Thermal properties of epoxy nanoclay composite materials

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Abstract— Composite materials are an emerging topic for research as a new competitive material in engineering. New classes of composite material manufactured from particles, nanoparticles and resins, and have experienced efficient and economical for the development and also replacement of new as well as deteriorating structures. In this study epoxy-nanoclay composite materials with varying compositions of nanoclay compared with pure epoxy and epoxy with 10, 20, and 30 by weight fraction of nanoclay are prepared for better insulating materials. The various thermal properties of the material were analyzed to demonstrate that the the prepared composite is a good insulator. An increase in specific heat maximum by 11.26%, thermal stability by 58.82% results in decrease in thermal conductivity maximum by 25.65%, diffusivity to 46.8% and also co-efficient of thermal expansion with an increase in nanoclay proportion is observed. DSC, TGA and TMA are used for determining the thermal properties. SEM and EDS analysis were used to show homogeneous mixture of epoxy and nanoclay.

Keywords: -Epoxy, Nanoclay, composite material, thermal properties, thermal insulator.

1. Introduction
Composite materials are made up of two or more distinct materials with extensively different physical or chemical properties, when united it produce a material with different characteristics from the individual components [1]. Due to the fact that the epoxy thermosets are thermally activated and temperature-dependent, it is essential to study the curing process, thermal analysis is the commonest method to be observed, as many common temperature-dependent properties like heat storage per degree change in temperature and modulus changes with the percentage of curing or magnitude of cross linking[2]. Fillers like aluminum and cupric oxide compared the thermal conductivity and thermal expansion coefficients of epoxy composite laminates prepared by filling with varying concentrations of ash, stone powder, alumina (Al₂O₃), milk of magnesia (Mg(OH)₂), carbide particles(SiC), and hematite powder show that fly ash filled GFRP laminate exhibited low thermal conductivity. GFRP laminates crammed with SiC showed high thermal conductivity and low thermal expansion coefficient[3, 4]. The composite containing hybrid filler consisting of spherical and fibrous filler were found to have enhanced thermal conductivity at low to intermediate filler content. Composites filled by SiC exhibited a low thermal expansion coefficient in comparison with other filled composites[5]. Utilizing an in-situ polymerization technique under ultrasonic treatment epoxy nanoclay materials containing organophilic montmorillonite and diglycidyl ether of Bisphenol-A were synthesized. X-ray diffraction measurements shows an increased separation of nanoclay layers with increase in ultrasonic stirring time[6, 7]. Few-layer graphene sheets were tested as additives in graphene-epoxy thermal conductive adhesives, which were fabricated by a re-expansion and exfoliation method. It shows that graphene sheets can efficiently enhance the thermal conductivity of epoxy matrix, with 4.01
W/mK for the utmost filling loading of weight 10.10%, which is enhanced by more than 22 times of the pure epoxy resin[8]. An epoxy thermal properties enhanced with graphite nanoplatelets (GNPs) or other carbon-based nanofiller that have desired properties and can be produced more easily with lower cost[9, 10].

Studies were found with varying constituent compositions. Most of them showed variations in thermal properties with respect to increase in thermal conductivity. The major constituents used with epoxy as filler materials in previous studies were Al₂O₃, Fe₂O₃, Mg(OH)₂, and SiC. The Study of thermal properties of composite material with respect to insulation by using Nanoclay as filler materials is a potential research gap. Composites with high insulation properties are an emerging requisite for several application purposes such as in cable coatings, cabin insulation of airplanes, cryogenics, aerospace etc. The main aim of this study is to investigate the effect of Nanoclay on thermal properties of Epoxy nanocomposites.

2. Preparation of Specimen

The chemical name of LY556 epoxy resin commercially available used is 2-(Chloromethyl) oxirane, 4[2-(4-hydroxyphenyl) propan-2-y1] phenol and the chemical name of hardener HY951 used is Triethylenetetramine supplied by Ciba-Geigy India Ltd. Company.

