Thermal Properties of Carbon Nano Tubes Reinforced Epoxy Resin Nano Composites

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The effects of reinforcement of Carbon Nano Tubes (CNTs) on thermal properties of epoxy resin based composites was studied. Epoxy resin was reinforced with CNTs type multi-walls (MWCNTs) to prepare nanocomposites with different volume fractions. Hand lay - up technique was used to prepare the nanocomposites.

Thermal tests included thermal conductivity measurement by using Lees disc and erosion rate test by using oxy-acetylene flame technique.
Thermal conductivity is calculated theoretically via simulation operation by using Nielsen model. Simulation programs of heat transfer in three dimensions for erosion test of epoxy nanocomposites specimens were carried out using finite difference method.

Thermal conductivity results show that the values increase progressively by increasing of volume fraction of \((\text{MWCNTs})\). Erosion rate behaves inversely, where it drops at high volume fractions of \((\text{MWCNTs})\) because of there help to transfer heat flow more than epoxy was alone. Ablation test results of experimental work and theoretical simulation were compared to understand the nature of adhesion mechanism between components of nanocomposite material. This comparison included the variation of the above measured and calculated properties in different volume fractions of the \((\text{MWCNTs})\).

**INTRODUCTION**

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 reach 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 change [1]. A nano composite, like a traditional composite has two parts, filler and the matrix. A traditional composite typically uses a fiber such as carbon fiber or fiber glass as the filler, in a nano composite the filler is a nano material. Nano material ranges in size from 1-100 nm [2-3].

The classes of nanocomposites that will be used in this work are the carbon nano tubes 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 [4]. Nano tubes composed of a single layer of graphene are called single-wall carbon nanotubes (SWNTs), where as those that have concentric multiple layers of graphene are called multi-wall carbon nano tubes (MWNTs). Typically SWNTs have diameters of order 1 nm, and lengths of order 100 nm to several μm. MWNTs 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) [5].
The high thermal conductivity of single wall carbon nanotubes (SWNT’s) makes them ideal for thermal management applications. To illustrate, in magnetic field aligned films of SWNT’s, a value of 250 W/m-K has been measured at room temperature[6]. For single tubes, theoretical calculations of the thermal conductivity give even higher values of about 10,000 W/m-K[7]. The polymer matrix is epoxy resin, a term which is often applied to both the prepolymer and to the cured resins, is a type of polymer which contain reactive epoxy groups, in its prepolymer[8]. Epoxy is a thermosets polymer that forms a strong gridley cross linked network of polymer chains. Epoxy has been widely used in commercial applications with fiber glass, graphite, and aromatic fibers. Applications include: aircraft components, pressure vessels, rocket motor cases, and car bodies [9]. 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 recent years be done measure the thermal conductivity by using different methods for two type of carbon nano tubes by H. Zhong and Jennifer R. Lukes[12], M. Fujii et al[13], Moisala and A.[14], Jonathan O’Reilly[15] and Ana L. et al [16], the researchers found through that these properties changed with measurement method.

Applications of polymer nanocomposites depend on: matrix, nanofillers, etc., 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 [17].

The aim of this work is to determine the effect of volume fraction of carbon nanotubes (equivalent to volume percentage 0.1%, 0.2%, 0.3% and 0.4%) on the thermal conductivity, the ablation time and rate of epoxy-matrix nanocomposites. Calculate the thermal conductivity of composites by
using Nielsen models. Simulate the ablation test of these composites by using finite difference method to predict ablation time as well as ablation rate. Comparing the results of experimental work and theoretical simulation to assist the results of both of these methods to produce good thermal insulators.

THEORETICAL APPROACH

Thermal conduction is the phenomenon by which heat is transported from high-to-low temperature regions of a substance. The property that characterizes the ability of a material to transfer heat is the thermal conductivity. It is best defined in terms of the expression [18]:

\[ Q = -\lambda \frac{dT}{dx} \]  

Where \( Q \) denotes the heat flux, or heat flow, per unit time per unit area (area being taken as that perpendicular to the flow direction), \( \lambda \) is the thermal conductivity coefficient, and \( \frac{dT}{dx} \) is the temperature gradient through the conductive medium. Equation (1) is valid only for steady-state heat flow, that is, for situations in which the heat fluxes do not change with time. In addition, the minus sign in the expression indicates that the direction of heat flow is from hot to cold, or down the temperature gradient.

