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Thermal Properties of Silicon Nitride Particles Filled Epoxy Composites

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ABSTRACT
The present work aims at developing a class of polymer composites consisting of thermoset polymer i.e. epoxy as a matrix material with a micro-size filler material i.e. silicon nitride as a reinforcing material. A set of composite with varying filler loading has been fabricated by simple hand lay-up technique. The effect of filler content on thermal properties of such fabricated samples are investigated and presented in this work. The various property evaluated are thermal conductivity, glass transition temperature and coefficient of thermal expansion of all sets fabricated samples. The values obtained under controlled laboratory conditions are analyzed to identify its behavior of the developed material and its effect on different properties of the material. From the experimental results, thermal conductivity of the sample increases appreciably when content of filler increases. After reaching the filler content of 30 wt. %, percolation occur and sudden enhancement in thermal conductivity value is obtained. After from thermal conductivity, other thermal properties like glass transition temperature and coefficient of thermal expansion also modifies as per the requirement of material for microelectronic material.

***Keywords**: Composites. Silicon nitride, Epoxy, Thermal, properties.*

INTRODUCTION

The group of material under the category of composite is very large, although their boundary depends on definition. Mostly, we define composite as any material that is a combination of two or more distinct constituents. Considering the definition, it would incorporate bricks, concrete, wood, bone as well as modern man-made composite such as plastic reinforced with long or short fiber. The man-made composite captured a huge market in around past five decades, where structure fabrication with low weight in combination with high strength and stiffness is of concerned. Apart from above definition of composite, in addition three other criteria have to be satisfied before we call material a composite. Firstly, all the constituents forming the composite have to be present in reasonable proportions. Secondly, all the constituents used for making composite should possess different properties such that the composite's properties are noticeably different from the properties of the constituents and the effect of any one constituent should not pre-dominant the composite properties. Lastly, a synthetic composite is usually produced by deliberately mixing and combining the constituents by various means.

Composite materials are extending the horizon of the designers in all branches of engineering. Composite materials are combines in such a way as to facilitate us to make enhanced use of their virtues while diminishing to some extent the effects of their insufficiencies. This process of optimization can release a designer from the constraints associated with the selection and manufacture of conventional materials. They can make use of tougher and lighter materials, with properties that can be tailored to suit particular design requirements. And because of the ease with which complex shapes can be manufactured, the complete rethinking of an established design in terms of composites can often lead to both cheaper and better solutions [1]. The term 'composite' provides slight indication of the huge series of different arrangement that are comprised in this class of materials. Composite materials create scope for ingenuity which may available to the materials scientist and his customer, the design engineer.

Again, by following the same definition, two or more distinct phase means they should have chemically distinct interphase and it is again important that specification of these constituent is possible by any mean. Among the two distinct constituent one should be a continuous phase which is often present in greater quantity in the composite, though it is not always true. This continuous phase is called matrix. The normal view is that it is the properties of the matrix that are improved upon when incorporating another constituent to produce a composite. The other constituents are known as reinforcing phase. In most cases the reinforcement is harder, stronger and stiffer than the matrix, although there are some exceptions. The geometry of the reinforcing phase is one of the major parameters in determining the effectiveness of the reinforcement; in other words, the mechanical properties of composites are a function of the shape and dimensions of the reinforcement.

Polymer matrix composites (PMCs) are the best established form of advanced composite materials. Of the two classes of polymers used as matrices, thermosets and thermoplastics, thermosets dominate the market for structural applications. Current research is being conducted on composite material that can be used for microelectronic applications. For these applications, high thermal conductivity, low coefficient of thermal expansion and high glass transition temperature are the most important requirements. Most metal matrix composites and ceramic matrix composites are thermally conductive but are highly dense and electrically conductive as well, which may not be suitable for electronic packaging application. So the present research has been focused on developing a composite, which are polymer matrix composites, where polymers are embedded with thermally conductive and electrically insulative ceramic particulate fillers.

