

THERMAL PROCESSES OF ABLATION CHARACTERISTICS OF SWCNTs / (PP – HDPE) BLEND NANOCOMPOSITES: EMPIRICAL AND SIMULATION INVESTIGATIONS

FAIZA M. SALIM

Department of Physics, Opened Education College, Ministry of Education, Iraq

ABSTRACT

Effect of reinforcement of single wall carbon nanotubes (SWCNTs) on thermal processes characteristics of polypropylene (PP) – high density polyethylene (HDPE) blend based nanocomposites in terms of empirical and simulation approaches were investigated. Extrusion and hot - press techniques were used after pre auxiliary procedures to prepare the blend and nanocomposites specimens. Thermal tests included thermal conductivity by using Lee's disc and ablation rate as well as thermal insulator index by using oxy-acetylene flame techniques. Simulation programs of heat transfer in three dimensions for ablation test of PP – HDPE blend nanocomposites specimens were carried out using finite difference method.

Thermal conductivity results show that the values increase progressively by increasing of volume fraction of SWCNTs. Simulation results prove that when the SWCNTs are parallel to heat flow, thermal conductivity values reached higher than that of random and perpendicular direction respectively. Ablation rate behaves inversely, where it drops at high volume fraction of SWCNTs; than blend was alone. Ablation 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 fraction and different orientation of the SWCNTs.

KEYWORDS: Ablation, Blend, Nanocomposites, Simulation, Thermal Conductivity

INTRODUCTION

The importance of polymers is mainly because polymers are still regarded as a cheap alternative material that is manufactured easily. A vigorous development of polymer composite and extensive utilization of polymer materials in technology has led in recent years to the polymer composites. Polymer blend, are known as the result of mixing two or more types of polymer, without any chemical reaction-taking place. Hence, no covalent bonding occurs between the components [1]. Polymer blending is commonly used to create materials with improved mechanical properties, but the resulting material properties can have a complex dependence on composition and processing conditions [2], so it's have become very important subject for scientific investigation in recent years because of their growing commercial acceptance, and they can possess unusual combinations of properties[3]. These blends are mainly classified as homogeneous, heterogeneous, miscible, and immiscible [4]. The properties of all blend components are present. Weakness of one polymer can, to a certain extent, be camouflaged by strength of the others [5].

There are several methods for producing polymer blends, the techniques used depend to a large extent on the nature of the polymer in particular, whether it is thermoplastic or thermosetting [6].

Polypropylene (PP) is a thermoplastic material. It is a linear structure based on the monomer C_nH_{2n} . It is manufactured from propylene gas in presence of a catalyst such as titanium chloride. Beside PP is a by-product of oil

refining processes. Most polypropylene used is highly crystalline and geometrically regular (i.e. isotactic) opposite to amorphous thermoplastics, such as polystyrene, PVC, polyamide, etc., which radicals are placed randomly (i.e. a tactic), it is said that PP has an intermediate level of crystalline between low density polyethylene (LDPE) and high density polyethylene (HDPE); On the other hand PP has higher working temperatures and tensile strength than polyethylene [7].

The ethylene (properly but infrequently called “ethane”) monomer is $\text{CH}_2=\text{CH}_2$ and so polyethylene is $[-\text{CH}_2-\text{CH}_2-]_n$ where the monomer double bond has been “opened” enabling the carbons to join together in a long chain. Polyethylene is the most popular plastic in the world [8]. Polymerization is accomplished by heat and pressure in the presence of a catalyst. The first polyethylene that was made is what we now call “low density” polyethylene, or LDPE. It is soft and waxy, flexible, and low-melting. It is used for the lids of margarine containers, for trash bags, squeeze bottles, and plastic film. The main reason that it exhibits these properties is that the polymer chains have many branches, of varying lengths, off of the main polymer backbone. The new material they produced has the same chemical composition as does LDPE, but is much stronger and more rigid, as well as being more dense and higher-melting. This “high density” polyethylene, or HDPE, owes its properties to the fact that it is easier for long strands of the molecule to form ordered, or crystalline, regions than is the case with LDPE. An increase in the density of polyethylene leads to an increase in its hardness, surface abrasion, tensile strength, modulus, thermal stability, chemical resistance and stress cracking resistance [9]. Polyethylene is limited as an engineering material because of its low strength and hardness. It is attacked by many oxidizing chemical agents and some hydrocarbon solvents [10]. From the above review, it is worth to investigate the effect of volume fraction of carbon nanotubes (equivalent to volume percentage 0.2%, 0.4%, 0.6%, and 0.8%) on the thermal conductivity and the ablation time as well as ablation rate in terms of empirical and simulation approach for SWCNTs / (PP – HDPE) blend nanocomposites.

