

Thermal conductivity and electrical conductivity of Epoxy Composites filled with Carbon Nanotube and Chopped Carbon Fibers

Sinaa I. Hussan

Department of Physics, College of Science, Baghdad University

Received 9/10/2011 – Accepted 17/1/2012

الخلاصة

تم في هذا البحث تحضير مادة متراكبة من راتنج الايبوكسي وانايبب الكربون النانوية وبنسب وزنية % (0.1, 0.2, 0.3) ومادة متراكبة من راتنج الايبوكسي واليايف الكربون المقطعة وبنسب وزنية % (10, 20, 30)، جميع العينات الخاصة بالتوصيل الحراري والتوصيل الكهربائي حضرت باستخدام طريقة القولية اليدوية واجري اختبار التوصيلية الحرارية باستخدام قرص لي لحساب معامل التوصيل الحراري في درجات حرارية مختلفة اظهرت النتائج تحسنا كبير في خواص المادة المتراكبة الحاوية على الكربون النانومتري لما تتمتع به من خصائص ادت الى تحسن الخواص الحرارية وزيادة معامل التوصيل الحراري لزيادة النسب الوزنية للكربون النانومتري. اما تأثير درجة الحرارة فقد ازداد معامل التوصيل الحراري لكلا المادتين المتراكبتين بزيادة درجات الحرارة. ظهرت النتائج العملية ان التوصيلية المستمرة تزداد مع زيادة درجات الحرارة (301-473) كلفن بزيادة نسبة المضافات ووجد ان افضل توصيلية في المتراكبات المتكونة من ايبوكسي مع الكربون النانومتري تقع بين $(7.31 \times 10^{-9} - 2.44 \times 10^{-9}) \Omega \cdot \text{cm}$ وتم حساب طاقة التنشيط ووجد انها تتناقص مع زيادة نسبة المضافات للمتراكبات جميعها.

ABSTRACT

In this research two composite material was prepared, the first prepared from epoxy resin (EP), which is a matrix, and carbon nanotube (CNT) of percentage weight (0.1, 0.2, 0.3)%, and the second prepared from epoxy resin and chopped carbon fibers (C.F) of percentage weight (10, 20, 30)%. All sample were prepared by hand layup process. by using lee disk to determine the coefficient of thermal conductivity at different temperatures. The results showed improvement of thermal conductivity values was measured for the composite materials consisting carbon nanotube. Also it was found that the thermal conductivity coefficient increased with the increasing percentage weight.

The effect of temperature on the thermal conductivity, the thermal conductivity coefficient increased by increasing the test temperature for both composite materials. it was found The D.C conductivity on wt.% filler content at (301-473) K electrical conductivity of all above composites increased with temperature for composites with filler contact, the excellent electrical conductivity of carbon Nano tube and epoxy $(7.31 \times 10^{-9} - 2.44 \times 10^{-9}) \Omega \cdot \text{cm}$. The activation energy of the electrical conductivity is determined and found to decrease with increasing the filler concentration.

Key word: - epoxy resin, carbon nanotubes, carbon fiber, thermal conductivity, electrical conductivity

INTRODUCTION

Carbon nanotubes possess the unique feature of having a superior combination of mechanical, electrical and thermal properties [1]. Nanotubes have been successfully investigated for field emission displays, micro-electronic devices, sensors and energy storage devices, for attenuation of electromagnetic radiation and microwave absorption [2]. The exceptional characteristics of carbon nanotubes make them ideal candidates for replacing conventional fillers in the matrix of composites. Inclusions of carbon nanotubes