Heat is transported in material by both lattice vibration waves (phonons) and free electrons. A thermal conductivity is associated with each of these mechanisms, and the total conductivity is the sum of the two contributions.

Non-metallic materials transfer heat by lattice vibrations so that there is no net motion of the media as the energy propagates through [19]. To measure the thermal conductivity methods are used depending on the nature of the substance under investigation. The poor conductor measurement by Lee's disc method.

Lee’s disc has determined the conductivity of small thin disc of material by a method, which is applicable over a wide range of temperatures [20]. The arrangement is shown in Fig. 2. The substance S was contained between two copper discs B and A, and the heater between B and a third copper disc C. The temperatures of all the copper discs were measured by thermometer.

When the discs had been assembled they were varnished to give them the same emissivity, and the whole apparatus was suspended in an enclosure of constant temperature.

It can be obtained \( Q \) in terms of \( IV \), since the total heat supplied must be equal to that given up by the various surfaces:

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\[ Q = \frac{IV}{\pi r^2(T_c + T_A) + 2\pi r \left[ d_A T_A + \frac{d_A}{2}(T_A + T_B) + d_B T_B + d_C T_C \right]} \] ...........(2)

So, thermal conductivity coefficient becomes:
\[ \lambda = \frac{Q d_A}{T_B - T_A} \left[ T_A + 2T_A\frac{d_A}{r} \left( \frac{d_A}{4} + d_B T_B \right) \right] \] ...........(3)

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**Fig.-2: Schematic arrangement diagram of Lee's disc method [20].**

The thermal conductivity however depends on the shape, orientation and distribution of particles or fibers in the matrix and falls between an upper bound is given by:
\[ \lambda_c = \lambda_m V_m + \lambda_d V_d \] ...........(4)

and a lower bound is given by
\[ \lambda_c = \frac{\lambda_m \lambda_d}{V_m \lambda_d + V_d \lambda_m} \] ...........(5)

The upper bound represents additives that are totally aligned in the direction of the measured thermal conductivity and have the length of the specimen while the lower bound represents additives that are totally aligned in the opposite direction of the measured thermal conductivity and have the length of the specimen. Different models were suggested to predict the exact thermal conductivity of a composite [21], same of these models is Nielsen Model which was used in this study [22]:
\[ \lambda = \frac{(1 + AB \phi)}{(1 - B \psi / \phi)} \] ...........(6)

Where:
\[ B = \frac{\lambda_f}{\lambda_m - 1} \]
\[ \psi = 1 + \left[ (1 - \phi m^2) / \phi m^2 \right] \phi \]
\[ \phi : \text{Volume fraction of additives}, \ \phi m: \text{maximum volume fraction}, \ A: \text{geometry of additives.} \]
Ablation phenomena is defined as; the degradation, decomposition, and erosion of a material caused by high temperature, pressure, time, percent oxidizing species, and velocity of gas flow.

Also, ablative plastic, is defined as; a material that absorb heat (with a low material loss and char rate) through a decomposition process (pyrolysis) that takes place at or near the surface exposed to the heat [23].