Theoretical Approach

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. The thermal energy associated with phonons or lattice waves is transported in the direction of their motion. Lattice wave contribution results from a net movement of phonons from high - to low - temperature regions of a cross body, which a temperature gradient exists [11]. Heat transfer by conduction involves transfer of energy within a material without any motion of the material as a whole .The rate of heat transfer depends upon the temperature gradient and the thermal conductivity of the material [12].

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 conductivity [13]:

$$Q = -K \frac{dT}{dx} \quad (1)$$

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), K is the thermal conductivity, and dT/dx is the temperature gradient through the conductive medium. The units of Q and K are W/m^2 and W/mK , respectively. 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.

The effect of using fibers, fillers, coatings, air gaps, carbon nanotube...etc. can be included by adding their

combined effects on the density, specific heat and thermal conductivity of the mesh that contains them. The thermal conductivity however, depends on the shape, orientation and distribution of particles or fibers in the matrix and falls between an upper bound given by [14]:

$$K = K_m V_m + K_f V_f \quad (2)$$

and a lower bound given by:

$$K = \frac{K_m K_f}{V_m K_f + V_f K_m} \quad (3)$$

The upper bound represents fibers that are totally aligned in the opposite directions of the specimen and have the length of the specimen while the lower bound represents fibers that are totally aligned in the direction of the specimen and have the length of the specimen. Different models were suggested to predict the exact thermal conductivity of a composite, one of these models is Micro structure, which is used in this study. In the case of composite materials (multiphase), the situation, is more complex. The thermal conductivity measurements depend on the model of the different distribution of component phases [14].

The thermal conductivity of multiphase micro-structures follows mixture rules. However, the weighting procedures which are necessary vary with the shape and distribution of the phases. Although they apply equally to either thermal or electrical conductivity, notations of thermal conductivity will be incorporated into the following equations. Parallel conduction applies in the first case, according to equation (2). Series conduction applies in second case according to equation (3). In this case, the thermal conductivity of the microstructure is smaller than that obtained from a linear interpolation of the volume fractions [14]. 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. The arrangement can be described as: 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 [15].

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. In the theory given below, the following symbols are used: IV = rate of supply of energy to the heater, after the steady state has been reached. Q = heat loss per second per sq.cm for 1°C excess of temperature of discs over that of enclosure. T = excess of temperature over that of enclosure. d = thickness of disc, r = radius of disc. It can be obtained e in terms of IV , since the total heat supplied must be equal to that given up by the various surfaces:

$$Q = \frac{IV}{\pi r^2 (T_c + T_A) + 2\pi r \left[d_A T_A + \frac{d_s}{2} (T_A + T_B) + d_B T_B + d_c T_c \right]} \quad (4)$$

So, thermal conductivity coefficient becomes:

$$K = \left(\frac{ed_s}{T_B - T_A} \right) \left[T_A + \frac{2T_A}{r} \left(T_A + \frac{d_s}{4} \right) + \frac{d_s T_B}{2r} \right]. \quad (5)$$

