Journal of Mines, Metals and Fuels, *71 (12A) : 86-90; 2023. DOI: 10.18311/jmmf/2023/45496*

Print ISSN : 0022-2755

Journal of Mines, Metals and Fuels

Contents available at: *www.informaticsjournals.com/index.php/jmmf*

Thermal Properties of Epoxy-GNP Based Nano-Dielectrics

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Abstract

This study highlights the thermal properties of nano-dielectrics materials composed of epoxy resin host and Graphene nano-platelets (GnP) have been studied. The introduction of the GnP nano-platelets (0.5, 1, 2, 3 and 5wt %) into the epoxy resin by the three roll mill technique following the Caframo mechanical mixer method is described. Asilane Coupling Agent (SCA) was used for the surface modification for better dispersion of filler in organic polymer matrix and for better compatibility between nano-platelets and host material. Thermal conductivity, glass transition temperature and thermal stability of nano-dielectrics were investigated based on the filler content. The synergistic effect was observed due to the introduction of GnP. The high-k nano-dielectric materials show better thermal conductivity and stability than that of the pure epoxy resins. The best performance of the composite is observed with 3wt% of graphene nano-platelets.

Keywords: *Graphene, Nano-dielectrics, Thermal Conductivity, Three Roll Mill*

1.0 Introduction

Fiber Reinforced Polymer (FRP) composites are better than traditional materials due to lesser weight, higher strength more stiffness, higher resistance to corrosion and fatigue. Also, these composites are more susceptibility to lightning strikes due to poor electrical, thermal and electromagnetic properties. Therefore, the present study is focused more on the lightning strike. However, using these composites in aircraft not only increase the additional weight but also reduces the performance of the aircraft[1]. Epoxy resin (Epon828) is one among the important matrix system commonly using in the advanced fiber reinforced polymer composites because of higher strength and stiffness, good dimensional stability, lesser shrinkage, better adhesion to different variety

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of nanofillers, fibers and better mechanical properties. The greater number of studies are made to observe the improvement of the multifunctional properties of the composites by addition of nano size fillers like carbon nanotube, graphene etc. GnP is the thinnest and strongest material. It consists of thick planner sheet type of carbon atoms which are arranged like honey comb type crystal structure[2]. Graphene is found to have unique features: superior electrical and thermal conductivities and because of platelet structure it offers superior vapor barrier properties[3] similar to nanoclay[4,5]. It is inexpensive and having better electrical, mechanical, thermal and barrier properties as graphene. It is observed that addition of small amount of nano size fillers improves some of the electrical, thermal and mechanical properties of the matrix systems. Therefore, GnP was chosen as a potential material for improving multifunctional properties of FRP composites.

A wide variety of processing techniques were explored to disperse graphene into polymer systems using conventional techniques like mechanical type mixing, sonication and the three roll mill. Drzal and Fukushima[6] have used sonication method. They reported percolation of less than 5wt% or about 2 wt%. Monti and coworkers[7] and Wajid and coworkers[8] have also used sonication method. They have observed significant electrical conductivity improvement at low loading (0.5-1.0 wt%) percentages. They have used a solvent as carrier and then removed it by evaporation and observed better improvement of grapheme dispersion in epoxy. However, they reported removal of solvent may degrade some mechanical properties of the matrix. Also, they observed the solvent evaporation takes longer times and this increases the re agglomeration of graphene platelets. To overcome this problem, Wajid and coworkers have incorporated a third material known as Polyvinyl Pyrrolidone (PVP) which may further degrade some mechanical properties of the modified composites. However, they have observed better improvement in tensile modulus and yield strength at 1wt% graphene. Prolongo and coworkers[3] have used sonication and three roll mill methods and have observed percolation occurrence at 5wt. %. According to the author there is very little reported data on three roll mill dispersion of graphene at lower loading of about 0.5-1.0 wt% percentage. However, Thostenson and Chou[9] and other researchers have used three roll mill methods for dispersion of CNT in epoxy effectively. They have observed the better improvement of CNT/epoxy nanocomposites electrical conductivity. By adding of small percentage of conductive graphene it is possible to convert epoxy in to a semiconductor and thus improve the conductivity of carbon/epoxy composites by few log cycles, however, it may not possible to make it conductive like metals. This implies that graphene modified carbon/epoxy is likely to be in the semi-conducting range.