in matrix in extremely small quantities to form Nano composites have shown to improve the mechanical properties to a large extent and the electrical properties by several orders of magnitude [3]. The electrical resistivity of polymer composites filled with carbon black (CB) or carbon fibers (CF) strongly depends on the filler content. Composite resistivity practically coincides with that of the polymer matrix at low concentrations of the filler. Conductive particles agglomerate in the composite as clusters. As the size and number of the clusters increases with increasing filler content, at some critical content, that is called the percolation threshold, the cluster becomes infinite and the material becomes conductive [4]. Polymers have a very low concentration of free charge carriers, and thus are nonconductive and transparent to electromagnetic radiation. Due to this reason they are not suitable for use as enclosures for electronic equipment because they cannot shield it from outside radiation. This drawback has led to the development of electrically conductive polymers such as inherently polyaniline conductive or polymers filled with conductive particles [5]. Indira Vir Singh et al [6] studied the effect of interface on the thermal conductivity of a carbon nanotube composite using a numerical approach. They suggested that the effect of interface on the conductivity of composite is small for short nanotubes, whereas for long nanotubes, it has a significant effect. Yang et al [7] studied the thermal and electrical transport in multiwall nanotube (MWNTs) using pulsed photo thermal reflectance and found that heat transport was dominated by phonons instead of electrons. They also observed that the thermal conductivity was independent of nanotube length. Fuji et al [8] measured the thermal conductivity of a single MWNT using a suspended sample-attached T-type Nano sensor and found to be around 2000 W/m-K. They also showed that the thermal conductivity increased with decreasing diameter of nanotubes. In 2002 Allaoui et al [9] Studied the effect of carbon walled Nano-tubes on the dielectric properties of epoxy matrix composite. The result exists increasing in conductivity by nine orders of magnitude at 4% weight fraction of carbon Nanotube.

MATERIALS AND METHODS

1-Materials :-

Epoxy resin LE-828(E-51), place of origin Anhui, china the Huangshan shanfu chemical Co. Ltd. The colorless transparent viscous liquid, the ratio resin at hardener [2:1]. Carbon fibers were used in this study the length of carbon fibers chopped (short) 1-2 cm, fiber diameter 7-8 μ m, and with density 1.75gm/cm³. Carbon Nano tube and chopped carbon fibers reinforced epoxy composites were fabricated by hand lay-up with variation of carbon fiber content which was obtained using

different percentage weight (10,20,30)% ,and carbon Nano tube (0.1,0.2,0.3)%, with the same total thickness of the specimens(3mm) and cut the specimen according lee disk the diameter 4 cm . CNT were first dispersed in chloroform solution under magnetic agitation to reduce the maximum size of the aggregates to about100 mm. After complete evaporation of chloroform the obtained CNT powder was then directly added to the epoxy resin and hardener mixture.

2- Measurements:-

Thermal conductivity:- Thermal conductivity coefficient was calculated to the data that measurement by using the lee's disk {manufacture by Griffin and George / England}, thermal conductivity coefficient was calculated by using the following equation [10]

$$K [T_B - T_A / d_s] = e [T_A + 2/r [d_A + d_s/4] T_A + 1/2r (d_s T_B)] \dots\dots(2)$$

$$H = IV = \pi r^2 e$$

$$(T_A + T_B) + 2\pi r e [d_A T_A + (1/2)d_s(T_A + T_B) + d_B T_B + d_C T_C] \dots\dots(3)$$

K: - Thermal conductivity Coefficient

e: - Represents the amount of thermal energy passing through unit area per second disk material

H: Represents the thermal energy passing through the heating coil unit of time

d:- Thickness of the disk (mm) , **r:**- The radius of the disk(mm).

d_s :- Thickness of the sample(mm) , **T:**- The temperature of the disk(°c).

Electrical conductivity:- electrical resistance of insulating materials , three electrodes cell or (guard ring electrode method) was used to study the effect of the filler addition and the temperature on volume resistivity of polymer composite. Resistivity (ρ) value was calculated by using the following relation[5]

$$\rho = R * A / \ell \dots\dots\dots 4$$

Where:

ℓ:-is the length (in units of meters), **A:** - is the cross sectional area (in units of m²)

ρ :- is the resistivity of the material (in units of Ω·m), **R** :- is the resistance of the object, measured in Ohm, equivalent to J·s/C