In the ablation process the high heat fluxes are dissipated by the material through a series of endothermic processes that finally lead to the loss and the consumption of the material itself. The working process of an ablative heat shield can be briefly summarized as follows: the ablative material keeps the surface temperature within a certain range, and as a consequence an increase of the heat flux will not cause a consistent temperature raise, but will cause an increase of the surface “recession rate”. Therefore, important parameters in the choice of a suitable ablator are the ablation temperature (the temperature at which the material degradation begins) and the density [24]. The most significant properties of an ablative material are specific heat, thermal conductivity, and density. In particular, the density is characterized by a lower limit dictated by the necessity of a low recession rate, and an upper limit dictated by the light weight requirements of all the aerospace parts. Furthermore, the degradation of an ablative material has to be an endothermic reaction, yielding a fair amount of gases. Such different properties are barely attained by a single material. Ablative materials have matrix and fillers, each of them contributing to different properties. In general, the degradation reaction affects mainly the matrix. In fact, most of the matrices of ablative materials are made out of polymers, taking advantage of the highly endothermic nature of polymer degradation in non-oxidative atmospheres, and of their many good properties such as low density, low thermal conductivity, high specific heat, in addition to excellent mechanical properties. In summary, the polymeric constituent in an ablator basically has to accomplish two functions, first it degrades thereby absorbing energy, and second it serves as a binder for the other components. The most commonly used resins are phenol formaldehyde, epoxies, silicones, and polytetrafluoroethylene ablation [24].

The ablation rate for ablative materials was calculated by dividing the original thickness of the specimen by the time to burn through as follows [25]:

\[ A_r = \frac{d_s}{b_t} \] ...............................(7)

Where: \( A_r \) : ablation rate, \( d_s \) : Thickness of Specimen, and \( b_t \) : burn through time, while the insulation index was calculated by using the equation below:

\[ I_r = \frac{b_t}{d_s} \] ...............................(8)
Ablative test was measured by three type’s technique: (i) Static Rocket test motor experiment, (ii) Laser ablation test and, (iii) flame test [25], which was used in this work.

**SIMULATIO APPROACH**

Partial differential equations are encountered in many branches of physics and engineering in which more than one dimension exist in the differential equations. Heat transfer equation is example of partial differential equations. The equation is transformed to ordinary differential equations when it becomes one dimensional only. Numerical solution of partial differential equation is an important class of solution since many of the above equations cannot be solved analytically. Scientists prefer finite difference method (FDM) since basic scientific experiments do not contain difficult geometries [26]. Finite difference method relies on using difference approximations to be substituted in the partial differential equations. Heat transfer equation in Cartesian coordinate is given by[27]:

\[
\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + Q \tag{9}
\]

Where \( T \) is the temperature, \( t \) is the time, \( x, y, z \) are the rectangular coordinates, \( \lambda \) is the thermal conductivity coefficient, \( \rho \) is the density, \( c \) is the specific heat, and \( Q \) is the latent heat of phase transformation. The finite difference equation of heat transfer using explicit method [28] is:

\[
T(x, y, z, t + \Delta t) = T(x, y, z, t) + \frac{\Delta t}{\rho c} \left( T(x + \Delta x, y, z, t) + T(x - \Delta x, y, z, t) - 2T(x, y, z, t) \right) \frac{\Delta x^2}{\Delta t^2} + \frac{T(x, y + \Delta y, z, t) + T(x, y - \Delta y, z, t) - 2T(x, y, z, t)}{\Delta y^2} + \frac{T(x, y, z + \Delta z, t) + T(x, y, z - \Delta z, t) - 2T(x, y, z, t)}{\Delta z^2} + \dot{Q} \Delta t \tag{10}
\]

Heat can be also transferred by convection or radiation that occurs generally at the boundary of the simulated piece. These methods can be used to fix the boundary problem and can be described by the following equations [29]:

\[
Q = hA(T_w - T_e) \tag{11}
\]

For convection heat transfer and:

\[
Q = F_e F_G \sigma A(T_1^4 - T_2^4) \tag{12}
\]

For radiation heat transfer where: \( h \) is the convection heat transfer coefficient, \( Q \) is the amount of energy transferred per unit time, \( A \) is the surface area, \( T_w \) is the surface temperature, \( T_e \) is the temperature of the fluid, \( F_e \) is the emissivity function, \( F_G \) is the geometric function, \( \sigma \) is the Stefan-Boltzmann constant, \( T_1 \) is the temperature of the radiating body and \( T_2 \) is the temperature of the irradiating body.
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In this study a simulation of the ablation of three-dimensional square insulators according to ASTM E285 - 80 standards is performed. The thermal properties of the insulator are known. This insulator is subjected to an oxy-acetylene flame of 2773 – 3273 K. The simulation also supposes a certain temperature at which the insulator is removed by gravity or the mechanical effect of the flame [30].