The thermal conductivity of the filled polymers is primarily determined by the type and amount of filler used. By the addition of conductive fillers in polymeric resin, thermal conductivity of the material can be improved. There are various categories of conductive fillers available. Among all fillers, additions of metallic filler in polymer are oldest. Apart from metallic filler, carbon-based fillers are other promising fillers to be used as reinforcement for enhancing the thermal conductivity of the polymers.

In microelectronics application, the requirement is quite different. Here high thermal conductivity is required for proper heat dissipation but at the same time electrical resistivity is mandatory for proper signal distribution and to avoid short circuiting. Because of high electrical conductivity of metallic and carbon based fillers, several ceramic materials gained more attention due to their high thermal conductivity and electrical resistivity. On that note, Agarwal and Satapathy [2] used micro size aluminium oxide as filler with two different matrix, one with thermoset polymer epoxy and other with thermoplastic polymer polypropylene. Sasikala and Sebastian [3] developed new class of composites by combining Mg2SiO4 with Polyteterafluoroethylene matrix. They also found improvement in thermal and dielectric property of the developed material. Jia *et al.* [4] used montmorillonite as filler material in epoxy matrix and found appreciable increase in the value of thermal conductivity. Fang *et al.* [5] used boron nitride in the form of nano-sheets and reported unbelievable enhancement in the value of thermal conductivity. Pan *et al.* [6] used surface modification technique over boron nitride particles and introduce them in PTFE matrix. In a very recent work, Agrawal and Chandrakar [7] modified the surface of boron nitride with the help of silane coupling agent and reinforce it in epoxy matrix. They evaluated different mechanical, thermal and dielectric property of the developed material. Pan *et al.* [8] also used AlN as filler in PTFE matrix and performed similar study. They reported excellent thermal stability of the developed material. Kumar and Reddy [9] worked on evaluating the mechanical and tribological properties of silicon nitride filled Nylon-6 polymer composites. Wang et al. [10] developed high strength polymer composite with silicon nitride as filler for dental application. Chen *et al.* [11] used silicon nitride with polyamide matrix and studied the dielectric properties of the material.

Against this background, in present work, a class of composite is fabricated in which the continuous phase is thermoset epoxy matrix and a discontinuous phase is micro-size silicon nitride particles. Simple hand lay-up method is used for fabrication of composites with wide range of filler content. The various thermal testing involves thermal conductivity measurement, coefficient of thermal expansion measurement and glass transition temperature measurement. The obtained results through experimentation will be properly analyzed and on the basis of results obtained, potential application of the developed material will be suggested.

MATERIALS AND METHODS

Material Used

Thermoset resin Lapox L12 is a liquid, unmodified epoxy resin of medium viscosity is used as the matrix material in present investigation. Hardener K6 is commonly employed with Lapox L12. The matrix material system selected is supplied by ATUL India Ltd., Gujarat, India. Silicon nitride of size 50 microns is used in present investigation supplied by Intelligent Materials Private Limited, Mohali. It is of high purity grade with alpha crystal structure. It delivers superior thermal shock resistance. It also has good fracture toughness. It has good oxidation resistance and creep resistance. Hence there are multiple reasons for selecting silicon nitride as filler material in present investigation.

Composite Fabrication

Simple hand lay-up technique is used in the present investigation for fabrication of silicon nitride particles in epoxy matrix. This method is considered as the simplest technique for composite fabrication. The fabrication of composite using hand lay-up method involves following steps:

1) The room temperature curing epoxy resin epoxy resin (Lapox-12) and corresponding hardener (HY 951) are mixed in a ratio 10:1 by weight as recommended.
2) Micro-size silicon nitride particles were then added to the mixture of epoxy and hardener which is later mixed thoroughly by hand stirring.
3) A coating of silicon spray is mandatory over the mould before pouring the

mixture into it, a silicon spray is done over the mold so that it will easy to remove the composite after curing. The uniformly mixed dough is then slowly poured into the mould.

4) The cast is than cured for 8 hours before it was taken from the mould.

Composites were fabricated with different weight fraction of filler ranging from 0 wt. filler *i.e.* neat epoxy to 50 wt. % filler. The composite fabricated under the investigation is given in table 1.

