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An Experimental Investigation on Thermal Conductivity of Epoxy/Zirconia Composites

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Abstract— An experimental study of the heat-transfer process within epoxy matrix composite filled with micro-sized zirconia particles are proposed in this paper. The composites are fabricated using simple hand lay-up technique for a wide range of filler content. The thermal conductivity values of all sets of fabricated composites are measured experimentally using Unitherm Model 2022. The tests are in accordance with ASTM E-1530 Standard. The result shows that the effective thermal conductivity (k_{eff}) increases with increase in the volume fraction of the zirconia in the epoxy matrix. The measured values are compared with the value obtained from numerical simulation. The simulated and experimental values are than compared with calculated effective thermal conductivity values obtained from other established correlations as well for validation. From the study, it is found that the numerical values are in good agreement with the experimental value whereas various theoretical models are far from satisfaction. This study reveals that the incorporation of zirconia particles results in enhancement of thermal conductivity of epoxy thereby increasing its heat transportation capability.

Key words: Polymer Matrix Composites, Epoxy, Zirconia, Thermal Conductivity, Numerical Simulation

I. INTRODUCTION

The trends approaching towards faster and denser electronic circuit are pushing the limits of conventional packaging materials. The average distance between the components reduces due to integration of large number of components on a single chip.

However, this performance and functions of a chip have come with a hidden cost i.e. heat. The heat produced by modern electronic components is greater and more highly concentrated as a higher clock speed, greater power and reduced size. Such overheating reduces the reliability of integrated chips or sometimes may also cause permanent damage. Therefore, it is desired to keep the temperature of electronic components below its critical value to avoid any permanent damage. As it is known, the trend in packaging electronic systems has been to reduce size and increase performance. Since there is a need of high performance and small size of electronic components, installation of separate heat sinks is not an option anymore. In addition, materials with their coefficients of thermal expansion similar to those of ceramic substrates and semiconductors are favorable to minimize the thermo-mechanical stresses. Hence, it is desired that the entire packaging of electronic devices must be made out of materials that can provide heat dissipation, package protection and power distribution. In other words, these need to develop advanced composite materials that are fabricated to meet the requirements of the electronic packaging or other heat management solutions.

Reports are available in the existing literature on experimental as well as numerical and analytical studies on thermal conductivity of some filled polymer composites. Most of the work was conducted taking metal powder as filler material. In this series, Rusua et al. [1] first used zinc powder as filler material and found appreciable increase in the thermal conductivity. Later Mamunya et al. [2] also reported the improvement in electrical and thermal conductivity of polymers filled with metal powders. Further Boudenne et al. [3] used aluminium as filler material in polypropylene matrix for improvement in thermal conductivity of the matrix body. Later they further went with similar study and this time they had taken copper as filler material for the improvement of thermal conductivity of polypropylene composites [4].

Carbon-based fillers with high thermal conductivity and low density appear to be the most promising fillers. Graphite, carbon fiber and carbon black are well-known carbon-based fillers. Graphite is considered as the best conductive filler because of its good thermal conductivity and low cost [6]. Carbon fiber, typically vapor grown carbon fiber (VGCF), is important carbon-based filler [6]. Studies conducted on modified thermal conductivity of polymer composites filled with carbon nanotubes have recently been reviewed by Han and Fina [7].

Metallic and carbon-based fillers are highly conductive thermally, but they are highly electrically conductive as well. There are certain areas where high thermal conductivity is required but at the same time electrical resistivity is of prime importance, like in electronic devices. Ceramic powder reinforced polymer materials have been used extensively for such applications because of their high thermal and low electrical conductivity. Some promising ceramic fillers such as SiC, AlN, Al_2O_3 and ZnO [8, 9] are in use to improve thermal conductivity of various polymers. In a more recent work Agrawal et al. [10] found increase in the value of thermal conductivity and glass transition temperature whereas decrease in the value of coefficient of thermal expansion for epoxy/AlN composites and polypropylene/AlN composites. They also reported that for wide range of filler content, dielectric constant of the composite remains constant for both sets of composites. Incorporation of multiple fillers into the polymer matrix for the improvement of thermal conductivity has also been reported.

A numerical approach to evaluate the effective thermal conductivity of granular or fibrous reinforced composite materials was proposed by Veyret et al. [11], whereas Kumlutas and Tavman [12] have developed a numerical model for particulate filled polymers which shows good agreement with the experimental values. Nayak et.al [13] has reported on the modified thermal conductivity of pine wood dust filled epoxy based composites using computational method.

