Study of effect acidic solution (HCl) and (EP/Al$_2$O$_3$ & EP/ TiO$_2$) hybrid on thermal conductivity of epoxy resin.

Abdul Adeem Zaily Hameed[1], Faik Hammad Anter[1], Muzhir Shaban Al-Ani[2]

[1]Department of Physics, College of Sciences, Anbar University

[2]Department of Computer Science, College of Science and Technology, University of

Human Development, Sulaimani, Iraq

E-mail: ab72d74@yahoo.com

Abstract

This research studies the effect of adding micro, nano and hybrid by ratio (1:1) of (Al$_2$O$_3$,TiO$_2$) to epoxy resin on thermal conductivity before and after immersion in HCl acid for (14 day) with normality (0.3 N) at weight fraction (0.02, 0.04, 0.06, 0.08) and thickness (6mm). The results of thermal conductivity reveled that epoxy reinforced by (Al$_2$O$_3$) and mixture (TiO$_2$+Al$_2$O$_3$) increases with increasing the weight fraction, but the thermal conductivity (k) a values for micro and Nano (TiO$_2$) decrease with increasing the weight fraction of reinforced, while the immersion in acidic solution (HCl) that the (k) values after immersion more than the value in before immersion.

دراسة تاثير المحلول الحامضي (HCl) والهجين (EP/Al$_2$O$_3$ & EP/ TiO$_2$) على التوصيلية الحرارية لراتنج الايبوكسي

عبد العظيم زعيلي حميد[1]، فائق حماد عنتر[1]، مزهر شعبان العاني[2]

[1]قسم الفيزياء، كلية العلوم، جامعة الانبار

[2]قسم علم الحاسوب، كلية العلوم، جامعة الموارد البشرية، السليمانية، العراق

الخلاصة

تم في هذا البحث دراسة تأثير إضافة الدقائق المايكروية والنانوية والهجين بنسبة (1:1) من (Al$_2$O$_3$، TiO$_2$) على راتنج الايبوكسي في اختبارات التوصيل الحراري قبل وبعد الغمر في المحلول الحامضي (HCl) لمدة (14 يوم) بتركيز (0.3 N) وبكسر وزني (0.02، 0.04، 0.06، 0.08) وسمك (6 mm). أظهرت نتائج اختبار التوصيل الحراري في الحالة الطبيعية أن الايبوكسي المقوى بدقائق المايكروية والنانوية (Al$_2$O$_3$) و الهجين (TiO$_2$ + Al$_2$O$_3$) يزداد مع زيادة النسبة الوزنية، ولكن قيم التوصيل الحراري (k) لدقائق المايكروية والنانوية (TiO$_2$) تتناقص مع زيادة النسبة الوزنية في حين تكون قيم (k) في حالة الغمر في المحلول الحامضي (HCl) اكبر من القيمة قبل الغمر.

Introduction

The result of the great scientific and technological development in the world, needed to find new alternative materials of metals and alloys which are lightweight materials with high mechanical specifications and give the durability and flexibility of material in addition that resistance to different environmental conditions and use in industrial products like airplanes, cars and other engineering designs, so been manufactured of composite material [1].

Aluminum oxide is a chemical composite has the formula Al$_2$O$_3$,

known as Alumina, there is in the form of two types differ from each other in the crystal structure, and thus also differ in their physical and chemical properties as well as applications, namely the pattern of alpha α and gamma γ. Alumina ceramic also feature very high mechanical strength, high thermal conductivity and high resistance to chemical and corrosion [2].

Titanium dioxide take at least eight structures alongside three structures found in nature and is the Rutile, Anatase and Brookite, TiO_2 is characterized by being a source of distracting light as a result of the coefficient of higher refractive index, stability and regular absorption and the low relative to visible light which is nontoxic and safe and is used in the paint, where he works the protective coating of chemical weathering and dissolution of photo synthesis organic links.

The titanium dioxide applications are: White Pigment, photo catalysis, catalyst support or promoter and gas sensor [3].