When fibers or powder fillers-reinforced plastics are exposed to ablative environments, 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 it from the decomposing polymer. In nanocomposite, pyrolysis reaction is found to occur in three general processes: (1) low temperature out gassing 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 [16]. Nanocomposite compounds provide high char yield, low oxygen to minimize CO and CO₂ formation, and many carbon – hydrogen bonds, which provide the evolution of H₂ and CH₄ for transpiration cooling. The nanocomposite must also have good forming characteristics; good adherence to the SWCNTs, and strength in the composite, and it must form a char that adheres well to the SWCNTs reinforcements. During ablation, some pyrolytic deposition of carbon from the CH₄ or other gases in the outer portions of the char can contribute to the strength and resistance to mechanical removal from the flow field. Addition of particulate additives to the resin can also contribute to strength of the char. The erosion rate for ablative materials is calculated by dividing the original thickness of the specimen by the time to burn through as follows [17]:

$$E_r = \frac{d_s}{b_t}. \quad (6)$$

Where: E_r : erosion rate, m/s, d_s : Thickness of specimen, m, and b_t : Burn through time, s. The insulation index is calculated by using the equation below:

$$I_T = \frac{b_t}{d_s} \quad (7)$$

Ablative test is measured in three type's technique: (i) Static Rocket Test motor experiment, (ii) Laser ablation test and, (iii) flame test [17, 18].

Simulation Approach

The theoretical simulation of ablative test of a thermal insulator is considered as an important process since it reduces many efforts, time and raw materials that are used in trial and error of the experimental procedure. This simulation is performed by using the values of thermal parameters of the specific material. Although this simulation is sometimes difficult to perform because of time and programming difficulties on personal computers, some approximations can result in reasonable results. Partial differential equations are encountered in many branches of physics and engineering in which more than one dimension exists in the differential equations.

Heat can be transferred by conduction, convection, or radiation. Heat conduction equation in Cartesian coordinate is given by [19]:

$$\frac{\partial T}{\partial t} = \frac{K}{\rho c} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + Q. \quad (8)$$

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

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 following equations [20]. For convection heat transfer:

$$Q = hA(T_w - T_\infty) \quad (9)$$

And for radiation heat transfer:

$$Q = F_\varepsilon F_G \sigma A (T_1^4 - T_2^4). \quad (10)$$

Where: Q is the amount of energy transferred per unit time. h is the convection heat transfer coefficient. A is the surface area. T_w is the surface temperature. T_∞ is the temperature of the fluid. F_ε is the emissive function. F_G is the geometric function. σ is the Stefan-Boltzmann constant. T_1 is the temperature of the radiating body. T_2 is the temperature of the irradiating body.

Experimental Approach

The experimental work is divided into three parts. The first part includes specimen preparation for five groups (pure blends resin, 0.2%, 0.4%, 0.6%, and 0.8% of SWCNTs vol. %). The second part includes three 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. Each PP and HDPE was solvated using toluene according to the blending ratios (80 PP vol.%) and (20 HDPE vol.%) with the volume fraction of SWCNTs which was (0.2, 0.4, 0.6, and 0.8) respectively. This would be an obstacle to the uniform dispersion of SWCNTs into blend matrix. Mixtures preparation includes the preparation of specimens; carbon nanotubes nanocomposites specimens by using ultrasonic dispersion method. Thermal conductivity coefficient of specimens was measured using Lee's disc method principle. Thermal conductivity coefficient was then calculated according to equation (5). The average of three measurements was taken for each specimen to minimize the possible errors. Thermal conductivity was calculated theoretically in three direction using microstructure model. The ablative test was carried out by using Flame test method. This test was done according to ASTM - E – 285 – 80. The erosion rate for each specimen was calculated using equation (6), while the insulation index was calculated according to equation (7). The average of 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 blend - nanocomposites were carried out using finite difference method. The program was written in FORTRAN90 language using a computer type Pentum4.