Resistivity is a measure of the material's ability to oppose electric current. Where Conductivity was calculated by using the following formula

$$\sigma_{d.c} = 1/\rho \dots\dots\dots 5$$

For nonmetallic materials, the electrical conductivity depends on temperature T:

$$\sigma_{d.c} = \sigma_0 \exp (- E_a / K_B T) \dots\dots\dots 6$$

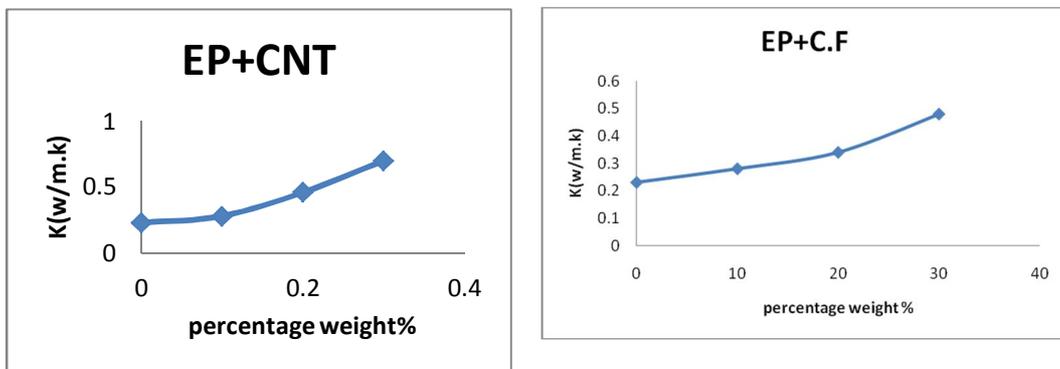
Where: E_a is the activation energy, K_B is the Boltzmann constant σ_0 is the minimum electrical conductivity at 0K.

RESULTS AND DISCUSSION

Thermal conductivity

Effect of percentage weight:-

Because epoxies are insulators and very poor thermal conductors, fillers and fibers must be introduced into the epoxy in order to provide thermal transfer. The thermal conductivity of an epoxy will be determined by the choice of filler, the percentage of filler loading. The process of thermal energy transfer depends on the structural nature of the material and style of the transition process varies depending on material and there are two ways for the transition of thermal energy are lattice waves and free electrons, Transmitted thermal energy in insulating materials by phonons and this process occurs as a result of oscillation molecules as they move to the frequency as a result of neighboring molecules are linked together and the bonds, transmitted pulse of heat to the upper end of the lower side is flexible waves called phonons[11]. The thermal conductivity coefficient of carbon nanotube $K_{CNT} = 3000 \text{ W/m.K}$ and carbon fiber $K_{C.F} = 15 \text{ W/m.K}$ [12]. The Figure (2) show that the thermal conductivity coefficient increases with increasing percentages weight for both types, so the highest value of thermal conductivity coefficient was at the ratio of carbon nanotube 0.3% and the ratio of carbon fiber 30%, The carbon nanotube composites show highly thermal conductivity values relative to carbon fibers composites, this result can be explained by the fact that the C.F is randomly orientated material which exhibited low heat flow and thermal conductivity coefficient (K). The modification of epoxy matrix might be caused the decreasing in the mean distance between neighboring chains and, hence, to increase the elastic constants caused by the intermolecular interaction. As a result, thermal resistant is decreased and, hence, thermal conductivity increased. This explanation is based on the liquid state theory