A metal mould of the required dimension is prepared initially, and then pre calculated amount of epoxy was taken and mixed with nanoclay in proportions of 10%, 20%, and 30% by weight fraction. The homogeneous mixture was achieved using the magnetic stirrer by rotating it at a speed of 600 rpm around 60 min this speed assists to break the clay and disperse into epoxy. A small amount of acetone is added at regular interval instead of heating the epoxy by hot plate while mixing to reduce the viscosity and also for easy dispersal of filler into the resin to get homogeneous mixture. Hardener was added to the mixture with a ratio of 5:1 as provided by manufacturer and allowed to cure at ambient temperature with 22 ± 2 °C and 56 ± 5% relative humidity for 24 hours instead of heating the epoxy by hot plate[11, 12]. Four compositions pure epoxy, epoxies with 10%, 20%, and 30% by weight fraction of nanoclay were prepared for study.

3. Results & Discussion

3.1. Thermal Conductivity

Thermal conductivity is the ability or the rate at which material transports heat energy. Thermal conductivity measured using Guarded Disc Method with specimen of size 10x10x3 mm³ as per ASTM standard E1225. Nanoclay, when added to epoxy, occupies the voids present in its structure and changes the orientation of the atoms[13]. Due to this the heat flow is resisted as nanoclay is an insulator having thermal conductivity of 0.11 W/mK. Hence, on addition of nanoclay in epoxy caused an overall decrease of the thermal conductivity. Thermal conductivity decreased from 0.421 W/mK to 0.369 W/mK, 0.333 W/mK, and 0.313 W/mK for 10%, 20%, and 30% weight fraction compositions respectively. (Fig.1)

![Figure 1. Variation of Thermal Conductivity with different Composition](image-url)
3.2 Specific heat
Specific heat is the quantity of heat essential to raise the temperature of the material of unit mass through one degree. Specific heat of the material was measured using Digital Scanning Calorimeter (DSC), using 5x5x3 mm³ size specimen as per ASTM standard E1296, using nitrogen as a purge. Specific heat with increasing amount of nanoclay attained a value of 787.53 J/kgK, 806.36 J/kgK, and 826.62 J/kgK from 742.94 J/kgK. An increase in specific heat (Fig. 2) shows that more amount of heat energy is required to raise the temperature of the material. Hence the material’s insulation is increasing with increase of nanoclay present in it. The reason is the high heat capacity of nanoclay, due to the presence of silicate in it. Silicates have a very high specific heat capacity which on mixing with epoxy increased the specific heat of the whole composite.

![Figure 2. Variation of Specific Heat with Different Composition](image)

3.3 Co-efficient of Thermal Expansion
The Co-efficient of thermal (CTE) expansion depicts a change in the size of material with a change in temperature. Specifically, it is a measure of the small change in size per degree change in temperature at a constant pressure. Co-efficient of thermal expansion was measured using Thermo-Mechanical Analyzer (TMA). The specimen used for this test was of 20x10x3 mm³ size as per E831. TMA is a technique where the change in dimension as a function of temperature is measured. CTE for neat and different compositions were found out to be 33.2x10⁻⁶ / °C, 30.2x10⁻⁶ / °C, 26.8x10⁻⁶ / °C and 23.8x10⁻⁶ / °C (Fig. 3). This reduction is attributed to the nanoclay particles presence. Nanoclay has very low co-efficient of thermal expansion whereas epoxy has a higher value. The silica present in nanoclay helps prevent the expansion of the material when subjected to higher temperatures.