RESULTS AND DISCUSSIONS

Influence of SWCNTs vol. % (empirical and simulation) on thermal conductivity of blend resin matrix was shown in Figure (1). Reinforcement by SWCNTs leads to increase thermal conductivity values with the increasing vol. %. This increment was depending on direction of SWCNTs with respect to heat flux and its type, which was SWCNTs. Generally, direction of SWCNTs (parallel, perpendicular, and random) and interface between the matrix and SWCNTs was clearly observed on these values of thermal conductivity. Figure (1) can be explained according to Erieman theorem, that in an amorphous substance each bond between neighboring atoms is equivalent to thermal resistance and calculates such an elementary thermal resistance. The thermal resistance of a macroscopic amorphous sample is, according to Eierman, a net work of elementary thermal resistances with atoms situated at the entanglement points. The elementary thermal resistance depends on the bonding forces operating between atoms. It decreases with increases in the elastic constant, which characterizes the bond. Therefore, the principal – valiancy chain of the polymers has a considerably lower thermal resistance than the Van der Waals bond. The thermal conductivity due to the Van der Waal bonds interacting between adjacent chains is much greater than thermal resistance in the primary- valence chain. To calculate the elementary thermal conductivity resistance due to Van der Waals forces, it is necessary to determine the corresponding elastic constants.

The Eierman theory makes it possible to account for the fall of thermal conductivity in an amorphous polymer above glass transition (T_g). It has been known that in amorphous polymers above (T_g), the thermal expansion is substantially increased, as a result of which the free volume increases. This leads to an increase in the mean distance between neighboring chains and, hence, to a decrease in the elastic constants caused by the intermolecular interaction. As a result, thermal resistance is increased and, hence, thermal conductivity decreases. Since the thermal conductivity of amorphous polymers depends on the Van der Waals bonds, the change in the temperature coefficient of thermal conductivity is intimately connected with the change in the cubic expansion coefficient at T_g .

Figure (1) shows the influence of (SWCNTs) vol. % and the direction of (SWCNTs) by simulation; simulation parallel direction (Simu. PAR dir.), simulation perpendicular direction (Simu. PER dir.), and simulation random direction (Simu. RAN dir.), on the thermal conductivity of nanocomposites and its nanocomparison experimental random direction (EXP. RAN. dir.) results. From the Figure it can be seen, that the values of experimental results (EXP. RAN. dir.) were located between perpendicular direction and random direction of (SWCNTs) nanocomposites with respect to heat flow direction. That can be explained as; most of (SWCNTs) were aligned in perpendicular direction of heat flow supplied which is led to low value of thermal conductivity comparing with simulation parallel direction values.

Figure (2) shows a comparison of influence of SWCNTs volume fraction on the ablation rate of blend resin 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 ablation rate of experimental values is lower than simulation values. Generally, the ablation rate for all blends resin nanocomposites were decreased when volume fraction increased, with different fractions, depending on direction of SWCNTs and interface composed between matrix and SWCNTs. Figure (3) shows a comparison of influence of SWCNTs volume fraction on the insulator index of blend resin matrix of simulation operation (SIMU) with that of the experimental (EXP) results of oxy-acetylene torch of three temperature- 353K, 453K, 653K. It can be seen from the Figure that the insulator index of experimental values is higher than simulation values. In general, the organic compound-based material under high temperature, all the organic compound will be decomposed at (673K - 773K), so the insulator index of 653K has adequate representation to show the insulation characteristic of the material.

Figures (2) and (3) can be explained by using Figures (4 – 8). Figures 4 - 8 show temperature distribution after operation seconds when SWCNTs of (0.2%, 0.4 %, 0.6%, and 0.8%) volume fraction is punctured by simulation operation of oxy-acetylene torch respectively. In each Figure, it can be seen three temperature distribution regions (0 – 1000, 1000 – 2000, and 2000 – 3000) K. Figures of simulation (4 - 8) can be explained by using ablation mechanism.