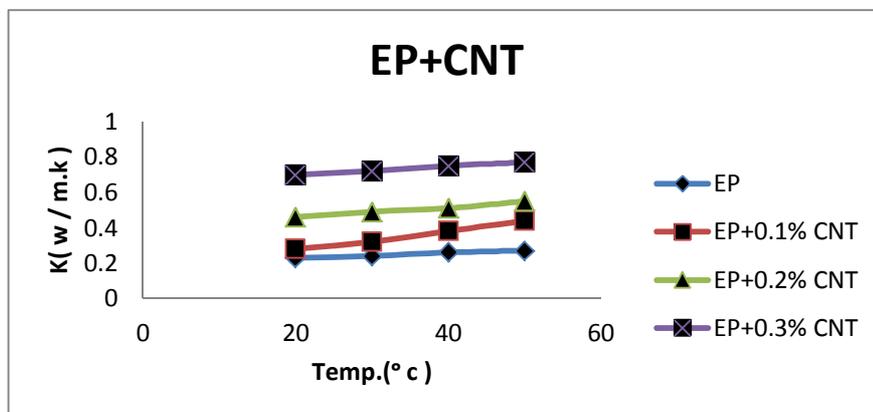
(a)

(b)

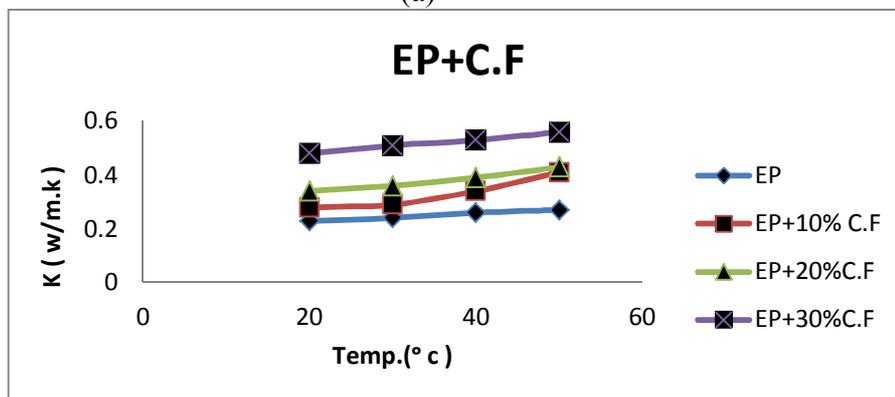
Fig.-1: Thermal conductivity of epoxy composites as a function of percentage weight a-Epoxy resin with carbon nanotube, b- Epoxy resin with carbon fibers

1-2 Effect of temperature:

Figure (3) show the variation of thermal conductivity (K) as a function of test temperature for EP/CNT and EP/C.F composites respectively. The results show that the thermal conductivity (K) has a common behavior for all composites; as the values for all composites increase linearly with increasing the test temperature. This result is due to the intermolecular vibrations increasing with increasing test temperature [13]. Thermal conductivity increases with increasing test temperature as in table (1). The increase test temperature lead to increased values of thermal conductivity of polymeric materials reinforced, with high temperature the molecules of material will absorb this heat energy and thus increase the capacity of oscillation about the equilibrium position, clash the environs of the molecules gain energy particles that make them oscillate with a capacity greater than it was the clash of these molecules in turn with its neighboring other molecules gain energy, and thus we believe that the heat transmitted through the vibration of molecules without moving from the position of equilibrium[14].



(a)



(b)

Fig.-2: Thermal conductivity of epoxy composites as a function of temperature
Epoxy resin with carbon nanotube ,b- epoxy resin with carbon fibers