Table 1 . Epoxy Composites Filled With Silicon Nitride

S.No.	Composition
1	Neat Epoxy
2	Epoxy + 10 wt % Silicon Nitride
3	Epoxy + 20 wt % Silicon Nitride
4	Epoxy + 30 wt % Silicon Nitride
5	Epoxy + 40 wt % Silicon Nitride
6	Epoxy + 50 wt % Silicon Nitride

Thermal Characterization

Thermal conductivity of a variety of materials is measure by The Unitherm Model 2022. The tests are in accordance with ASTM E-1530 Standard. Special containment cells are available for fluids, pastes, and powders. 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.

In present work thermal conductivity of samples are measured as a function of filler content as well as working temperature. The device used had provision to control the inside temperature of the apparatus thus change the ambience condition for monitoring the variation of thermal conductivity with respect to ambient temperature.

In the present work, Glass transition temperature (T_g) and Coefficient of thermal expansion (CTE) of the composites are measured with a Perkin Elmer DSC-7 Thermal Mechanical Analyzer. At first, the thermal mechanical analyzer sample stage is purged with nitrogen gas. The sample length is set between 6-8 mm and the width and thickness is about 2-3 mm. During the measurement, the specimen is heated from 30 to 150°C at a heating rate of 5°C/min. For each measurement, two heating scans are used. The first heating scan is used to eliminate any possible internal stress and moisture in the sample which is likely to be generated during the curing and sample preparation processes. The second heating scan is used to determine the T_g and CTE of the material.

RESULTS AND DISCUSSION

Thermal Conductivity

The thermal conductivity value of epoxy matrix and its micro-composites at various level of silicon nitride loading are shown in figure 1. The epoxy used in present work has a very low thermal conductivity of 0.211 W/m-K and by adding the micro-size silicon nitride particulates, the thermal conductivity increases with increasing silicon nitride content. By addition of 10 wt % of silicon nitride, the conductivity of composites increases to 0.35 W/m-K.

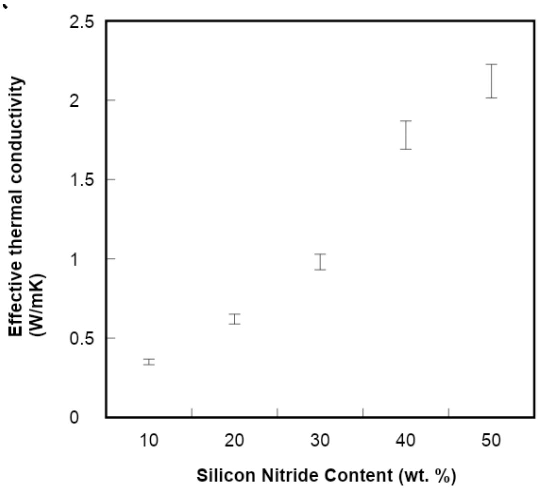

Fig. 1 Thermal Conductivity of Epoxy Filled with Silicon Nitride

This is an increment of 65 %. The increment continuous with filler content and reaches 0.98 W/m-K when 30 wt. % of filler is added giving an increment of 364 %. This phenomenon can be explained by the dependence of thermal conductivity of the composites on the content of conductive filler. It is further notified that when filler content increases beyond 30 wt. %, sudden rise in the value of thermal conductivity is obtained. Here, the thermal conductivity reaches to 1.78 W/m-K and 2.12 W/m-K with filler content of 40 wt. % and 50 wt. % respectively. This is an increment corresponding to 739 % and 900 % respectively. It can be seen from the figure that for low filler content, rate of increase of thermal conductivity is low, whereas when filler content increased beyond 30 wt. %, increment rate increases. When the conductive filler content was low in matrix, the filler were randomly distributed in matrix with no contact among themselves. When the content of filler increased continuously, the filler could come in contact and form the thermally conductive path within the matrix body, leading to the higher thermal conductivity. Hence it is always advisable to add filler in matrix beyond its percolation threshold to achieve high value of effective thermal conductivity.

