Ablation characteristics of carbon nanotubes reinforced novolac resin nanocomposites: Experimental and simulation approach

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Abstract

Ablation rate and thermal conductivity for phenol- formaldehyde type novolac resin reinforced with single walled carbon nanotubes (SWCNTs) have been studied via experimental and simulation of Oxy – acetylene flame and Lee's disc techniques respectively. Simulation programs of heat transfer in three dimensions of ablative test for novolac and novolac nanocomposites specimens were carried out using finite difference method (FDM). Theoretical thermal conductivity was calculated according to microstructures model. Hot-press technique was used to prepare the nanocomposites as well as novolac specimens using flash molds at standard conditions. Thermal conductivity results show, that the values increase progressively by succession of volume fraction of SWCNTs. Ablation rate behaves inversely, where it drops at high volume fraction of SWCNTs. The thermal conductivity – ablation rate relationship, displays two mechanisms, the first, associated with the starting of ablation test, is recognized by ideal distribution of SWCNTs, which leads to good thermal dispersion due to the formation of segregated network of thermal conducting paths. The second mechanism is associated with in- run ablation test recognized by shearing cracks appearance, which leads to earlier char production mechanism. Simulation thermal conductivity results, , and when it compared with the experimental results, it observed, that the experimental results, were located between the parallel and random direction simulation values of SWCNTs, which is evidenced that the additives arrangement closed to parallel direction more than random or perpendicular direction with respect to heat flux direction.

Keywords: Ablation, simulation, nanocomposites, and carbon nanotubes.

Introduction

Nanotechnology is the science of the extremely tiny. It involves the study and use of materials on an unimaginably small scale. Nano refers to a nanometre (nm). One nanometre is a millionth of a millimeter or about one eighty thousandth the width of a human hair. Nanotechnology describes many diverse technologies and tools, which don't always appear to have much in common. Therefore it is better to talk about nanotechnologies, in the plural. One thing that all nanotechnologies share is the tiny dimensions that they operate on. They exploit the fact that, at this scale, materials can behave very differently from when they are in larger form. Nanomaterials can be stronger or lighter, or conduct / insulate heat or electricity in a different way. Carbon nanotubes, long, thin cylinders of carbon, were discovered in 1991 by S. Iijima [1]. They can be thought of as a sheet of graphite (a hexagonal lattice of carbon) rolled into a cylinder. These intriguing structures have sparked much excitement in the recent years and a large amount of research has been dedicated to their understanding. Currently, the physical properties are still being discovered and disputed. To make things more interesting, besides having a single cylindrical wall (SWCNTs), nanotubes can have multiple walls (MWCNTs)--cylinders inside the other cylinders [2].

Nanomaterials are materials containing a controlled morphology of nanoscale dimensions. The simplest example is a powder consisting of particles with diameters between 1 and 100 nm (nanoparticles). The transition from micro to nano particles offers several advantages. First, it implies an enormous increase in surface area. Bulk properties become governed by surface properties. For instance, the material can be made light absorbing by coating the particles with a dye. Second, the particle size reduction induces both mechanical advantages and quantum effects [3]. Nanotechnology is likely to have a profound impact on our economy and society in the early 21st century; it is widely felt that nanotechnology may lead to the next industrial revolution [4].