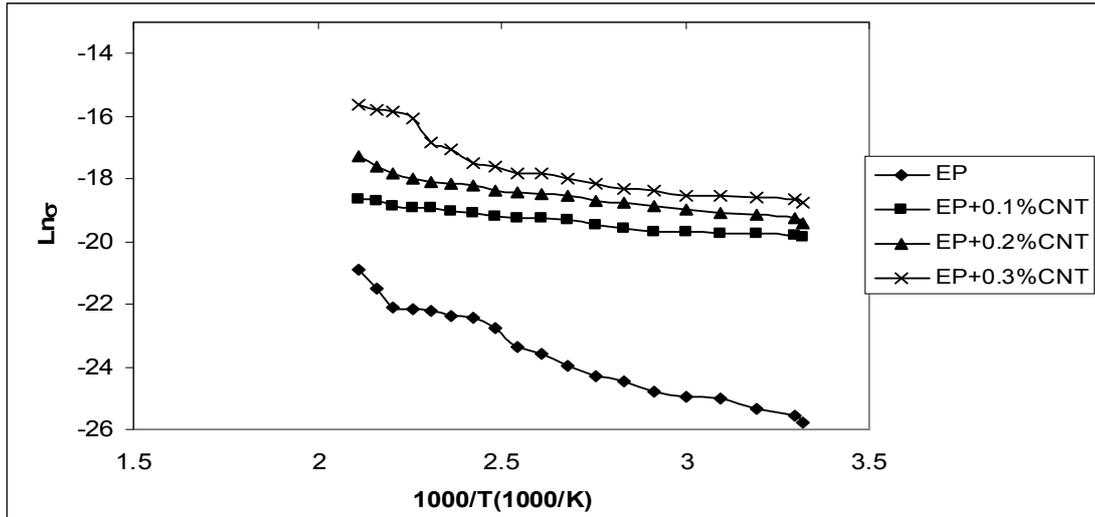
Table-1: values of thermal conductivity of epoxy composites with carbon nanotube and chopped carbon fibers

Sample	K(W/m.K) at 20 °C	30 °C	40 °C	50 °C
EP	0.23	0.24	0.26	0.27
EP+0.1% CNT	0.28	0.32	0.38	0.44
EP+0.2% CNT	0.46	0.49	0.51	0.55
EP+0.3% CNT	0.70	0.72	0.75	0.77
EP+10%C.F	0.28	0.29	0.34	0.41
EP+20%C.F	0.34	0.36	0.39	0.43
EP+30%C.F	0.48	0.51	0.53	0.56