Glass Transition Temperature

Glass transition temperature of epoxy composites filled with silicon nitride as a function of silicon nitride content is shown in figure 2. It is an important property of polymer, as at this temperature polymer changes its behaviour from glassy state to rubbery state. When this change occurs, material suddenly changes its property and become brittle in nature. With this brittle nature, it will be very difficult to handle the material and little impact may break without any noticeable deformation. It is the fact that once the material cross the glass transition temperature, it property will not again change from brittle to rubbery even if the temperature falls.

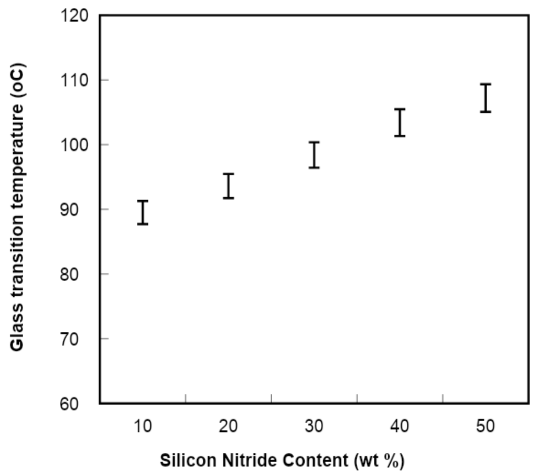

Fig. 2 Glass Transition Temperature of Epoxy Filled with Silicon Nitride

From the figure it is clear that the glass transition temperatures of epoxy composites were higher as compared to that of neat epoxy and it increases with increase in silicon nitride content. Glass transition temperature increases from 86°C for neat epoxy to 107.2°C for 50 wt. % silicon nitride filled epoxy composites. The increment is measured to be of 24.65 % which is an appreciable improvement over neat epoxy and increases the working range of the material from 86°C to 107.2°C which increases the safe limit of the material.

Coefficient of Thermal Expansion

The application where material undergoes fluctuating thermal loading condition, coefficient of thermal expansion became an important property. It is always advisable that the CTE value should remain lowest to avoid thermal fatigue which may arise due to fluctuating temperature. In microelectronic application, when the device works, temperature of the system increases and when the device does not work, the temperature goes down. Because of this variation in temperature which is continuous, the dimension of the material changes as increased temperature expands the material. Hence, continuous change in working temperature may even cause failure of material. Therefore, the study is mandatory and reduction of the property is favorable.

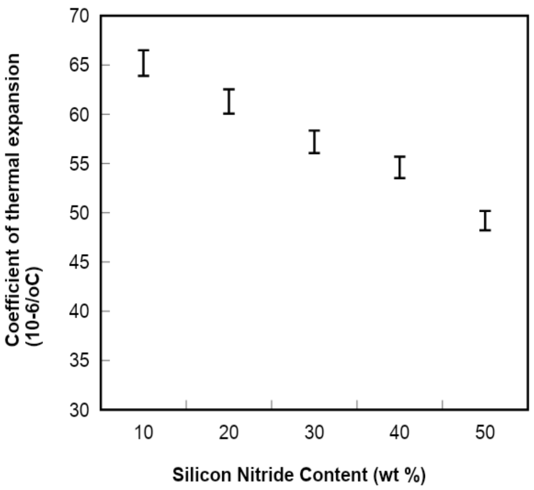

Fig. 3 *Coefficient of Thermal Expansion of Epoxy Filled with Silicon Nitride*

Keeping this in mind, inclusion of silicon provided is beneficial as with increase in content of silicon nitride, CTE of epoxy matrix decreases. The same can be seen in figure 3. It is expected because intrinsic CTE of silicon nitride is much lower than that of epoxy matrix. CTE of silicon nitride is $2.5 \times 10^{-6}/^{o}C$ which is a very low value. Also, the addition of silicon nitride particles into epoxy results in a reduction in the value of CTE of the composites due to the restricted mobility of the polymer molecules arising out of adsorption of silicon nitride surfaces. The CTE of the composite reduces from $68 \times 10^{-6}/^{o}C$ to $49.2 \text{ x } 10^{-6}/^{o}C$ for 50 wt. % of silicon nitride. The decrement in CTE observed for present combination is 27.64 %. The appreciable decrement in CTE results in much better material to be used in said application with very low thermal fatigue.