Theoretical Approach

The recent advances of nanotechnologies in the past decades have resulted in the burst of promising synthesis, processing and characterization technologies, which enables the routine production of a variety of nanomaterials with highly controlled structures and related properties [5]. Many properties of the nanoscale materials have been well studied, including the optical, electrical, magnetic and mechanical properties. However, the thermal properties of nanomaterials have only seen slower progresses. This is partially due to the difficulties of experimentally measuring and controlling the thermal transport in nano scale dimensions. Moreover, the theoretical simulations and analysis of thermal transport in nanostructures are still in infancy [6]. More importantly, as the dimensions go down into nanoscale, the availability of the definition of temperature is in question. In non-metallic material system, the thermal energy is mainly carried by phonons, which have a wide variation in frequency and the mean free paths (mfp). For macroscopic systems, the dimension is large enough to define a local temperature in each region within the materials and this local temperature will vary from region to region, so that one can study the thermal transport properties of the materials based on certain temperature distributions of the materials. But for nanomaterial systems, the dimensions may be too small to define a local temperature [7]. Recent advances in experiments have showed that certain nanomaterials have extraordinarily thermal properties compared to their macroscopic counterparts. As mentioned above, as the dimension goes down to nano scales, the size of the nanomaterials is comparable to the wavelength and the mean free path of the phonons, so that the phonon transport within the materials will be changed significantly due the phonon confinement and quantization of phonon transport, resulting in modified thermal properties [8]. The special structure of nanomaterials also affects the thermal properties. For example, because of it tubular structures of carbon nanotubes, they have extreme high thermal conductivity in axial directions, leaving high anisotropy in the heat transport in the materials [9]. The interfaces are also very important factor for determine the thermal properties of nanomaterials. As a result, the nanomaterials structures with high interfaces densities would reduce the thermal conductivity of the materials [10]. The rigidity of the nanotubes, combined with virtual absence of atomic defects or coupling to soft phonon modes of the embedding medium, should make isolated nanotubes very good candidates for efficient thermal conductors [11]. The high thermal conductivity of carbon nanotubes were first proved by some theoretical calculations [12]. Savas Berber et al combined the equilibrium and nonequilibrium molecular dynamics simulations with Tersoff potential to determine the thermal conductivity of carbon nanotubes and its dependence on temperature [13].

Thermal conductivity, *K*, of a solid along a particular direction, taken here as the *z* axis, is related to the heat flowing down a long rod with a temperature gradient *dT*/*dz* by:

$$\frac{1}{A}\frac{dQ}{dt} = -K\frac{dT}{dz} \qquad (1)$$

where *dQ* is the energy transmitted across the area *A* in the time interval *dt*. In solids where the phonon contribution to the heat conductance dominates, l is proportional to *C*v*l*, the product of the heat capacity per unit volume *C*, the speed of sound v, and the phonon mean free path *l*.

Thermal conductivity of multiphase nano-structures follows mixture rules. However, the weighting procedures, which are necessary, vary with the shape and distribution of the phases [15].

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 [16]. Among the common plastics, the novolac resin gives the highest yield of carbon during thermal pyrolysis, and they have been widely used as a surface charring ablative materials. Since a char is relatively weak, and is removed mechanically by high shear forces associated with the stream of gases during re-entry, nanofibers, nanosilicon dioxide, nanorefractory oxides, nanomineral asbestos, or even nanoglass have been added to assist the char retention [16]. The ablation rate for ablative nano-composites was calculated by dividing the original thickness of the specimen by the time to burn through as follows [17]:

$$A_r = \frac{d_s}{b_t} \qquad (2)$$

where: A_r : ablation rate, m/s, d_s : thickness of specimen, m, and b_t : burn through time, s.

Simulation Approach

The theoretical simulation of ablative test of a thermal insulator is considered an important process since it reduces many efforts, time and raw materials that are used in trail and error of the experimental procedure. This simulation is performed by using the values of thermal parameters of the specific material. 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 [18]. Heat transfer equation in Cartesian coordinate is given by:

$$\frac{\partial T}{\partial t} = \frac{K}{^{\circ}c}\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) + Q \text{..................(3)}$$

Where T is the temperature, t is the time, x, y, z is the rectangular coordinates, K is the thermal conductivity coefficient, ρ is the density, c is the specific heat, and Q is the latent heat of phase transformation [18].

Experimental Approach

Phenol – formaldehyde resin material (novolac type) designated by (PFN) in form of solid was used as a purity (matrix) in preparation of nanocomposite materials. Carbon nanotubes (30 nm in diameter) with volume fractions (0.1%, 0.2%, 0.3%, and 0.4%) were used as reinforcing materials for novolac resin nanocomposites manufactured by Fluka Chemist Foundry (F.C.F.)**.** Preparation of novolac nanocomposites specimens included two steps; mixtures preparation by blower mixing method and Hot-press step of mixtures. Novolac in form of solid was solved using ethanol to obtain a suitable matrix. Then carbon nanotubes were impregnated in matrix by blower technique, followed by drying the mixture in air using dispersion method on a dry plate for three hours. The mixture was pre- cured using an oven at (353 K) for three hours. Hot–press technique was used in this work to prepare the nanocomposites specimens of PFN matrix, using flash mold according to standard conditions.