The important objective of this research work is to find and analyze the thermal conductivity and thermal stability and also to address the thermal dissipation problems by developing a high performance polymer composite.

2.0 Experimental

2.1 Material

EPON 828 type epoxy resin system used because of wide range of applications in the advanced composite structures filed. An aromatic amine curing agent (Epicure W) with Amine Hydrogen Equivalent Weight (AHEW) of 43-46 g/mol was used as a curing agent. The matrix to curing agent mixing ratio of 100:26.4 by weight was used. Resin and the curing agent used in this experiment are manufactured by USA based M/s Miller-Stephenson Inc. xGnP M-25 (Graphene nanoplatelets) used in this experiment is manufactured by M/s XG Sciences Inc., USA. It is found that the xGnP having a maximum of 3wt. % of silica as impurity. Also, the average platelets diameter found to be about 25 µm.

2.2 Fabrication of Composites

Graphene-epoxy nanocomposites were prepared using three roll mill methods. The EXAKT 80E, a commercially scaled laboratory three roll mill manufactured by M/s EXAKT Technologies Inc. used in this fabrication procedure. It has 80mm diameter and 200mm length three chrome coated plated hard steel rolls. The processing control parameters such as start gap setting, final gap setting, RPM and number of passes at every gap setting are considered in this method to observe effective dispersion of nano platelets into a polymer system. Effective processing parameters were identified through several experiments. Gap settings start of 40µm and its progressive reduction to 30 and 25µm at 200rpm and passed three times at every gap setting were found to be good for better dispersion of graphene into epoxy

mixture. After dispersing of graphene in the epoxy resin, epicure W curing agent was added and mixed at the rate of 500rpm for the duration of 10 minutes using Caframo make mechanical mixer. Before curing, the epoxy resin was modified and transferred to aluminum mold of diameter 90mm and then degassing at 60°C for 30 minutes in order to remove air bubbles. Curing of both base and epoxy-GnP nanocomposites samples done in aluminum mold for the duration of about 2.5 hours at 177 °C temperature.

3.0 Measurement

The thermal conductivity heat flow measurement system (Unitherm TM Model-2022) was used to evaluate thermal conductivity of the nanocomposite samples as per ASTME-1530 standard. The sample of size 3±0.35mm thickness and 50mm diameter was placed between two polished surfaces by different temperature controllers under uniform compressive load. The lower polished surface consisting of calibrated transducer for heat flow measurement. The establishment of the temperature axial gradient at stack was observed due to flow of heat from upper surface to lower surface in the sample. The difference in the temperature across the sample is measured using the transducer heat flow output at thermal equilibrium. The thermal conductivity was calculated using temperature difference value and the sample thickness. The temperature variation in the sample was measured using temperature sensing elements placed at the metal conductive surfaces on both sides of the sample. Using these values, the thermal conductivity was calculated using the equation:

$$kc = \frac{Q * l}{A(T1 - T2)} \text{ W / mk} \quad (1)$$

wherein, Q represents the heat flow in W, A represents the area of cross section in m^2, (T_1-T_2) represents the temperature difference between upper and lower plate in Kelvin and lre presents the thickness of the sample in mm.

3.1 Theoretical Approach

The thermal conductivity was calculated using the Maxwell model equation:

$$kc = km\frac{Kf + 2Km + 2\phi(Kf - Km)}{kf + 2km - (kf - km)} \quad (2)$$

Wherein, k_c, k_m and k_f are represents the composite, matrix and fillers effective thermal conductivities respectively, and, φ represents the fraction of the volume inclusions. This model was developed considering lower fraction volume of the filler phase in the matrix system for lower dispersion.

3.2 Thermal Conductivity of Epoxy-GnP Nanocomposite Using FEM Model

Finite element method is one of the important techniques used to find the numerical solution for a wide range of physical problems. A complete finite element analysis is based on the logical interaction consisting of the three stages of computation. The systematic development of the input data file is presented in this section. In the 3D model, the heat flux was analyzed only in x-direction. A constant temperature was considered along the block surface which is perpendicular to the direction of x with one of the surface set at 220°C and the other one set at 25°C. The surfaces of the other block, which is parallel to the direction of x were considered as adiabatic. It is observed that the transfer of heat due to conduction in the block and it is found to be steady-state problem. Flux density heat was determined using FEM technique and the nano-composite thermal conductivity (λ) was calculated using the equation (3):

$$\lambda = \frac{\phi X d}{\Delta T} \quad (3)$$

Wherein represents the flux density of the heat in the x-direction, d represents the block thickness in the x-direction and ΔT represents the difference in temperature at the surfaces of the perpendicular to the x direction.