We Can Conclude

Reinforcement of PP-HDPE blend resin with SWCNTs has been improved the ablation rate as well as insulator index and thermal conductivity of nanocomposites in different volume fraction, depending on distribution of SWCNTs. Extremely results of ablation rate have been shown that the reinforcement by SWCNTs for the blends had better than the reinforcement by macroscopic carbon fibers. From simulation results it can be seen that there was high influence of SWCNTs direction with respect to heat flux, on thermal conductivity values. Simulation results of ablation show that the best values of ablation rate as well as insulator index are for 0.8 vol. % groups with respect to SWCNTs nanocomposites, which agree with experimental results.

There is a high influence of SWCNTs (direction and dispersion), with respect to heat flux, on thermal conductivity values. Nanocomposites were produced have high ablation resistance and insulator index at temperature exceed 3000K; because an earlier char operation has been taken place. 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 (insulator index) for nanocomposites.

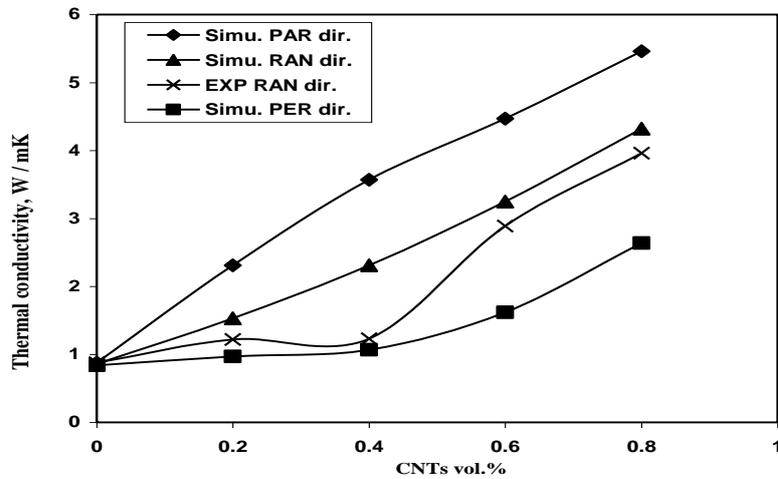


Figure 1: Influence of SWCNTs Vol % and Direction on the Thermal Conductivity of Blend of Simulation Results and its Comparison Experimental Random Direction Results

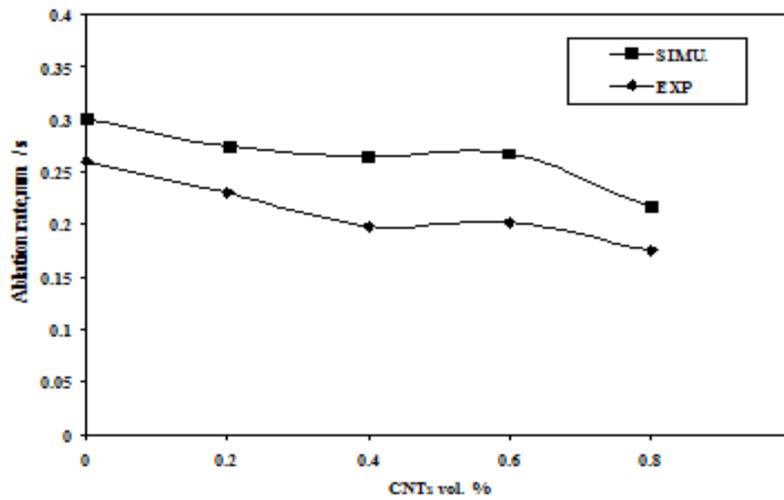


Figure 2: Comparison is between Influence of SWCNTs Volume Fraction on the Ablation Rate of Blend by Simulation Operation and the Experimental Results