Nano composite materials are especially important due to their bridging role between the world of thermal conducting polymers and that of inorganic materials. Inorganic nanoparticles of different nature and size can be combined with the thermal conducting polymers, giving rise to a host of nanocomposites with interesting physical properties and important application potential. Inorganic materials used for this purpose are generally of two types: nanoparticles and some nanostructured materials or templates. Depending upon the nature of association between the inorganic and organic components, nanocomposites are also classified into two categories: one in which the

inorganic particle is embedded in organic matrix and the other where organic polymer is confined into inorganic template [4].

The thermal conductivity factor for the test specimen, as shown in Fig.1, in this instrument, the heat is transferred from the heater to the followed disc till it reaches the last disc, and the temperatures (T_A, T_B, T_C) for the three discs can be specified by using the thermometers inside them respectively,

One of the most important influences is to ensure that the surfaces of the copper discs are clean and compatible to obtain the best heat transfer through them. The dimension of specimen (disk) [r = 3 cm, d = 0.5 cm]. The value of thermal conductivity (k) can be calculated by the following Eq. (1) [5].

$$k (T_B − T_A)/d_s = e [T_A + 2/r (d_A+ 1 /4d_s) T_A + 1 / 2r d_s T_B] \qquad (1)$$

where (e) represents the amount of thermal energy transferred through unit area of the disc per second (W / m^2.K) and it calculated from the following Eq. (2):-

$$IV = \pi r^2 e (T_A+T_B) +2 \pi re [d_A T_A + d_S 1 /2(T_A+T_B) + d_B T_B + d_c T_C] \qquad (2)$$

where (T_A, T_B, T_C) represent the temperature of discs (A, B, C) respectively.
d: disc thickness (cm), r: disc radius (cm), I: current (Ampere), V: voltage (volt).

When putting specimen between (A, B) discs and applied power for circuit and let it for (l) hours to reach all discs at equilibrium case in temperature and recorded the values of (T_A, T_B, T_C) and let it (discs) to cool gradually for (45 min) and repeat the experimental again for all discs.
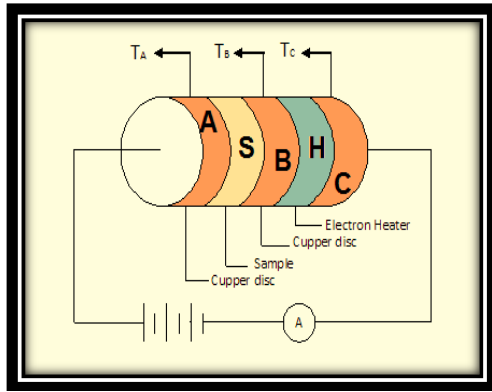
Fig.1: Electric circuit used in thermal conductivity instrument.

Firas, 2010 [6], studied the thermal conductivity measurement was done for specimens of Polystyrene/ titanium dioxide, Polycarbonate/ titanium dioxide and Polymethylmetha acrylate/ titanium dioxide composites for weight ratio of 1.9:0.1 and 1.8: 0.2 wt% for different thickness of the samples. The experimental results show that the thermal conductivity is increased with the increasing of thickness of layers and with the weight ratio of TiO_2.

Asutosh, (2013) [7], prepared the epoxy composites with high content of micro-filler (Al_2O_3) up to 22.1 vol. %. Experimental thermal conductivity tests were evaluated in each specimen and compared with the proposed model. The results show that the (Al_2O_3) particles show a percolation behavior at this volume fraction (16vol %) at which a sudden jump in the thermal conductivity is noticed

Sarah, (2014) [8], studied the effect of adding titanium dioxid (TiO_2) particles with average particles size (70.94 nm) and Alumina (Al_2O_3) with average particles size (65.05 nm) on the some mechanical and thermal properties. The results showed that the thermal conductivity increase with weight fraction increased of titanium dioxide nanoparticles alumina nanoparticles composite and hybrid.

Summit Bhanariya, (2015) [9], explained that effective thermal conductivity of Ep/TiO_2 composites

and showed that with increase in the TiO_2 content in the composite the effective thermal conductivity improves quite notably. This indicates that the incorporation of micro sized TiO_2 helps in the enhancing the heat conduction capability. The correlation proposed in this work provide value of effective thermal conductivity for different volume fraction of particulates are found to be in good consensus with the measured value. There is increase in the gap in-between the theoretical and experimental lines of magnitude of effective thermal conductivity.