Numerous theoretical and empirical models have been proposed in the past to estimate and predict the effective thermal conductivities of particulate filled composites. Comprehensive review articles have discussed the pertinent applicability of many of these analytical models. The simplest alternative for a two-component composite system would be with the arrangement of materials in either parallel or series with respect to heat flow which gives the upper or lower bounds of effective thermal conductivity.

For series conduction model [14]

$$\frac{1}{k_c} = \frac{1-\phi_f}{k_m} + \frac{\phi_f}{k_f} \qquad (1)$$

Where, k_f, k_m, k_c are thermal conductivities of filler, composite matrix and conductivity of the composite as a whole and Φ_f is volume fractions of filler.

The correlation represented by Equations (1) is derived on the basis of the rules-of-mixture.

Maxwell [15] has obtained an exact expression for thermal conductivity, using potential theory for an infinitely dilute composite of spherical particulates dispersed randomly and devoid of mutual interaction in a homogeneous medium, which is given by

$$k_c = k_m \left[\frac{k_f + 2k_m + 2\phi_f (k_f - k_m)}{k_f + 2k_m - 2\phi_f (k_f - k_m)} \right] \qquad (2)$$

Eq. (2) is well known for dilute composites which is the earliest flux law in which a cube of suspension for a single particle was considered.

Lewis and Nielsen [16] derived a semi-theoretical model for a two phase system which assumes an isotropic particulate reinforcement and also takes into consideration the shape of particle as well as its orientation

$$k_c = k_m \left[\frac{1 + AB\phi}{1 - B\phi\psi} \right] \qquad (3)$$

Where,

$$B = \left[\frac{(k_f/k_m) - 1}{(k_f/k_m) + A} \right] and, \psi = 1 + \left[\frac{1-\phi_m}{\phi_m^2} \right]$$

Zirconia powder with a moderate thermal conductivity and low cost therefore emerges as a suitable filler material to be used in polymeric materials. In view of this, in the present work, zirconia is chosen as the ceramic filler to be dispersed within epoxy resin. The objective of this work is to analyze the heat transfer through the ZrO_2-epoxy composites and to evaluate the equivalent thermal conductivity of these composites by numerical methods. It reports the estimation of the equivalent thermal conductivity of this particulate-polymer composite system using finite element method. Later, the numerically obtained values are compared with the values obtained from theoretical model.

II. MATERIALS AND METHODS

A. *Material considered*

Matrix materials are the base of composite fabrication. The presently used matrix is a thermoset polymer epoxy. The epoxy resin Lapox-12 is used in the present work which belongs to the epoxide family. Bisphenol-A-Diglycidyl-Ether (commonly abbreviated to DGEBA or BADGE) is the common name of the presently used epoxy resin. It provides a solvent free room temperature curing system when it is combined with the hardener tri-ethylene-tetramine (TETA) which is an aliphatic primary amine with commercial designation HY 951. The various physical and mechanical properties of epoxy resin are presented in Table 1.

Characteristic Property	Values	Units
Density	1.1	g/cm^3
Tensile strength	50	MPa
Cross breaking strength	130	Mpa
Impact strength/Energy	17	kJ/m^2
Thermal conductivity	0.363	W/m-K
Coefficient of thermal expansion	5.80×10^{-6}	/^{o}C

Table 1: Important Properties of Epoxy Resin

Zirconium dioxide (ZrO_2), sometimes known as zirconia (not to be confused with zircon), is a white crystalline oxide of zirconium. Its most naturally occurring form, with a monoclinic crystalline structure, is the mineral baddeleyite. A dopant stabilized cubic structured zirconia, cubic zirconia, is synthesized in various colours for use as a gemstone and a diamond simulant. Zirconia is chemically unreactive. Zirconium dioxide is one of the most studied ceramic materials. Zirconia adopts a monoclinic crystal-structure at room temperature and transitions to tetragonal and cubic at higher temperatures. The main reason for the selection of zirconia in present study is because of its good thermal conductivity (16.7 W/m-K) and low cost.

B. *Composite Fabrication*

Composite samples of various compositions are prepared by hand lay-up technique. Hand lay-up technique is the oldest and simplest technique for composite fabrication. The epoxy-zirconia composites are prepared in the following steps:

– Uncured epoxy and its corresponding hardener are mixed in a ratio of 10:1 by weight as per recommendation.
– Micro-sized zirconia particles are mixed with the epoxy in different proportions.
– The uniformly mixed dough (epoxy filled with zirconia) is then slowly decanted into the glass molds so as to get disc type specimens (diameter 50 mm and thickness 3 mm) coated beforehand with wax and a uniform thin film of silicone-releasing agent.
– The castings are then left at room temperature for about 24 hours and then the glass molds are broken and the samples are released.