CONCLUSION

This experimental investigation has led to the following specific conclusions:

1) Epoxy matrix composites reinforced with micro-size silicon nitride is possible by simple hand-lay-up technique.
2) The epoxy has a very low thermal conductivity and by adding the micro-size silicon nitride particulates, the thermal conductivity increases. By the addition of 10 wt. % of silicon nitride, the conductivity of composites increases to 0.35 W/m-K. The increment continuous with filler content and reaches 0.98 W/m-K when 30 wt. % of filler. It is further notified that when filler content increases beyond 30 wt. %, sudden rise in the value of thermal conductivity is obtained. Here the thermal conductivity reaches to 2.12 W/m-K with filler content of 50 wt. %.
3) Glass transition temperature is an important property of polymer, as at this temperature polymer changes its

behaviour from glassy state to rubbery state. Glass transition temperatures of epoxy composites were higher as compared to that of neat epoxy and it increases with increase in silicon nitride content. Glass transition temperature increases from 86 °C for neat epoxy to 107.2 °C for 50 wt. % silicon nitride filled epoxy composites. The increment is measured to be of 24.65 %.

4) Addition of silicon nitride particles into epoxy results in a reduction in the value of CTE of the composites due to the restricted mobility of the polymer molecules arising out of adsorption of silicon nitride surfaces. The CTE of the composite reduces from 68 × 10-6/°C to 49.2 x 10-6/°C for 50 wt. % of silicon nitride. The decrement in CTE observed for present combination is 27.64 %.

REFERENCES

1) Zhou, W., Zhang, F., Yuan, M., Li, B., Peng, J., Lv, Y. & Dang, Z. M. (2019). Improved dielectric properties and thermal conductivity of PVDF composites filled with core–shell structured Cu@ CuO particles. Journal of Materials Science: Materials in Electronics, 30(20), 18350-18361.
2) Agrawal, A., & Satapathy, A. (2015). Effect of Al2O3 addition on thermo-electrical properties of polymer composites: An experimental investigation. Polymer Composites, 36(1), 102-112.
3) Sasikala, T. S., & Sebastian, M. T. (2016). Mechanical, thermal and microwave dielectric properties of Mg2SiO4 filled Polyteterafluoroethylene composites. Ceramics International, 42(6), 7551-7563.
4) Jia, Z. R., Gao, Z. G., Lan, D., Cheng, Y. H., Wu, G. L., & Wu, H. J. (2018). Effects of filler loading and surface modification on electrical and thermal properties of epoxy/montmorillonite composite. Chinese Physics B, 27(11), 117806.
5) Fang, H., Bai, S. L., & Wong, C. P. (2017). Thermal, mechanical and dielectric properties of flexible BN foam and BN nanosheets reinforced polymer composites for electronic packaging application. Composites Part A: Applied Science and Manufacturing, 100, 71-80.
6) Pan, C., Kou, K., Jia, Q., Zhang, Y., Wu, G., & Ji, T. (2017). Improved thermal conductivity and dielectric properties of hBN/PTFE composites via surface treatment by silane coupling agent. Composites Part B: Engineering, 111, 83-90.
7) Agrawal, A., & Chandrakar, S. (2020). Influence of particulate surface treatment on physical, mechanical, thermal, and dielectric behavior of epoxy/hexagonal boron nitride composites. Polymer Composites, 41(4), 1574-1583.
8) Pan, C., Kou, K., Wu, G., Zhang, Y., & Wang, Y. (2016). Fabrication and characterization of AlN/PTFE composites with low dielectric constant and high thermal stability for electronic packaging. Journal of Materials Science: Materials in Electronics, 27(1), 286-292.
9) Kumar, K. S., & Reddy, A. C. Mechanical and Tribological Behavior of Particulate Filled Silicon Nitride Reinforced Nylon-6 Polymer Composites.(2020). Composites Part B: Engineering, 85(7), 1324-1328.
10) Wang, F., Guo, J., Li, K., Sun, J., Zeng, Y., & Ning, C. (2019). High strength polymer/silicon nitride composites for dental restorations. Dental Materials, 35(9), 1254-1263.