Thermal conductivity coefficient of specimens was measured by using Lee's disc method principle. The ablative test was carried out by using Flame test method. This test was done according to ASTM - E – 285 – 80 [19] .By this test, ablation rate (A_r) and insulation index (I_T) were determined . Experimental set up consists of a welding torch, equipped with mix of oxygen–acetylene gases. A steel shutter fixed between the torch and the specimen, which was controlled on starting and terminating of the test. Thermocouple type (K) was mounted against the backside of the specimen and the leads are connected to a digital temperature recorder type (CRL – 405, control and read out LTD). A digital stopwatch was used to record the burning time setup between the temperature recorder and the shutter. According to standard test, the torch was ignited and the gas flow rate was adjusted until the flame was stabilized to give a blue conical shape with height of (30 mm). The torch flame was allowed to contact the specimen at an angle of 90° using a controlling shutter, subjected between the torch and the specimen, and the distance between the torch tip and the specimen was kept (20 mm) for all measurements. The burning (hollow) time of the specimen was measured using a controlling digit stop watch triggered by temperature recorder contacted with the back face of the specimen across thermocouple type – K. The ablation rate for each specimen was calculated using equation (2). The average of three measurements was taken for each specimen to reduce error.

Resulrs And Discussion

Influence of single walled carbon nanotubes (SWCNTs) vol. % on the experimental thermal conductivity as well as theoretical calculations of novolac matrix were shown in Fig. (1). Generally, reinforcement by single walled carbon nanotubes (SWCNTs) leads to increase thermal conductivity values with the increasing volume fraction. This increment was differentiated in novolac nanocomposites depending on capability of single walled carbon nanotubes (SWCNTs) thermal conductance. According to Fig. (1), thermal conductivity values were increased gradually with respect to increasing of volume fraction of single walled carbon nanotubes (SWCNTs).

Influence of interface between the matrix and the reinforcement materials was clearly observed on thermal conductivity. In polymeric materials, heat was transferred as elastic wave, and since an interface was existed, that led to restraint of transfer's motion of these waves. Transfer of thermal energy as elastic waves, are still complex process and difficult, since there is disconnected in structure and transference from structure to another one, i.e., the wave loss a part of its energy at interface region between the matrix and reinforcement material. Figure (1) show the influence of single walled carbon nanotubes (SWCNTs) vol. % and the direction of single walled carbon nanotubes (SWCNTs) on the thermal conductivity of novolac matrix and its comparison experimental random direction results. From the Figures it can be seen, that the values of experimental results were located between parallel direction and random direction of single walled carbon nanotubes (SWCNTs) with respect to heat flow direction. That can be explained as; most of single walled carbon nanotubes (SWCNTs) were aligned in parallel direction of heat flow supplied which is led to high value of thermal conductivity.

Fig. (2) shows the influence of single walled carbon nanotubes (SWCNTs) vol.% on the experimental ablation rate as well as simulation calculations of novolac matrix for oxy-acetylene torch heat source . Figure (2) has shown the influence of volume fraction of single walled carbon nanotubes (SWCNTs) on ablation rate and it can be seen from the Figure that, the ablation rate for all novolac nanocomposites was decreased when volume fraction increased. But with different volume fraction, dependence on additives type (single or multi wall) and interface composed between the matrix and additives materials.

Fig. (3) and (4) show the temperature distribution after 179 seconds when 0.1 SWCNTs vol.% and after 312 seconds when 0.4 SWCNTs vol.% of novolac matrix was punctured respectively, and that return to the thermal, physical, and chemical properties of the single walled carbon nanotubes. Ablation phenomena can be explained by using ablation mechanism; when a thermal flux was applied on the surface of nanocomposite material, they first act as heat sinks: as heating progresses, the outer layer of polymer may become viscous and then begins to degrade, producing a foaming char. The char is a thermal insulation; the interior is cooled by volatile material percolating through 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. The rate of ablation slows as the rate of char surface recession equals or exceeds the recession rate of the interface between the char and virgin polymer. Since this part provides the essential gas for transpiration cooling of the char, the decomposition products are important. With the continuous of thermal decomposition reactions the pyrolysis gases were produced, which were exceeded inside the constitute char structure, which was characterized with low porosity and permittivity. With the rising of temperature, the thermal decomposition operation was continued; with continuous production of these gases, which leads to raise the internal pressure. This, internal pressure was continued, with increment of temperature, till reaching the maximum value. At that, thermo-chemical expansion will take place, which is caused, the increment of porosity and permittivity of the nanocomposite material. By that, the exceed gases could pass through the nanocomposite material, and in general, this current of flow gases was associated, a high shear forces, caused removal of carbonaceous char, so, the progress gases in carbonize zone direction, will be worked to inhalation the thermal energy, which is reached the pyrolyzed zone, because of, transferring of heat by convection. If the pyrolysis and thermal expansion reactions were continued, the porosity and permittivity well were increased, and that leads to increment of flow rate of gases and decrease of internal pressure. At that, sudden high shrinkage well be taken to the material, which is returned to the fact, that the elastic recovery was taken.