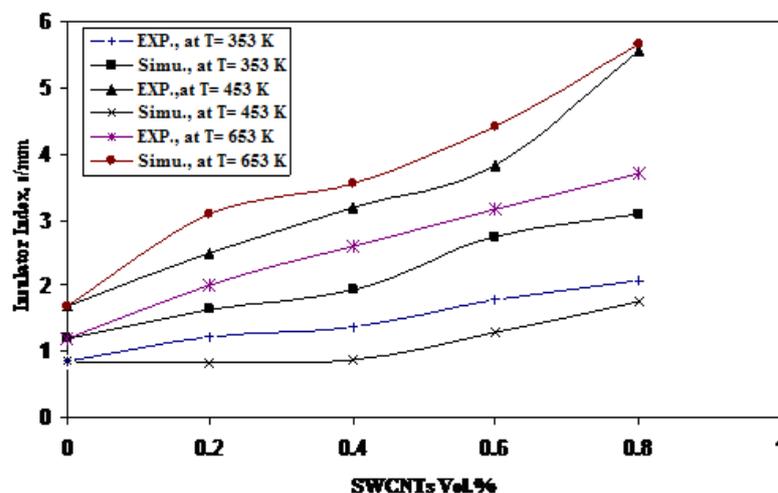


Figure 3: Comparison between Influence of SWCNTs Volume Fraction on the Insulator Index by Simulation Operation and the Experimental Results

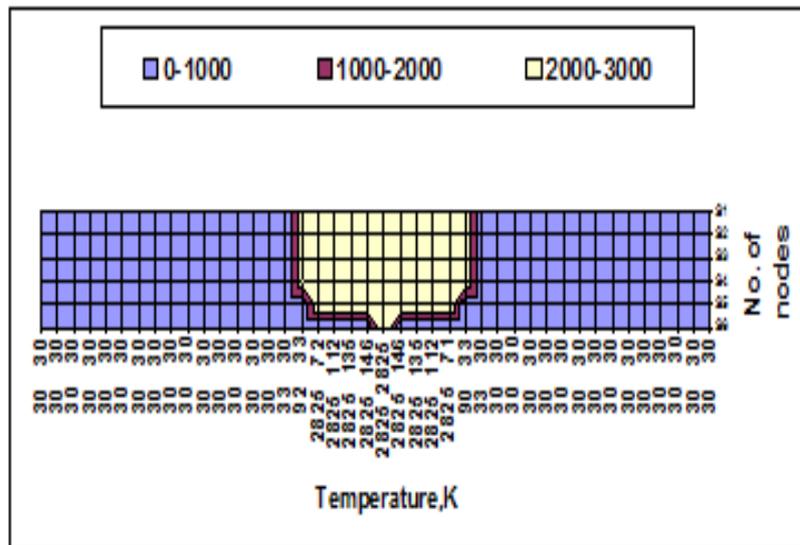


Figure 4: Temperature Distribution after 18.13 Seconds When Blend is Punctured by Simulation Operation of Oxy-Acetylene Torch Temperature

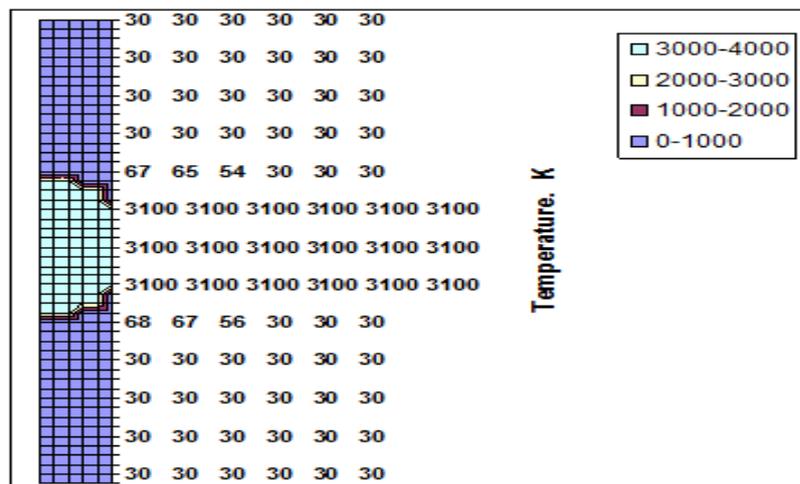


Figure 5: Temperature Distribution after 22.10 s When 0.2 SWCNTs Vol. by Simulation Operation of Oxy-Acetylene Torch Temperature