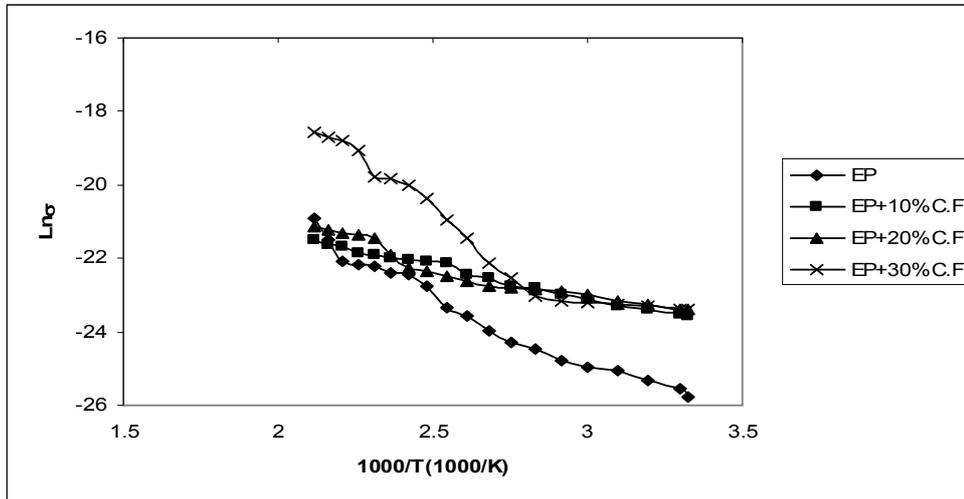
Electrical conductivity:-

D.C conductivity

In polymers at 0 K all the trapped electrons are in deep traps. But at a particular temperature and on application of the applied field some of the electrons can excite into shallow traps or to conduction level. It has been reported in the literature that these electrons can take part in conduction. The increase in temperature does not alter the total amount of space charge but increases the portion of this space charge in the conduction band which increases exponentially on increase of temperature. D.C conductivity was calculated using eq.(5), The D.C conductivity dependence on wt.% filler content at (301-473) K, and show that the increase in D.C conductivity of all sample with the concentration (10,20, and 30)%of chopped carbon fibers and (0.1,0.2,0.3)% of carbon nanotube filler, At low filler content (20%) was mainly due to the polymer itself and not to the filler. This increased could be attributed to increased segmental mobility of the polymer chains near the filler particles [15]. At 0.3% (CNT) filler concentration the increase in electrical conductivity could be ascribed to increase of ionic charge carriers which might be increased due to increasing filler content for example of Carbon nanotube the conductivity increased between $(6.91 \times 10^{-11} - 5.84 \times 10^{-11}) \Omega \cdot \text{cm}$. It has been observed that d.c. conductivity suddenly increases after 333K in all the samples. This is because Tg (glass transition temperature) epoxy is around 333K, below Tg d.c. conductivity does not increase much, after Tg where epoxy comes in amorphous phase and sudden change in conductivity occurs. This is because after Tg free volume increases and chains start moving, which makes the movement of charge carriers easy and hence they take place in conduction process after release from traps, makes the movement of charge carriers easy and hence they take place in conduction process after release from traps [16].



(a)



(b)

Fig.-3:the variation of $\ln \sigma_{d.c}$ with reciprocal absolute temperature for epoxy composites a- Epoxy with carbon Nano tube b- epoxy with chopped carbon fibers

Activation energy :-

The variation of conductivity with test temperature is the main tool in investigating the properties of composites it is very useful to determine in the extrinsic rang the activation energies of impurity centers and in the intrinsic rang the main energy gap. Plots the $(\ln. \sigma)$ vs. Reciprocal of the absolute temp. $(10^3 / T)$, we can measure the activation energy by taking the slope of straight line of $(-\Delta E/K)$. The d.c conductivity for EP Composites has been studied as function of $10^3 / T$ at RT and annealing temp. (301-473)K we found that there are two stages of conductivity throughout the heating temperature rang. In this case the first activation energy (E_{a1}) occurs at higher temperature within rang (393- 473)K,

while the second activation energy (E_{a2}) occurs at low temperature within rang (301- 383)K, and the conduction mechanism of this stage is due to carriers transport to localized states near the valence and conduction bands. The values of E_{a1} and E_{a2} decrease with the increasing of content CNT or C.F as shown in table (3) .that this may be due to saturate the dangling bonds,i.e there is reduction in the density of state which occurs at Fermi level which caused to the transfer from conductivity near Fermi level to the thermal activation conductivity at band gap.

To calculate the activation energy for the thermal activation processes Arrhinus eq.(6) has been used . At low temperatures the thermal activation of the conductivity was almost negligible, activation energy of thermal degrees (301-383)K except for the transition of positive energy levels localized in the energy gap and as a result of a proposed high density of localized energy levels in the energy gap[17], after increasing the temperature above T_g the conductivity increased strongly . So, the activation energy values were calculated for this region because that the second region (393-473) K the result of activation energy at the granular ion by thermal emission (thermal stimulation cross-border movement), and listed in Table(3). The activation energy values decreased with increasing of wt% filler content of epoxy composition. The low activation energy for epoxy – carbon nano tube between (0.54-0.27) e.V should be to the electronic conduction mechanism which was resulted for a new kinetic path formation in polymer matrix. It has been reported that for these types of composites ionic, electronic and even mixed conducting process are possible .This value is compared with epoxy pure and that activation energy of 1.33 eV[18].

Table-2: Values of $\sigma_{d.c}$ and activation energy of epoxy composites

Additives	$\sigma_{d.c}$ (R.T)	E_{a1} (e.v)	E_{a2} (e.v)
EP	$6.27 \cdot 10^{-12}$	1.40	1.02
EP+0.1%CNT	$7.31 \cdot 10^{-9}$	0.54	0.43
EP+0.2%CNT	$3.66 \cdot 10^{-9}$	0.36	0.32
EP+0.3%CNT	$2.44 \cdot 10^{-9}$	0.30	0.27
EP+10%C.F	$6.91 \cdot 10^{-11}$	0.75	0.46
EP+20%C.F	$6.87 \cdot 10^{-11}$	0.66	0.27
EP+30%C.F	$5.84 \cdot 10^{-11}$	0.58	0.51