3.3 Thermogravimetric Analysis

The thermogravimetric analyzer (TGA) model Q50 of TA instruments were used and it was operated in nitrogen atmosphere. The flow of nitrogen gas was monitored as per ASTM D 3850 - 06. The composites relative thermal stability was calculated based on the decomposition temperatures comparison at different weight loss percentages. The thermograms recorded was carried out in the presence of nitrogen environment at 10°C/min scanning rate in the range of temperature from ambient to 800°C. A sample of mass of about 6-8 mg was used for the experiments. The instrument was first calibrated using sample of pure calcium oxalate.

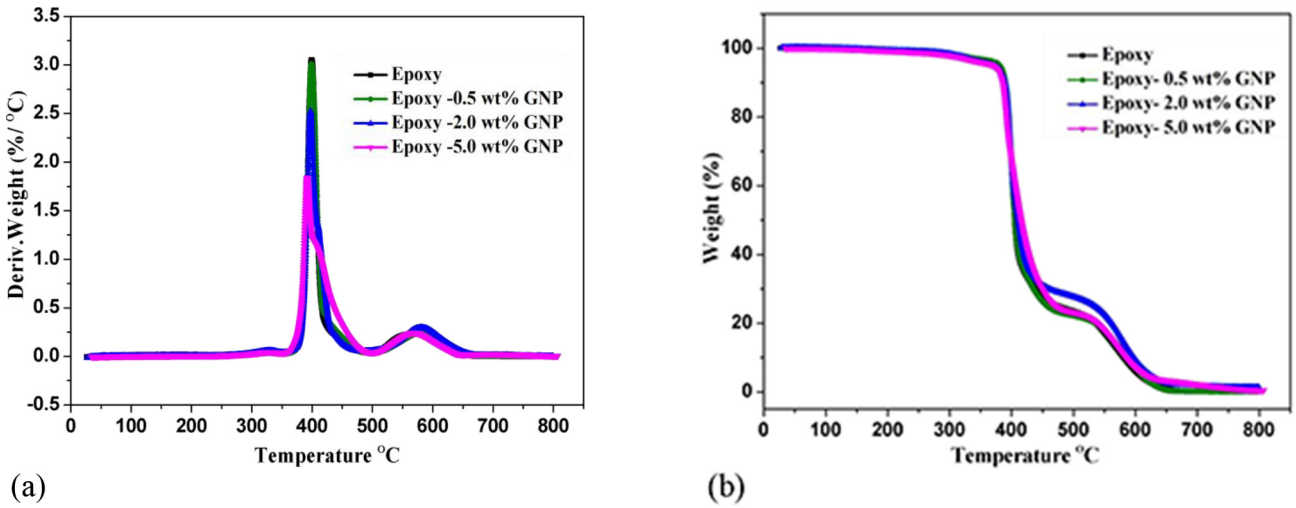


Figure 1: (a) TGA and (b) DTG curves of the epoxy-GnP nano composites.

4.0 Results and Discussions

4.1 Thermal Conductivity

The analytical results obtained from the Maxwell model (Equation 2), Finite Element Model (FEM) and the experimental results are tabulated together for comparison, and are shown in Table 1. The result obtained both from Maxwell model and FEM agree with the experimental results obtained. Based on the assumptions made, a better correlation of experimental data is achieved with Maxwell model rather than the FEM model. It is also observed that the thermal conductivity increases with grapheme content in the epoxy increases. The change in the thermal conductivity appears to be linear. But a sharp percolation threshold is observed in the electrical conductivity. It is observed that the modified nano-composites thermal conductivity depends on the platelets size, dispersion, content and contact resistance between the platelets and the matrix interface. Therefore, interface between the platelets and the matrix play a critical role in the thermal conductivity improvement process. Network created by small size platelets of 1, 5, 15 μm may show low thermal conductivity as compared to bigger size platelets of 25μm due to high contact resistance.