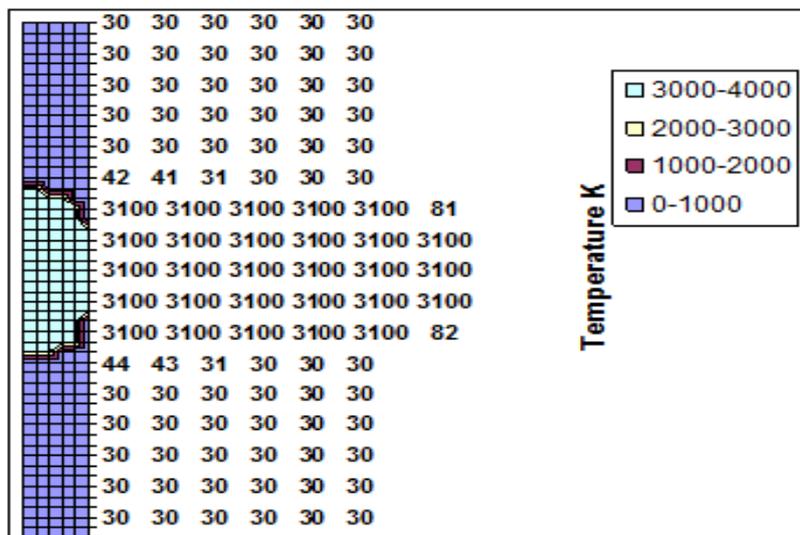


Figure 6: Temperature Distribution after 29.67 s When 0.4 SWCNTs Vol. % by Simulation Operation of Oxy-Acetylene Torch Temperature

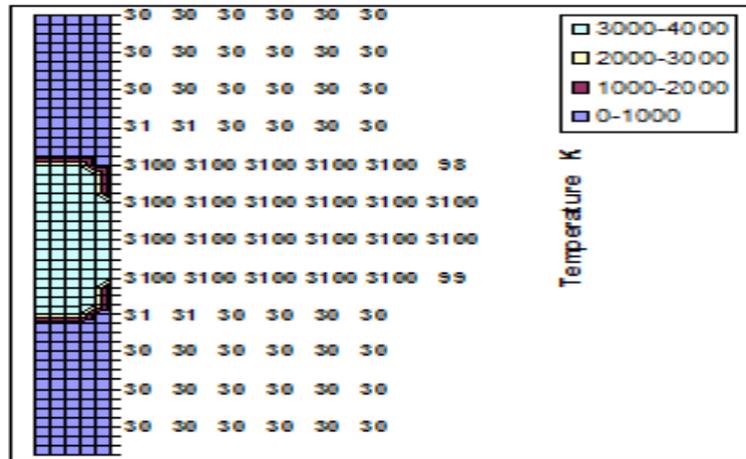


Figure 7: Temperature Distribution after 34.14 s When 0.6 SWCNTs Vol. % by Simulation Operation of Oxy-Acetylen Torch Temperature

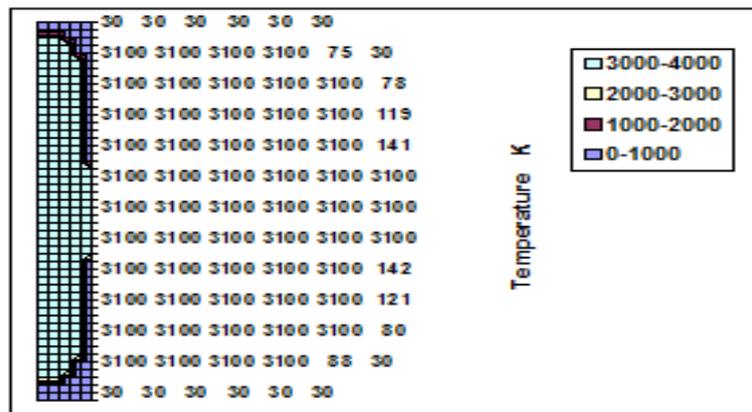


Figure 8: Temperature Distribution after 38.78 s When 0.8 SWCNTs Vol. % of Blends Resin in Punctured Simulation Operation of Oxy-Acetylen Torch Temperature