Composite samples of 6 different compositions with varying zirconia content are made and are shown in table 2.

S. No.	Composition
1	Neat epoxy
2	Epoxy + 1.41 vol % ZrO_2
3	Epoxy + 3.35 vol % ZrO_2
4	Epoxy + 5.236 vol % ZrO_2
5	Epoxy + 7.85 vol % ZrO_2
6	Epoxy + 9.42 vol % ZrO_2
7	Epoxy + 11.31 vol % ZrO_2

Table 2: Epoxy Composites Filled with Micro-Sized Zirconia Powder

C. *Thermal Conductivity Characterization*

Thermal conductivity of a variety of materials is measure by The Unitherm Model 2022 .These materials are polymers, composites, ceramics, glasses, rubbers, some metals and other materials of low to medium thermal conductivity. Only simple relatively small test sample is required. Non-solids, such as pastes or liquids can be tested using special containers. Thin films can also be tested accurately using a multi-layer technique. The tests are in accordance with ASTM E-1530 Standard.

A sample of the material which is tested is held under a uniform compressive load between two polished surfaces, each controlled at a different temperature. The lower surface of sample is part of a calibrated heat flow transducer. The heat flows from the upper surface, to the lower surface, through the sample, so that an axial temperature gradient is established in the stack. After reaching thermal equilibrium, the temperature difference across the sample is measured along with the output from the heat flow transducer. These values and the sample thickness are then used to calculate the thermal conductivity. The temperature drop through the sample is measured with temperature sensors in the highly conductive metal surface layers on either side of the sample. For one-dimensional heat conduction the formula can be given as equation 4

$$Q = kA\frac{T_1 - T_2}{x} \qquad (4)$$

Where Q is the heat flux (W), K is the thermal conductivity (W/m-K), A is the cross sectional area (m2) T_1-T_2 is the difference in temperature (K), x is the thickness of the sample (m). The thermal resistance of a sample can be given as

$$R = \frac{T_1 - T_2}{Q} \qquad (5)$$

Where, R is the resistance of the sample between hot and cold surfaces (m2-K/W). From Equations 4 and 5 we can derive that.

$$k = \frac{x}{RA} \qquad (6)$$

In Unitherm model 2022, use the heat flux transducer which measures the Q value and between the upper plate and lower plate the temperature difference can be obtained. Thus the thermal resistance of sample can be calculated between in the upper and lower surfaces. The thermal conductivity of the samples can be calculated using the input value of thickness and taking the known cross sectional area, the thermal conductivity of the sample can be calculated using equation 6.

D. *Numerical Method*

The Finite Element Method (FEM), originally introduced by Turner in 1956, is a powerful computational technique for approximate solutions to a variety of "real-world" engineering problems having complex domains subjected to general boundary conditions. FEM has become an essential step in the design or modeling of a physical phenomenon in various engineering disciplines. The basis of FEM relies on the decomposition of the domain into a finite number of sub-domains (elements) for which the systematic approximate solution is constructed by applying the variation or weighted residual methods. In effect, FEM reduces the problem to that of a finite number of unknowns by dividing the domain into elements and by expressing the unknown field variable in terms of the assumed approximating functions within each element. These functions (also called interpolation functions) are defined in terms of the values of the field variables at specific points, referred to as nodes. Nodes are usually located along the element boundaries and they connect adjacent elements. The ability to discretize the irregular domains with finite elements makes the method a valuable and practical analysis tool for the solution of boundary, initial and eigen value problems arising in various engineering disciplines.

III. RESULTS AND DISCUSSION

A. *Numerical Model*

1) *Description of the problem*

Using the finite-element program ANSYS, thermal analysis is carried out for the conductive heat transfer through the composite body. In order to make a thermal analysis, three-dimensional physical models with spheres-in-a-cube lattice array have been used to simulate the microstructure of composite materials for different filler concentrations. Furthermore, the equivalent thermal conductivities of these epoxy composites filled with micro size zirconia particle up to about 11.3% by volume is numerically determined using ANSYS.

