_3 \right) + 2\pi r e \left[ d_1 T_1 d_3 \left( \frac{T_1 + T_2}{2} \right) + d_2 T_2 + d_3 T_3 \right] \]

K : thermal conductivity coefficient (W/m°C).

\[ e : \text{represents amount of thermal energy passing through unit area per second disk material}. \]

\[ d_1, d_2 : \text{represent thickness of the disk (mm)}. \]

\[ d_3 : \text{thickness of the sample (mm)}. \]

2.4.3. Electrical conductivity
In the insulating materials the electrical resistance, three electrodes cell or (guard ring electrode method) was used to study the effect of the temperature and the filler addition on volume resistivity of polymer composite. Resistivity (\( \rho \)) value was calculated by using the relation [20]:

\[ \rho = \frac{RA}{L} \]

\( L \) : the length (m).

\( \rho \) : the resistivity of the material (\( \Omega \cdot m \)).

\( A \) : the cross sectional area (m²).

R : the resistance of the object (\( \Omega \)).

Where conductivity was calculated by using the equation: 

\[ \sigma = \frac{1}{\rho} \]
\[ \sigma = \frac{1}{\rho} \quad \ldots \quad (4) \]

### 2.4.4. Dielectric strength

In this test we used instrument (Rang HV - 50 Hz, 30 Kv) and the specimen used in ASTM standard in dimension length (10 mm) and the diameter (10 mm).

The breakdown strength (dielectric strength) is calculated from the equation [21]:

\[ E_{br} = \frac{V_{br}}{h} \quad (V/m \text{ or } Kv/m) \quad \ldots \ldots (5) \]

where \( h \) represents the thickness (mm).

\( V_{br} \): the maximum breakdown (Kv).

### 2.4.5. Dielectric constant and dielectric loss factor

Complex permittivity (\( \varepsilon \)) is defined as the product of the relative permittivity multiplied by the vacuum permittivity constant (\( \varepsilon_0 = 8.85 \times 10^{-12} \text{F/m} \)). In equation (6), \( D \) and \( E \) are the electric permittivity, electric flux density (\( q/m^2 \)) and electric field intensity (\( V/m \)) respectively.

\[ D = \varepsilon E \quad \ldots \ldots (6) \]

Complex relative permittivity (\( \varepsilon_r \)) consists of two real and imaginary parts. The real part (\( \varepsilon \)) is known dielectric constant or charge storage and the imaginary part (\( \varepsilon' \)) is known as dielectric losses or loss factor (\( \varepsilon'' = \varepsilon' - j \varepsilon'' \)). The imaginary part indicates the ability of material in absorption of ratio frequency waves. So, high value of this parameter (loss factor) indicates materials with high absorption properties [22].

The loss tangent known as dielectric loss or tan \( \delta \), is described by equation (7). This parameter represents the ability of converting the stored energy in the material to heat energy. High loss factor (\( \varepsilon'' \)) and high loss tangent (tan\( \delta \)) show high ability of the materials in absorbing the radio waves [23].

\[ \tan \delta = \frac{\varepsilon''}{\varepsilon} = \sigma \varepsilon_0 \varepsilon_r \quad \ldots \ldots (7) \]

### 3. Results and Discussion

#### 3.1. X-ray diffraction

The patterns of X-ray diffraction (XRD) are carried out using (Shimadzu XRD-6000) with Cu K\( \alpha_1 \) radiation powder diffractometer. X-ray diffraction patterns of pure and reinforcement epoxy with MWCNTs are shown in Figure (1). The crystalline phase of CNT is represented by a strong 26.36° (002) reflection. The intensity of the (002) peak associate with CNT is stronger than other x-ray diffraction peaks due to presence of the more tangled nanotubes in the pattern of 6% CNT.

![Figure 1. X-ray patterns of pure and reinforcement epoxy](image)

\( \text{Intensity (a.u.)} \)

\( 2\theta \text{(degree)} \)

Pure Epoxy 2%CNT 4%CNT 6%CNT

(002)
3.2. Mechanical properties

- **Hardness**

In this study, it was found that the hardness increased with the increasing of the weight fraction of MWCNTs due to stacking and overlap, which decrease the movement of polymer molecules and increase the resistance of material to scratch, cut and becoming high resistance to plastic deformation. The hardness of materials depends on the kind of the forces according to the atoms in the material because the strong interlink between the phases of MWCNTs and epoxy increases the cohering of mixture which results in increasing the hardness. The result is shown in Figure (2).