From literature thermal diffusivity of epoxy is observed between 0.85×10^{-3} cm^2/s to 1.10×10^{-3} cm^2/s. The density and specific heat of the base epoxy was measured and from literature thermal diffusivity value, the base epoxy thermal conductivity computed is between 0.12 W/mK and 0.16 W/mK. Average of the two range (0.14 W/mK) was considered as the thermal conductivity of the base epoxy. In literature the epoxy thermal conductivity is reported is about 0.14 W/mK. The thermal conductivity calculated based on the lower limit of the diffusivity and measured specific heat and density of epon 828 is 0.145 W/mK. Thermal conductivity of 1 wt% graphene/epon 828 is 0.27 W/mK, which is almost double of the base epoxy 828. It is observed that the thermal conductivity of the epoxy-GnP nanocomposites increased significantly by 92% in comparison to the base epoxy.

Table 1: Values of thermal conductivity of epoxy-GnP nano composites

Sl No	Sample code	Thermal conductivity(W/m^2)		
		Theoretical	*Simulation*	*Expt.*
1	Epoxy	0.13	0.15	0.14
2	Epoxy-0.5wt% GnP	0.15	0.18	0.17
3	Epoxy-1.0wt% GnP	0.18	0.21	0.27
4	Epoxy- 2.0wt%GnP	0.21	0.25	0.29
5	Epoxy-3.0wt% GnP	0.26	0.28	0.30
6	Epoxy-5.0wt% GnP	0.29	0.30	0.32

4.2 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is one of the technique of the thermal analysis used to quantify weight change and thermal decomposition of the polymer. The TGA and the derivative of the weight change curves of epoxy-GnP nanocomposites are shown in Figures 1(a) and (b), respectively. From thermograms of Figure 1 the deterioration temperature weight loss is determined and are shown in Table 2. The Table shows temperatures and corresponding weight loss, T_0 represents onset decomposition temperature, T_{10} represents temperature at 10% weight loss, T_{20} represents

Table 2: Decomposition temperatures of epoxy-GnP

Sample code	Decomposition temperature at different weight loss in °C(±3%)				
	T_{10}%	T_{20}%	T_{5}0%	T_{m}ax	Residue(%)
Epoxy	389	394	404	800	0.2741
Epoxy-0.5wt%GnP	390	395	406	805	0.1203
Epoxy-2.0wt%GnP	392	398	410	810	1.289
Epoxy-5.0wt%GnP	395	401	416	815	0.5235

temperature at 20% weight loss, T_{50} represents temperature at 50% weight loss, T_{max} represents maximum temperature. These are the main characteristic which described the heat stability of the epoxy-GnP nanocomposites. The increased value of T_0, T_{10}, T_{20}, T_{50} and T_{max} support the fact that there is increase in thermal stability of epoxy-GnP based nanocomposites. The relative thermal stability of epoxy-GnP based nanocomposites is determined by comparing the weight loss and different decomposition temperatures. From the Table it is observed that the thermal stability improves slightly up to 5wt% of GnP loading. In all the samples, it is observed that the first stage of thermal degradation is between 385 to 450°C, which is mainly due to the degradation of the cross linking and/or degradation of polymeric back bone, while the second stage occurs between 450 – 560°C during which the C-C and C-O bonds on the main chain are destroyed. The TGA profile of all the samples shown in Figure 1 are all most identical and materials start decomposing at 385°C and they are completely degrading at 660°C. The temperature at which the maximum rate of decomposition takes place is 385-400°C for all the samples. It is observed that the decomposition temperature of composite is not very much affected by the GnP addition into the epoxy. This may be because of the better dispersion of the GnP in the polymer matrix, which may help to develop efficient interfacial interaction within the composite. From the thermograms it is been observed that the total weight loss increases as the content of GnP increases.

5.0 Conclusions

Epoxy-GnP based nano dielectric material of different weight percentages was fabricated using three roll mill method to study the thermal properties of the nanocomposites. Following are the conclusions of the study:

1. The thermal conductivity is observed to increase with increase in filler percentage up to 3wt % of Gnp loading and the value reduced beyond 3 wt % of GnP loading.
2. A better thermal stability is observed with GnP of 0.5wt % in the composite as confirmed by TGA analysis.

6.0 Acknowledgment

The authors are thankful to the Composite Materials Research, Center, Mechanical Engineering Department, Engineering College, University of North Carolina A&T State, Greensboro, NC-27411, USA and Kalpataru Institute of Technology, Tiptur for the support and encouragement.

7.0 References

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