2) *Assumptions*

In the analysis of the ideal case it will be assumed that

- The composites are macroscopically homogeneous.
- Locally both the matrix and filler are homogeneous and isotropic.
- The thermal contact resistance between the filler and the matrix is negligible.
- The composite lamina is free of voids.
- The problem is based on 3D physical model.
- The filler particles are in a square periodic array/uniformly dispersed in matrix.

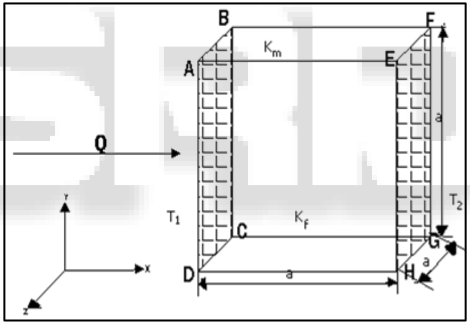

Fig. 1: Boundary conditions

B. *Numerical Analysis*

In the numerical analysis of the heat conduction problem, the temperatures at the nodes along the surfaces ABCD is prescribed as T_1 (=100^0C) and the convective heat transfer coefficient is assumed to be 2.5 W/m^2-K at ambient temperature of 27°C. The heat flow direction and the boundary conditions are shown in Fig. 1. The other surfaces parallel to the direction of the heat flow are all assumed adiabatic. The temperatures at the nodes in the interior region and on the adiabatic boundaries are unknown. These temperatures are obtained with the help of finite-element program package ANSYS. Thermal conductivities of epoxy composites filled with micro size zirconia particles up to 11.3 % by volume are numerically estimated by using the spheres-in-cube model. A typical 3-D model showing arrangement of spherical fillers with a particle concentration of 3.35 vol% within the cube shaped matrix body is illustrated in Fig. 2. The temperature profiles obtained from FEM analysis for the composites (spheres-in-cube arrangement) with particulate concentrations of 1.4, 3.35, 5.236, 7.85, 9.42 and 11.31 vol. % are presented in Fig. 2.

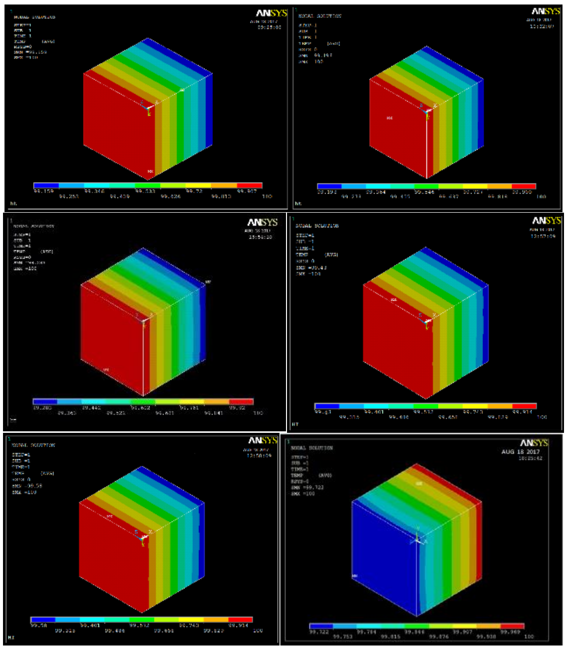

Fig. 2: Temperature profile for composite with particle ranging from 1.41 to 11.31 vol%

C. *Comparison of values obtained from different methods*

The numerical results are compared with the experimental results and also with the values calculated using some of the existing theoretical and empirical models. Rule of mixture model, Maxwell's equation and Lewis and Nielsen's equation are presented in Table 3. It presents a comparison among the results obtained using these models with regard to the corresponding values of equivalent conductivity obtained by numerical simulation as well as experimentally determined values. Similar comparison of simulated values of thermal conductivity of the composites obtained by FEM, analytical model and measured values are presented graphically as shown in Fig 3.

Sr. No	Zirconia particles (vol. %)	Equivalent thermal conductivity of the composite [W/mK]				
		Rule of mixture model	Maxwell model	Lewis and Neilson model	FEM values	Experimental Result
1	1.41	0.368	0.377	0.375	0.385	0.382
2	3.35	0.375	0.398	0.393	0.410	0.405
3	5.236	0.382	0.418	0.412	0.442	0.432
4	7.85	0.393	0.449	0.441	0.494	0.478
5	9.42	0.399	0.468	0.459	0.584	0.562
6	11.31	0.408	0.492	0.483	0.654	0.628

Table 3: Equivalent Thermal Conductivities Obtained From Different Methods

It is evident from this figure that there is appreciable increase in thermal conductivity as the concentration of zirconia particle is increasing. It is also clear that the FEM results are in better agreement with the experimental results in comparison to those obtained from other theoretical models.