ACKNOWLEDGEMENTS

The work reported in this paper was supported by laboratories of University of Technology, Iraq, Center of Materials Science, Ministry of Science and Technology, Iraq, University of Baghdad, and the University of Mustansiriyah.

REFERENCES

1. N. Taleb Ahmed, "Study the visco-elastic properties of polymer blends irradiated by gamma ray", M.Sc. Thesis, The University of Mustansiriyah, Iraq, (2012)
2. P. H. Laurent "Robotics and radiation hardening in the nuclear industry", Master's thesis, University of Florida, American, (2000).
3. S. Zheng, J. Huang, J. of Applied Polymer Science, Vlo.69, No.4, PP. (675-684), (1998).
4. M. S. Bhatangar "Polymers Chemistry & Technology of Polymers, Processing and Applications", Chand S. & Company LTD New Delhi, Vol.2, (2004).
5. L. A. Utracki, "Polymer Blends and Alloys", Hanser Press, New York, (1990).
6. R. Donald, W. Askelane, and P.P phule, "The Science Engineering of Materials", 4th ed., John Wiley, New York, (2003).

7. V. R. Gowariker, N. V. Viswanathan, and Jayadev Sreedhar, Polymer Science, New Age International (P) Limited publishers, Bangalore, (2001).
8. M. T. Awwad and L. Shbeeb, Am. J. Appl. Sci., Vol. 4 (6), PP. (390-396), (2007).
9. R. M. S. Al-Ubaidy, "The Influence of Additives on Some Physical and Mechanical Properties of Polymer Blends", Ph. D. Thesis, University Of Technology, Iraq, (2009).
10. V. D. Vegt, "From Polymers to Plastics", Delft University, the Netherlands, (1999).
11. J. S. Blakmore; "Solid State Physics", W. B. Saunder Company, London, (1974).
12. W. D. Bowen and D. R. Uhlmann; "Introduction to Ceramic", 2nd edition, John Wiley and Sons, New York (1976).
13. M. W. Zemanesky; "Modern University Physics", Addison Wesley Publishing Company, New York, (1972).
14. A. J. Yusuf, "Simulation of Thermal Insulation, Mechanical, and Electrical Characteristics of Sacrificed Nanocomposites", M.Sc. Thesis, The University of Mustansiriyah, Iraq, (2013).
15. H. A. Muhsen, "Thermal and Mechanical properties of carbon Nanotubes Reinforced Epoxy Resin Nano Composites", M.Sc. Thesis, The University of Mustansiriyah, Iraq, (2011).
16. Jose-Yacaman, M.; Rendon, L.; Arenas, J.; Serra Puche, M. C. (1996). "Maya Blue Paint: An Ancient Nanostructured Material". *Science* **273** (5272): 223. Doi.10.1126/science.273.5272.223. PMID 8662502.
17. B. K. G. Theng "Formation and Properties of Clay Polymer Complexes", Elsevier, NY 1979; ISBN 978-0444417060
18. Manias, Evangelos (2007). "Nanocomposites: Stiffer by design". *Nature Materials* **6** (1): 9. doi:10.1038/nmat1812. PMID 17199118.
19. E. Schmid, G. Spitz and W. Losch, "Theoretical Physics on the personal computer ", Springer-Verlag. (1989).
20. A. Bejan; "Heat Transfer", John Wiley and Sons, England, (1993)