MATERIALS AND METHODS

The experimental work is divided into three parts. The first part includes specimen preparation for five groups (pure epoxy, 0.1 vol. %, 0.2 vol. %, 0.3 vol. %, and 0.4 vol. %). The second part includes two empirical tests: the first set of tests includes the thermal conductivity coefficient measurement using Lee's disc method; the second set of tests includes ablative test using flame technique. The third part includes a computer simulation for ablative test using finite difference method.

The polymer (Epoxy Resin), designated (EPO- 105) in the form of liquid used in this work. The required (EPO- 105) of 300 gm was mixed with 150 gm Hardener. Hardener was mixed thoroughly until a homogenous state of the mixture was obtained. Added were used as reinforcing materials for epoxy resin composites, these added are carbon nanotubes type.

Preparation of epoxy resin composites specimens included mixtures preparation by hand mixing method. Mixtures preparation includes the preparation of epoxy specimens; carbon nano tubes composites specimens by using hand lay-up method, Specimens preparation according to standard methods for thermal conductivity test, Lee Disc B.S-Griffin-George LTD and Ablative test, ASTM E- 285-80[30, 31].

Thermal conductivity coefficient of specimens was measured by using Lee's disc method principle [20]. Thermal conductivity was then calculated according to equation (3). The average of three measurements was taken for each specimen to minimize the possible errors. Thermal conductivity was calculated theoretically in three directions using Nielsen Model [21].

The ablative test was carried out by using flame test method. This test was done according to ASTM - E – 285 – 80 [30]. By this test, ablation rate \((A_r)\) was determined. The ablation rate for each specimen was calculated using the equation (7). The average of the three measurements was taken for each specimen to reduce error.

Simulation programs of heat transfer in three dimensions of ablative test for five groups of epoxy nano composites were carried out using finite difference method. The program was written in FORTRAN90 language using a computer type Pentum4. The program was starting to solve heat conduction equation in three directions (10) and equations (11) and (12) for the boundaries.
RESULTS AND DISCUSSION

Thermal properties results were shown in Figures 3, 4, 5 and 6. Influence of CNTs vol. % (empirical and simulation) on thermal conductivity of epoxy matrix was shown in Figure 3. Reinforcement by CNTs leads to increase thermal conductivity values with the increasing vol. %. This increment was depending on direction of CNTs with respect to heat flux and its type, which was MWCNTs. Generally, direction of CNTs (parallel, perpendicular, and random) and interface between the matrix and CNTs was clearly observed on these values of thermal conductivity. Influence of interface between the matrix and the reinforcement materials was clearly observed on thermal conductivity. Figure (3) shows the influence of (MWCNTs) vol. % and the direction of (MWCNTs) by simulation; theoretical parallel direction (Theo. PAR dir.), theoretical perpendicular direction (Theo. PER dir.), and theoretical random direction (Theo. RAN dir.), on the thermal conductivity of epoxy matrix and its comparison experimental random direction results. From the Figures it can be seen, that the values of experimental results (EXP. RAN. dir.) were located between parallel direction and random direction of (MWCNTs) with respect to heat flow direction. That can be explained as; most of (MWCNTs) were aligned in parallel direction of heat flow supplied which is led to high value of thermal conductivity. Interfaces in nanotube/polymer composites as well as concentration of defects in the multi-walled carbon nanotubes are known to affect the thermal conductivity. The influence of the nanoscale structure of the tube, the structure of the nanocomposite, and properties of the nanotube/matrix interface will affect the bulk thermal conductivity.