So, we can Conclude:-

1. The thermal conductivity test of Nano composite material of (epoxy

- +carbon Nano tube) gives higher values compared with composites material of (epoxy + chopped carbon fibers).
2. Thermal conductivity increase by increasing temperature test for all samples.
 3. The electrical conductivity of all above composites increased with increased temperature for composites epoxy.
 4. The activation energy decreased with increase of weight percentage for both additives

REFERENCES

1. Baughman, R.H., Zakhidov A.A., and de Heer W.A.,” Carbon Nanotubes--the Route toward Applications”. Science, 297, (792),(2002).
2. Harris P.J.” Carbon Nanotube Composites”. International Materials Reviews, 49,(1), : 31-43, (2004).
3. Nanni F., Travaglia P., Valentini M.,” Effect of carbon nanofibres dispersion on the microwave absorbing properties of CNF/epoxy composites”. Composites Science and Technology, 69,(3), p.485-490,(2009).
4. Yuri C., Ryuji O.,Shigeo A. and Masao S.,” Electrical properties of epoxy resin filled with carbon fibers” J. OF Mat. Sci., 34 ,:5589 – 5599,
5. Navin CH. and Archana N., 2008" *Investigations on d.c. conductivity behavior of milled carbon fiber reinforced epoxy graded composites*" Bull. Mater. Sci., 31(4):665-668,(2008).
6. Singh, I.V., M. Tanaka, and M. Endo,” Effect of interface on the thermal conductivity of carbon nanotube composites”. International Journal of Thermal Sciences, 46, (9),: 842-847, (2007).
7. Yang, D.J. “Thermal and electrical transport in multi-walled carbon nanotubes”. Physics Letters A, 329, (3): 207-213,(2004).
8. -Fujii, M. “Measuring the Thermal Conductivity of a Single Carbon Nanotube”, Physical Review Letters, 95, (6), :65502,(2005).
9. Allaouiet A.,Bai S. ,Cheng H. and.Bai J. , "Composite Science and Technology", 62, :5691-5692, (2002)
- 10.Perepechko I.L., “An Introduction to Polymer Physics”, Ch.4, Translated from the Russian by Artavaz. Beknazarov, First Published, (1981).
- 11.Incropera P.F. ,Dewitt D.D, “fundamental of heat transfer”,John wi;ey & Sons.Inc,(1981).
- 12.Fisher F.T.,. Bradshaw R.D., Brinson L.C.; “Effects of nanotube waviness on the modulus of nanotube-reinforced polymers”, Appl. Phys. Lett. ,24,(80),: 4647-4648, (2002).
- 13.Piokowska E.and Goleski A.,”Int.polym.Sci.Tech.”1, (12),:102,(1985).

14. Hone J., Llaguno M.C., Nemes N.M., Johnson A.T., Fisher J.E., Walters D.A., "Thermal properties of carbon nanotube and nanotube based materials", *Appl. Phys.* 74, :339- 343, (2002).
15. Kawamoto Y., Nagura N., and Tsuchihashi S., "D.c Conductivity of Ge-S-Ag and As-S-Ag Glasses" *Journal of American Ceramic Society*, 57(11): 489 – 491 (2006).
16. Sankara S., Arayanan Potty N., and Abdul Khadar M., " *Dielectric properties of nanophase Ag₂HgI₄ and Ag₂HgI₄-Al₂O₃ nanocomposites*" *Bull. Mater. Sci.*, 23(5): 361–367, (2000).
17. Sindhu S., Anantharaman M. R., Thampi B., Malini K. A. and Kurian P. " *Evaluation of a.c. conductivity of rubber ferrite composites from dielectric measurements*" *Bull. Mater. Sci.*, 25 (7): 599–607, (2002).
18. Tsangaris G.M., and Kazilas M.C., 2008" *Conductivity and percolation in epoxy resin/conductive filler composites*" *J. Phys. D: Appl. Phys.*, 16(21): 41-45.