Experimental part
1. Materials
The material used as matrix in preparing the composite materials is epoxy resin type (Polyprime EP from Hankl company) with a density 1.03 g/cm^3 and low viscosity. process foundation with particles be easier, The hardener relative to the resin are (1: 2) the duration of resin hardening is 48 hours at a temperature room degree as they are leaving it for two weeks so as to complete the processing (Full Curing) and then samples are cut up within the standard used in the search for the tests (r = 4 cm).

2. Reinforcement material
This study used two types of particulate materials, aluminum oxide (micro and nano) (Al_2O_3) and titanium dioxide (micro and nano) (TiO_2) have been mixing all the (micro and nano) with epoxy resin separately with weight percentages by (0.02, 0.04, 0.06 and 0.08 wt%), and then (Al_2O_3, TiO_2) crushed together by ratio (1:1) a mixing with epoxy s, to get on hybrid composite.

2.1 Aluminum dioxide (Al_2O_3)
Two kinds of aluminum dioxide micro (Al_2O_3) with different particles

sizes are used in this research. (Al_2O_3) micro particles' from England (RIEDEL-DE HAEN AG), (Al_2O_3) Micro particles' properties are shown in Table1. And (Al_2O_3) nanoparticles from China (MTI) company. (Al_2O_3) nanoparticles properties are shown in Table 2.

Table 1: Properties of micro alumina by the manufacturer.

Density	Purity	Particle Size	Type	Color
3.38 (g/m^3)	99.5%	3 (μm)	α	White

Table 2: Properties of nano alumina by the manufacturer.

Density	Purity	Particle Size	*Type*	Product
3.97 g/cm^3	> 99 %	20-30 nm	α	Al_2O_3 (white, alpha type, Crystalline Structure)

2.2 Titanium dioxide (TiO_2)

Two types of Titanium dioxide (TiO_2) with different particle sizes are used in this research: (TiO_2) Microparticals England supplied by a (AVOCHEM limited) company. (TiO_2) Microparticals properties are shown in Table 3. And (TiO_2) nanoparticals china supplied. (TiO_2) nanoparticals properties are shown in Table 4.

Table 3: (TiO_2) microparticals properties.

Density	Molecular mass	Type	Purity	Particle size	Color
4.23 (g/cm^3)	79.866 (g/mol)	Anatase	99.5	30 (μm)	White

Table 4: (TiO_2) nanoparticals properties.

Density	Purity	Particle size	Product
4.2 g/cm^3	99.8%	<50 nm	TiO_2 (white, Anatase type, Crystalline Structure)

Preparation of samples

Hand lay-up method was used for preparing the samples. First step: Preparation of molde. The molde used in the casting process is the base of each glass plates coated with thermal paper molde (so as to prevent the adhesion of the resin on plate of glass and easily manufactured by cutting output) with a high degree of subject plates equator (ensure flush surface mediated settlement balance) aspects of the molde of thickness glass rulers (6 mm).

Second step: molding of samples. The main method of preparation and casting of samples consist of the following steps as shown in Fig. 2: weighted amount of required epoxy proportion and hardener that added by ratio (1:2), weighted amount of additive materials (Al_2O_3 and TiO_2) micro, nanoparticles and hybrids in (0.02, 0.04, 0.06, 0.08) wt%, mixing addivite materials and matrix at room temperature. In a special pot mixing by the electric mixer to a maximum of $(1-10)$ min.