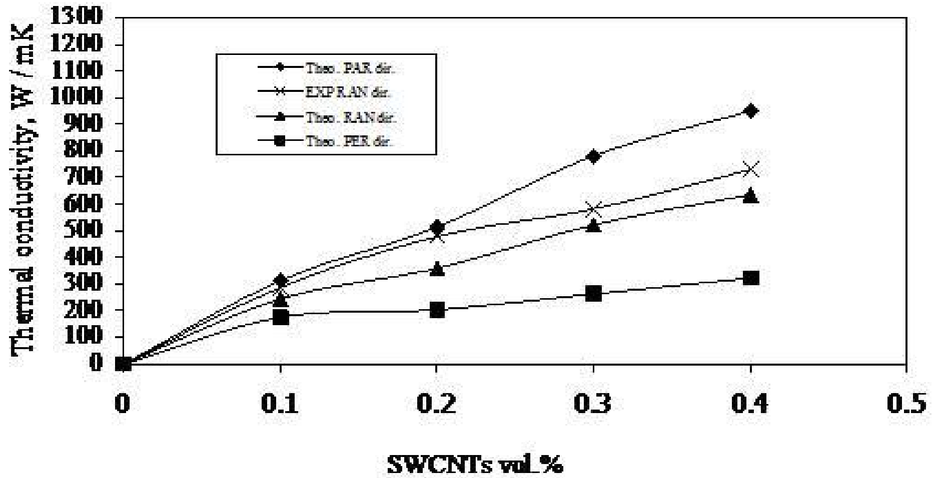

Fig. 1: Influence of SWCNTs vol% and direction on the thermal conductivity of PFN of theoretical results and its comparison experimental random direction results.

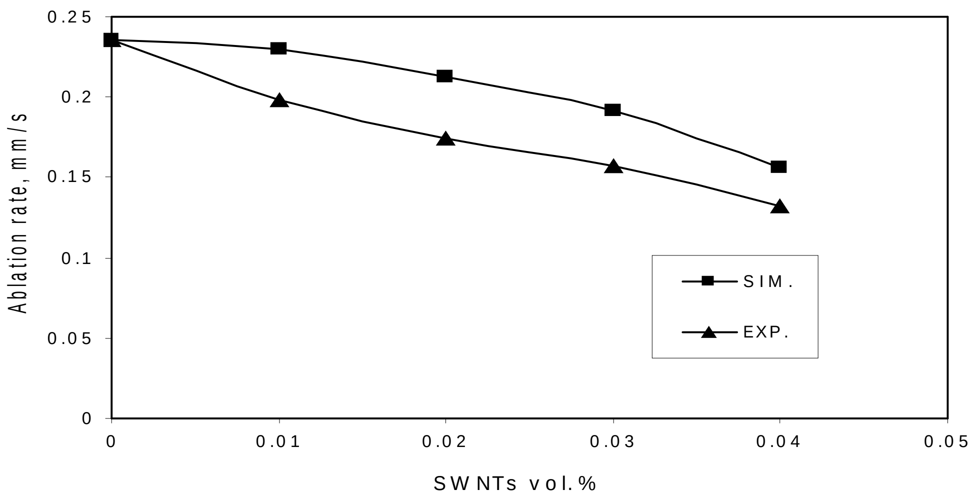

Fig. 2 : Influence of SWNTs vol.% on the ablation rate of PFN for oxy - acetylene torch temperature .