Though the results obtained from Lewis and Neilson model are giving better results as compare to the other theoretical models but still it is far from satisfaction when the experimental results are compared with the value obtained from the finite element method simulation. It is noticed that while the FEM analysis can very well be used for predictive purpose in determining the equivalent thermal conductivity for a wide range of particle concentrations. The difference between the simulated values and the measured value of conductivity may be attributed to the fact that some of the assumptions taken for the numerical analysis are not real. The shape of zirconia particle is assumed to be spherical, while in actual practice they are not perfectly spherical.

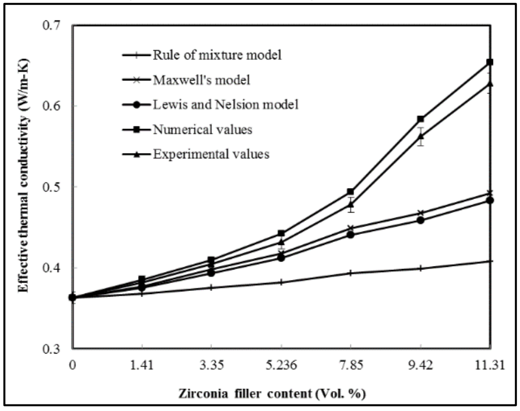

Fig. 3: Equivalent Thermal conductivity from different methods

Moreover, although the distribution of zirconia particulates in the matrix body is assumed to be in an arranged manner, it is actually dispersed in the resin almost randomly. However, it is encouraging to note that the incorporation of zirconia particle results in enhancement of thermal conductivity of epoxy resin. With addition of 1.4 vol. % of zirconia particle, the thermal conductivity improves by about 5.23 % and with addition of 11.31% of zirconia particle the thermal conductivity improves by about 73 % when compared with neat epoxy resin. It can be seen from the graph that for less filler concentration, the slope of the curve is less and as the filler volume fraction increases, the curves representing FEM and experimental values become steeper. It might be due to the fact that with increase in filler concentration, the inter-particle distance reduces and the conductive chains begin to form which increase the thermal conductivity quite reasonably.

The percentage errors associated with the FEM values and with values obtained from theoretical models with respect to the experimental values is given in Table 4. It is seen from this table that for low volume fraction of filler the entire model are in good agreement with the experimental values but as the volume fraction of the filler is increasing deviation between the values obtained from the models and the experimental values are registered. It can be seen that while the errors associated with rule of mixture model goes up-to 35.1 % as the filler content rises to 11.31 % and Maxwell's model and Lewis and Neilson model shows maximum error percentage of around 21 % and 23 % respectively.

Sr. No.	Equivalent thermal conductivity associated error (%)			
	Rule of mixture model	Maxwell's model	Lewis and Neilson model	FEM Simulation
1	3.66	1.30	1.83	0.78
2	7.40	1.72	2.96	1.23
3	11.57	3.24	4.63	2.31
4	17.7	6.06	7.74	3.34

5	29.0	16.7	18.3	3.91
6	35.1	21.6	23.1	4.14

Table 4: Percentage Errors with Respect to the Experimental Values

The value obtained from FEM simulation are in closest approximation with the experimental values where the maximum error percentage goes to around 4.14 % which is well within range as compared to the other existing correlations. It leads to a conclusion that for a particulate filled composite of this kind the FEM can very well be used for predictive purpose in determining the equivalent thermal conductivity for a wide range of particle concentration

IV. CONCLUSIONS

This numerical and experimental investigation has led to the following specific conclusions:

- The addition of conductive fillers in the polymer matrix is an effective way to increase thermal conductivity of polymers for several industrial applications.
- Successful fabrication of epoxy composites filled zirconia particles by hand lay-up technique is possible.
- Finite element method (FEM) can be gainfully employed for determination of effective thermal conductivity of these composites with different amount of zirconia content.
- A good agreement of FEM results with those obtained from experimental efforts validates the usefulness of this numerical method.
- Incorporation of zirconia particles results in increase of thermal conductivity of epoxy and thereby improves its conduction capability. With addition of 1.41 vol% of ZrO_2 particle (100 micron size), the thermal conductivity increases by about 5 % as compared to neat epoxy and it increases by as high as 73 % by adding 11.31 % of same particle.

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