Pour liquid mixture to form a torrent in the middle of the molde so that the flow take place to all areas of ongoing

and regular template that the template is filled to the desired level.
The cured time takes (48) hours to hard and then put in oven with temperature

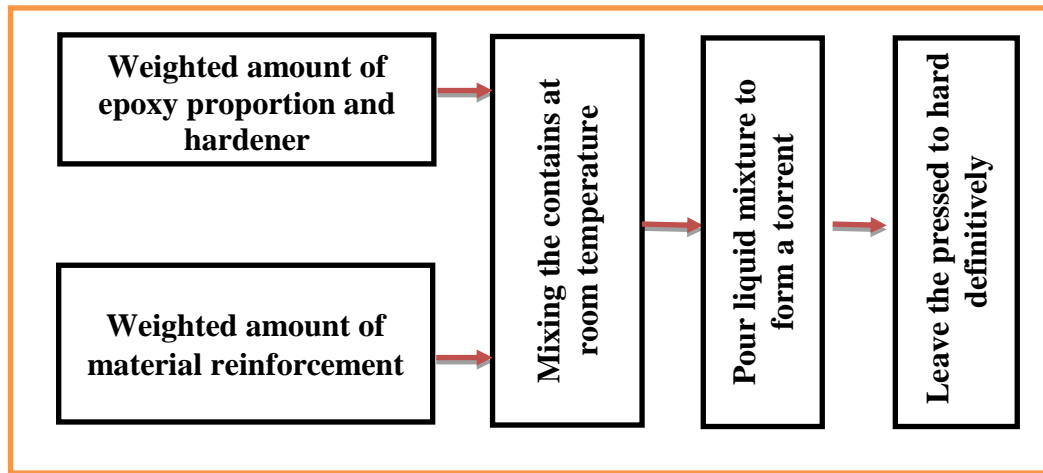50 ^{o}C for 5 hours to complete the formability.

Fig .2: Modeling of samples.

Third step: the samples cut in diameter according to specifications and global measurements (ASTM) for shows in

Table 5 of refinement with smooth sheets (silicon carbide) and different degrees of softness.

Table 5: Sample's dimensions of thermal conductivity.

Standard Specifications	*Sample's dimensions*	*Test*
Lees' Disk **ASTM**	6 mm $r = 40$ mm	*Thermal conductivity*

Thermal conductivity instrument
Lee's disc instrument is used to calculate thermal conductivity of the samples under test. The instrument which consists of three discs of brass and a heater. The heat transfers from the heater to the next two discs then to the third disc across the sample. The temperatures of the discs (T_A, T_B, T_C) as show in Fig. 1 can be measured with the thermometers which are located in them. The surfaces of these discs should be clean and well touched so as to obtain the optimum heat transfer through them.

After from (6.3 Volt) the power supply was supplied to the heater, the current value through the electrical circuit was about (0.23A), then the temperatures of the discs were recorded after reaching the thermal equilibrium (nearly after 120 min).
The values of thermal conductivity are calculated by applying the Eqs. (1 and 2).

Results and discussion
The values of thermal conductivity are calculated by Eqs. (1,2). To measure thermal conductivity of

samples in natural condition and after immersion (14 day) in a acidic solution of normality (0.3N).

Fig.4 shows thermal conductivity increases with increasing the weight fraction for micro and Nano (Al_2O_3) and hybrid (Al_2O_3 + TiO_2) before immersion.

The value of thermal conductivity for Al_2O_3 microparticals increases from 0.431 W/m.K at weight fraction 0.02 to value 0.54 W/m.K at weight fraction 0.08, while for (Al_2O_3) nanoparticles the thermal conductivity increases from 0.5242 W/m.K at 0.02 to value 0.5812 W/m.K at weight fraction 0.08 (wt%),

Its notice from that the value thermal conductivity for Al_2O_3 nanopartecals samples more than that Al_2O_3 microparticles for the same weight fraction.

The reason of that is related to the grain size of nano particle which permeate into the matrix (Epoxy) this helped to high stacking density of Al_2O_3 nanopartecals, which leads to reduce air spaces already exist in composite material this results in reduced air spaces that function as

insulator so increasing thermal connectivity of composite and this agree with [10], as (k) dependent on the density of insulation.

Also from Fig. 4 it was found that thermal conductivity for TiO_2 micro particulate and TiO_2 nanoparticals decrease with increasing the weight percentage.

Thermal conductivity value of TiO_2 microparticals 0.4826 W/m. K at 0.02 (wt%) decrease to 0.3723W/m.K at 0.08 weight fraction (wt), while for (TiO_2) nanoparticals the thermal conductivity decrease from 0.5495 W/m.K at 2% to value 0.4296 W/m.K at 0.08 weight fraction (wt%).