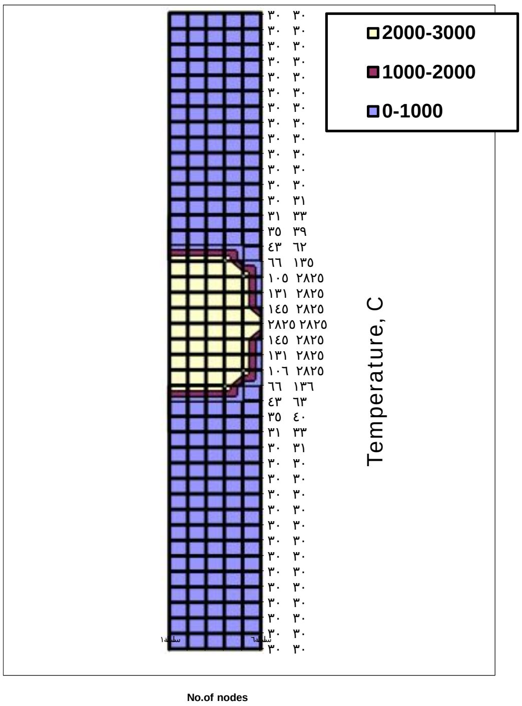

Fig. 3: Temperature distribution after 179 seconds when 0.01 SWCNTs vol.% of PFN is punctured by simulation operation of oxy-acetylene torch temperature.

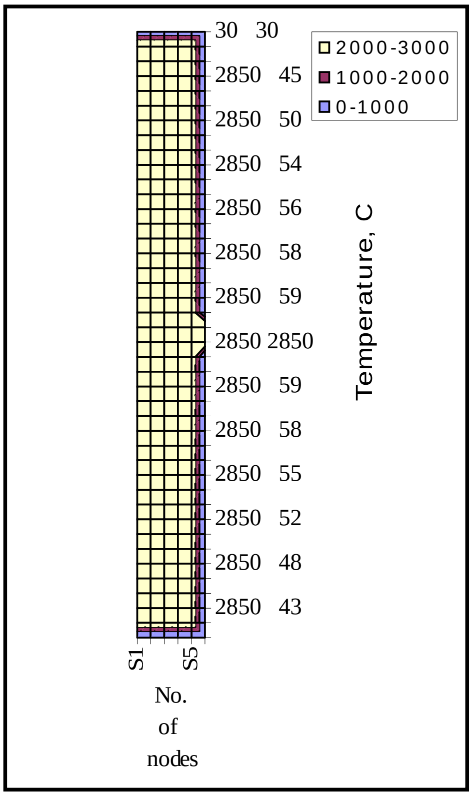

Fig. 4: Temperature distribution after 312 secondes when 0.04 SWCNTs Vol. % of PFN is punctured by simulation operation of oxy-acetylene torch temperature.

Conclusions

From this study, the following remarkable points can be concluded:

1- In thermal conductivity results (experimental and theoretical), 0.4 vol.% specimens had given high values of thermal conductivity.

2- Experimental results of ablation have been shown, that 0.4 vol.% specimens had better results.

3- Results of thermal transfer indicted, that the increment of thermal conductivity and decrement of ablation rate lead to better thermal distribution, which leads to increment of thermal insulation efficiency for composites.

4- Nanocomposites were produced have high ablation resistance at temperature exceed 2773K; because of earlier char operation has been taken place.

5- According to the theoretical results, thermal conductivity has obtained three sets of values; represent arrangement direction of carbon nanotubes with respect to heat flux. In addition, it was concluded that the experimental results of thermal conductivity were fallen in between the parallel direction and random direction values, evidence to the nearest arrangement of additive to the parallel direction more than randomly direction with respect to heat fluxes.

6- Simulation results of ablation shown, that the best values of ablation were for 0.4 vol.% specimens which coincides with experimental results.

Nomenclature

A_r: ablation rate, m/s

d_s: thickness of ablation specimen, m

K: thermal conductivity coefficient, W/mK

Q: latent heat of phase transformation, W/m^{2}K

F.C.F.: Fluka Chemist Foundry

b_t: burn through time, s

C: specific heat, J/Kg ^{0}C

K: Kelvin

T: temperature, K

t: time, s

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