![Figure 3. Variation of Coefficient of Thermal expansion with Different Composition](image)

3.4 Thermal Stability
The thermal stability of the material is nothing but the measure of temperature at which the degradation of the material starts to takes place and the temperature at which the material decomposes completely. Thermo-Gravimetric Analyzer (TGA) is used to measure thermal stability, where 5x5x3 mm³ specimen was used according to ASTM standard E2550. At higher temperatures prepared composite materials starts to decompose by destroying its components in form of gases. TGA was operated at a rate of 10 °C/min with nitrogen flow. The pure epoxy decomposes at 170 °C. The temperature sustaining capability increased due to addition of nanoclay to 210 °C, 240 °C, and 270 °C for 10 %, 20 % and 30 % weight fraction composition(Fig.4). The decomposition of epoxy starts with the release of both CO and CO₂, since epoxy is a resin that contain Carbon and Oxygen as its main constituents (around
This loss renders the material useless since other properties are also compromised. These factors resulted in measuring the thermal stability of the material only half the way of its weight loss.

Figure 4. Variation of Weight of different composition with Temperature

3.5 Thermal Diffusivity
Thermal diffusivity is the measure of the capability of a substance to conduct heat energy relative to its heat capacity. The thermal diffusivity of the material was calculated by the given formula:

\[ \alpha = \frac{k}{\rho C_p} \]

Where \( \alpha \) - Thermal diffusivity \( \text{m}^2/\text{s} \), \( k \) - thermal conductivity \( \text{W/mK} \), \( C_p \) - specific heat at constant pressure \( \text{J/kgK} \), and \( \rho \) - density \( \text{Kg/m}^3 \). The value of thermal diffusivity decreased from \( 4.85 \times 10^{-7} \text{ m}^2/\text{s} \) for pure epoxy to \( 3.68 \times 10^{-7} \text{ m}^2/\text{s} \) for 10 wt \%, \( 3.04 \times 10^{-7} \text{ m}^2/\text{s} \) for 20 wt \%, and \( 2.58 \times 10^{-7} \text{ m}^2/\text{s} \) for 30 wt \% composition. The decrease in the value of thermal diffusivity is due to the fact that in the formula the value of thermal conductivity decreases with an increasing nanoclay composition whereas the value of density and specific heat increases. This decrease in the value of thermal diffusivity is a required parameter, as it signifies the penetration of heat into the material.
3.6 SEM and EDS Analysis

SEM analysis was done to see the microstructure of the specimen for ascertaining the presence of nanoclay in epoxy matrix. The microstructure of a material can strongly affect the thermal and physical properties, which in turn govern the application of these materials in industrial practices. The specimen of the given size was placed in the instrument and images at a magnification of 5.0 KX at 5 KV were taken for pure epoxy sample and at 15.0 KX and 5 KV for composite containing nanoclay[15]. It is observed that the image of epoxy with nanoclay contains circular particles showing the presence of nanoclay in the matrix, which is absent in the image of pure epoxy. (Fig.6 & 7)
EDS analysis was done to show the chemical composition of the material. The same specimen was used for both SEM and EDS tests. Image site of pure epoxy and composite is shown in Fig. 8 & 9. The EDS test revealed the chemical composition of the specimen which showed the presence of silica with 0.73%, Na with 0.73%, Cl-0.64%, and Au-1.89 wt % in the sample of epoxy with nanoclay (Fig. 10 & 11). This proved the presence of nanoclay in epoxy and also showed that the composition was homogeneous.

4. Conclusions
The composite was fabricated by varying the proportion of nanoclay and they were subjected to various tests to determine variations in thermal conductivity, thermal stability, specific heat, thermal diffusivity and coefficient of thermal expansion. The decrease in thermal conductivity was found to be 12.35%, 20.90%, and 25.65% respectively for the different composition in increasing order of nanoclay quantity. An increase of 6%, 8.54%, and 11.26% specific heat, further thermal stability increase 26.67%, 40%, and 58.82% observed with increase in filler. This indicates that the composite material can be used as an insulating material beyond 170 °C. CTE decreases maximum to 28.31% results decrease in thermal diffusivity to 46.8%, which is highly required for an insulating material.

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