Figure 4 shows a comparison of influence of CNTs volume fraction on the erosion rate of epoxy matrix of simulation operation (SIMU.) with that of the experimental (EXP.) results of oxy-acetylene torch. It can be seen from the Figure that the erosion rate of experimental values is lower than simulation values. Figure 4 can be explained by assistant of Figures 5 and 6 which is shown the temperature distribution after (13.40 and 23.37) seconds when CNTs of 0.1.% and 0.4 % volume fraction is punctured by simulation operation of oxy-acetylene torch respectively. In there Fig.s, it can be seen three temperature distribution regions (0 – 1000, 1000 – 2000, and 2000 – 3000) 0C. Figures of simulation (5 and 6) can be explained by using ablation mechanism; The good ablative characteristics of the resins under study may also be due to the fact that reinforcing MWCNTs may act as a heat dissipater or provide a much better network for transferring heat in a random manner. This may divert the heat path away from the targeted direction much more than the uncomposited resin would do. Hence the MWCNT's network will actually act as an additional heat barrier. At the same time it will act as a mechanical stabilizer to the charred layers, which
protect this porous layer. Thus, will hinder the erosion process and in turn enhance the insulation process by maintaining the thickness of these layers. Moreover, in the ablation process the high heat fluxes are dissipated by the material through a series of endothermic processes that finally lead to the loss and the consumption of the material itself. The working process of an ablative heat shield can be briefly summarized as follows: the ablative material keeps the surface temperature within a certain range, and as a consequence an increase of the heat flux will not cause a consistent temperature raise, but will cause an increase of the surface “recession rate”. During ablation, some pyrolytic deposition of carbon from the CH$_4$ or other gases in the outer portions of the char can contribute to the strength and resistance to mechanical removal from the flow field. The char is a thermal insulation; the interior is cooled by volatile material percolating through it from the decomposing polymer. During percolation, the volatile materials are heated to very high temperatures with decomposition to low molecular weight species, which are injected into the boundary layer of gases. This mass injection creates a blocking action, which reduces the heat transfer to the material. Thus, a char-forming resin acts as a self-regulating ablation radiator, providing thermal protection through transpiration cooling and insulation. Ablation of the char occurs by sublimation of carbon and oxidation in the boundary layer with concomitant vaporization. In epoxy resins, pyrolysis reaction is found to occur in three general processes: (1) low temperature outgassing of free epoxy present in the resin material, (2) formation of water from post-cure reaction at 423 K – 673 K, and (3) thermal fragmentation of the polymer structure above 803K, to yield lower molecular weight species, which evolve, with hydrogen gas, as the primary product (in the absence of oxygen) at 973 K, and above. Epoxy compounds provide high char yield, low oxygen to minimize CO and CO$_2$ formation, and many carbon – hydrogen bonds, which provide the evolution of H$_2$ and CH$_4$ for transpiration cooling. The epoxy resin has good forming characteristics; good adherence to the CNTs, and strength in the composite, and it form a char that adheres well to the CNTs reinforcements.

**We can conclude**

1. Reinforcing of epoxy resin with CNTs has Improved the ablation and thermal properties of nanocomposites in different volume percent, depending on distribution of CNTs.
2. The thermal conductivity increased linearly with nanotube concentration to a maximum increase of 40% at 0.4 vol.% carbon nanotubes.
3. Results of ablation have been shown in CNTs had better than results of macroscopic carbon fibers.
4. From simulation results it can be seen that there was high influence of CNTs direction with respect to thermal flux, on thermal conductivity values.

5. Simulation results of ablation show that the best values of erosion are for 0.4 vol. % groups with respect to CNTs nanocomposites, which agree with experimental results.

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Fig. 3: Influence of CNTs vol% and direction on the thermal conductivity of epoxy of simulation results and its comparison experimental random direction results.

![Graph showing thermal conductivity vs CNTs vol% and direction](image)

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Fig. 4: Comparison between influence of CNTs volume fraction on the erosion rate of epoxy by simulation operation and the experimental results.

![Graph showing ablation rate vs CNTs vol%](image)
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Fig. -5: Temperature distribution after 13.40 seconds when 0.4 MWCNTs vol.% of epoxy is Punctured by simulation operation of oxy-actylene torch temperature

Fig. -6: Temperature distribution after 23.37 seconds when 0.4 MWCNTs vol.% of epoxy is Punctured by simulation operation of oxy-actylene torch temperature
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