![Figure 2. Variation of Hardness with CNT concentration](image)

3.3. Thermal properties

- **Thermal conductivity**

The epoxies are insulators and very weak thermal conductors, fillers and fibers must be introduced within epoxy in order to provide thermal transfer. The thermal conductivity of an epoxy will be determined by the percentage of filler loading, and the choice of filler, the process of thermal energy transfer depends on the structure nature of the material and there are two ways for the transition of thermal energy which are lattice waves and free electrons. Transmitted thermal energy in insulating materials is by phonons and this process occurs as a result of oscillation molecules as the move to the frequency as a result of neighboring molecules are linked together the bonds. Thermal conductivity coefficient of MWCNTs $K_{CNT} = 3000 \text{ W/m} \cdot \text{˚C}$. Figure (3) shows that the thermal conductivity coefficient increase with the increasing of weight fraction of MWCNTs.

The modification of epoxy matrix might cause decrease in the mean distance between neighboring chains, hence to increase elastic constant reason the intermolecular interaction, the result, thermal resistant is decreased, and, hence thermal conductivity is increased.

![Figure 3. Variation of thermal conductivity coefficient with CNT concentration](image)
3.4. Dielectrical properties

3.4.1 Electrical conductivity

Electrical conductivity was calculated from equation (4), the results are show in figure (4). In 'figure(4)' observed increasing of electrical conductivity with the increase of the frequency and we can observed in the same figure increased the electrical conductivity with increase the weight fraction of (CNT), specially at the higher electrical conductivity in the weight fraction (0.06) of (CNT)% . This increased could be attributed to increase segmental mobility of polymer chains near the filler particles [27].

![Electrical conductivity vs Frequency](image)

**Figure 4.** Variation of Electrical conductivity with Frequency for different concentration of MWCNT

Also the electrical conductivity increased with increasing weight fraction of MWCNTs, that could be describe to increase of ionic charge carriers which might be increased due to increasing filler content [28], this shown in this figure (4). The electrical conductivity increases with the increase of frequency we can explain this relation according to the resistivity where the effect of the frequency on resistivity of carbon nanotubes/epoxy. It is interesting that when the higher frequency the impedance of the sample decreases significantly indicating that the impedance of the sample is dominated by the capacitance of epoxy matrix [29]. Inasmuch, the conductivity equals reciprocal the resistivity, hence the conductivity increases with the increase of frequency.

3.4.2 Dielectric constant, Dielectric loss factor and Dielectric strength

'Figure (5)', represents the relation between dielectric constant and frequency, figure (6) represents the dielectric loss factor with frequency, from both figures observed same behavior, when the frequency is increasing the dielectric constant and dielectric loss factor decrease in the other hand the dielectric constant is increasing with increase weight fraction of CNTs, while the behavior of dielectric loss factor is opposite that. Several articles have studies the complex permittivity of different types of the carbon of nanotubes at low frequencies (1 MHz), studied showed an extremely dependence of the real and imaginary of relative permittivity on frequency and weight fraction of the (CNTs) in the polymer matrix. From the result both parts of relative permittivity at megahertz frequency were very high but at gigahertz frequency they showed extremely low values [30].
Figure 5. Variation of Dielectric Constant with Frequency for different concentration of MWCNT

In most of nanocomposite the imaginary part of permittivity is smaller than the real part [31]. Whereas, according to equation (7) the increase of the loss factor (imaginary part of permittivity $\varepsilon'$) of nanocomposites leads to materials with high absorption properties are not suitable for use in electromagnetic waves reflector structures [32].

Figure 6. Variation of Dielectric loss factor with Frequency for different concentration of MWCNT

'Figure (7)' represented the relation between the break down and weight fraction of CNTs%. The results showed in this figure the increase of the break down strength with the increase of the weight fraction and we can explain this relation. In most the polymers/CNTs composite because the agglomeration of filler particles at vicinity of favorable the bundle structure is formed [33]. In this respect, it becomes apparent that filler EP/CNT composites contain few CNT weight content are dispersed as isolated agglomerates in the epoxy rather than network of linked particles.
Figure 7. Variation of Break Down with CNT concentration

Conclusions
In this study, MWCNTs used as a filler in epoxy resin. Four samples with different weight fractions (0, 2, 4, 6) wt% of MWCNTs were made. The results showed the epoxy composites filled with a few weight fraction CNTs give better mechanical properties than pure epoxy, also give better thermal and electrical properties, because the (CNTs) have a good mechanical, thermal and electrical properties.

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