The reason that when adding TiO_2 micro particulate to epoxy resin lead to reduces the structural vibrations of epoxy resin caused by high temperature and this leads to lower thermal connectivity value, and when increase weight fraction of particulate TiO_2 in composite material lead that to reduces thermal conductivity because TiO_2 microparticals is lousy of heat conduction due to being a ceramic oxide. This agree with [11].
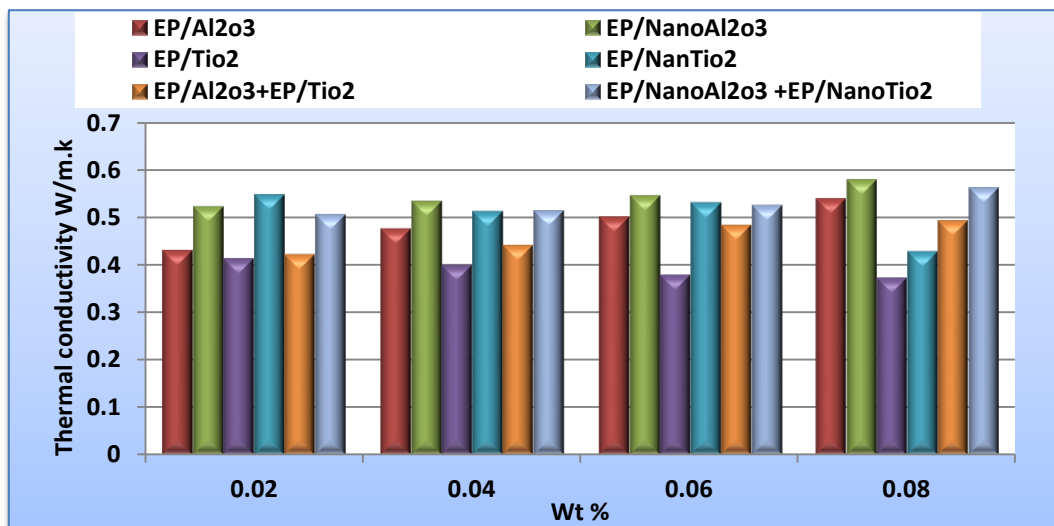

Fig. 4: Thermal conductivity value before immersion with weight percentage for (EP/Al₂O₃ & EP/TiO₂) composites.

After immersion in chemical solutions (HCl) from Fig. 5. Notice that (k) values increasing with the time of immersion and because it was due to enter the acidic solution (HCl) through the interfacial and cracks already exist in the material, working on poor of powerful molecular binding for matrix and bonds relaxant result the increase in plasticity of matrix where heat transfer is by rotational motion and vibrations for molecular chains, and as a result of bonds relaxant increasing molecular chains scalability on movement as well as the interaction of chemical solutions of material degradation which increases the thermal conductivity, this results agree with [12].
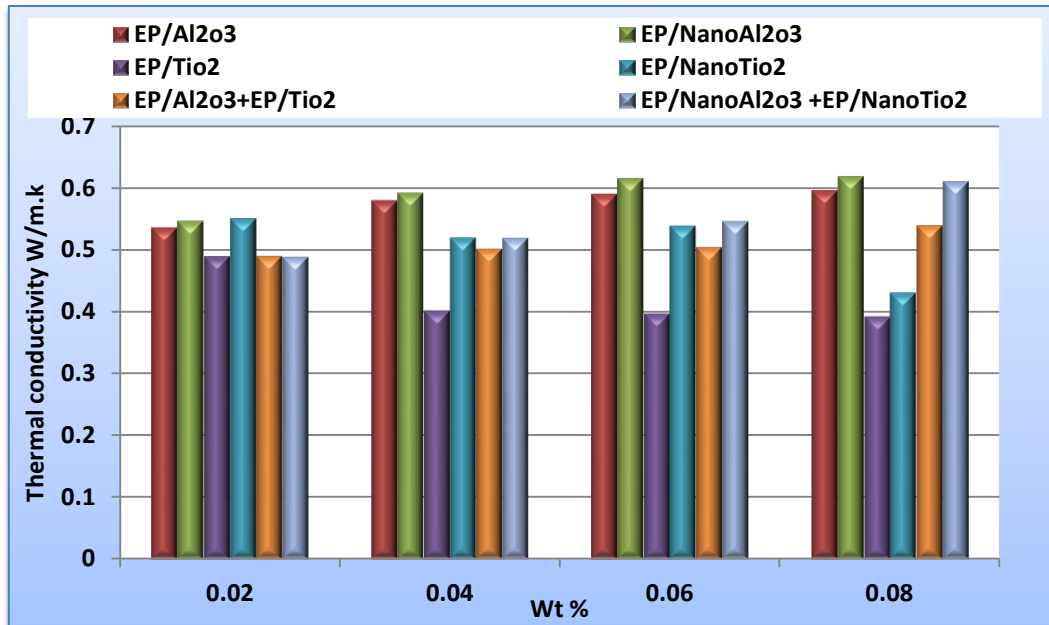

Fig. 5: Thermal conductivity vis weight percentage for (EP/Al₂O₃ &EP/ TiO₂) composites after immersion in (HCl).

Conclusions

Thermal conductivity (k) increases with increasing the weight fraction for EP/Al_2O_3 micro and Nano and hybrid $(EP/Al_2O_3 + EP/TiO_2)$ before immersion in (HCl) for time (14day), and decrease with increasing the weight fraction value forTiO_2 microparticales and nanoparticls, while after immersion in chemical solutions (HCl) that (k) increasing with time of immersion. The composite (EP/TiO_2) showed best value of thermal conductivity at weight percentage 0.08 was 0.3723 W/m.K and less value was 0.4126 W/m.K at weight percentage 0.02.

References

[1] Mikell P. Groover, (1996) "Fundamentals of Modern Manufacturing", prentice- Hall, Upper Saddle River, New Jersey.

[2] Petrtti Auerkari, (1996) "Mechanical and Physical properties of engineering alumina ceramics".

[3] Kop ،Erhan, (2007) "Synthesis and characterization of mechanical, thermal and flammability properties of epoxy based nanocomposites", M.Sc. Thesis, Chemical Engineering Department, University of Middle East Technical.

[4] Sandhya. K.P. (2014) "Synthesis, Characterization and Applications of

Hybrid Nanocomposites of TiO_2 with Conducting Polymers" Ph.D, Department of Applied Chemistry, Cochin University of Science and Technology, Cochin - 682 022, Kerala

[5] Bhatnagar M.S., (2004) "A Textbook of Polymers, [Chemistry and Technology of Polymers], (Processing and Applications)", Volume II, S. Chand & Company Ltd, 1st Ed.,

[6] Firas J. Al-Maliki, Iraqi Journal of Physics, 8, 12 (2010) 29 – 32.

[7] Asutosh Panda, "A Study on thermal conductivity of Epoxy/Al_2O_3 composites" M.Sc. Thesis. Department of Mechanical Engineering, National Institute of Technology Rourkela, India, (2013)

[8] Sarah Khudair Taha, "Study some of mechanical and thermal conductivity properties of Epoxy-TiO_2 and Al_2O_3 nanocomposites and their Hybrid composites" M.Sc. Thesis. University of Baghdad. Iraq, (2014).

[9] Sumit Bhanariya, (2015) "An assessment of effective thermal conductivity of Epoxy – TiO_2 composites" M.Sc. Thesis. Department of Mechanical Engineering . National Institute of Technology. Rourkela – 769008. India. June.

[10] Abd, Muhannad Mahdi, (2012) "Comparsion study of some mechanical and dielectrical properties of TiO_2 and SiO_2 (nano – micro particles /Epoxy composites", Ph.D., University of Baghdad.

[11] P.I. Ten, M. Janfar, H.M. Akil, K.N. Seetharmn, A.N.R wagiman, K.S.Beh., 19, 4 (2008) 308-315.

[12] Ali Hassen, "The study of the mechanical and thermal behavior of hybrid composites materials", Department of Applied Sciences - University of Technology. (2002)