A STUDY ON THERMAL AND DIELECTRIC CHARACTERISTICS OF SOLID GLASS MICROSPHERE FILLED EPOXY COMPOSITES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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In
Mechanical Engineering

By

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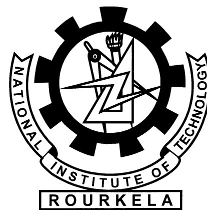

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C E R T I F I C A T E

This is to certify that the thesis entitled ***A Study onThermal and Dielectric Characteristics of Solid Glass Microsphere Filled Epoxy composites*** submitted by **DEBASMITA MISHRA** to National Institute of Technology, Rourkela for the award of the degree of **Doctor of Philosophy** in *Mechanical Engineering* is anauthentic record of research work carried out by her under my guidance and supervision.

The work incorporated in this thesis has not been, to the best of my knowledge, submitted to any other University or Institute for the award of a degree or diploma.

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Abstract

This thesis reports on the research dealing with the processing and characterization of solid glass micro-sphere filled epoxy composites. The first part of the work includes the development of two theoretical correlations based on one dimensional heat conduction models for estimation of effective thermal conductivity of polymer composites with single and multiple fillers.The second part depicts the details of the test procedures and test results in regard tothe physical, mechanical and micro-structural characteristics of the epoxy composites filled with solid glass microspheres (SGM) and/or micro-sized boron nitride (BN). The last part throws light on the thermal and dielectric characteristics of the composites with different filler type and concentrations. The estimation of effective thermal conductivity of the composites using finite element method (FEM) and using the proposed theoretical models is done and the results are validated by corresponding experimental results.

The effects of inclusion of SGM and/or BN on the effective thermal conductivity (k_{eff}), glass transition temperature (T_g), coefficient of thermal expansion (CTE), electrical resistivity (ρ) and dielectric constant (D_k) of epoxy composites are studied. With the addition of SGM, the thermal conductivity, dielectric constant as well as volume resistivity value decreases. Again, the embedment of both SGM and BN fillers results in lowering the CTE of the composites whereas the T_g of the composites is improvedsubstantially. This work shows that the FEM serves as a very good predictive tool for assessment of thermal conductivity of composites.The proposed theoretical correlations too can serve as very good empirical models for spherical inclusions to estimate k_{eff} for composites within the percolation limit.

With light weight and improved insulation capability, the solid glass micro-spheres filled epoxy composites can be used for applications such as insulation boards, food containers, thermo flasks, building materials, space flight and aviation industry etc.Similarly, with enhanced thermal conductivity, improved glass transition temperature, reduced coefficient of thermal expansion and modified dielectric characteristics, the epoxy composites with appropriate proportions of solid glass micro-spheres and boron nitride can be used in micro-electronics applications like electronic packaging, encapsulations, printed circuit board substrates etc.

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Chapter 1

INTRODUCTION

1.1 Background and Motivation

Requirement of Thermal Insulation

Insulation to retard the flow of heat is important for comfort and in some cases, for the survival of humans and animals. Insulation also prevents damage to various articles by freezing or high temperatures, and lowers heating and cooling costs. Contrary to popular belief, insulation is not used to keep cold from entering an area, but is used only to retard the flow of heat. Heat can flow in one direction only -- from a warmer body to a less warm body--so insulation serves to retard this flow. In a refrigerator, for example, insulation slows down the flow of heat from the room air to the interior of the refrigerator. In a building, insulation keeps heat in during winter and out during summer.

Air is a poor conductor of heat, and when trapped in a hollow area is an excellent insulator. Other insulating materials, some of which depend on air pockets for much of their insulating effect, include mineral wool, fiberglass, asbestos, wood, concrete, vegetable fiber, vermiculite and foamed plastics such as polystyrene. These substances retard the conduction and convection of heat. Aluminum sheets and aluminum foil, on the other hand, prevent the radiation of heat, by reflecting it back towards its source.

Buildings can be insulated by using building materials that themselves are good insulators or by leaving spaces in walls and ceilings and by filling the spaces with an insulating material. Such simple building materials as the snow blocks of Eskimo igloos, the straw of thatched roofs, and the sun-baked clay houses in Northern Africa, the Middle East, and Latin America provide good insulation.

Materials designed exclusively as insulation commonly come as loose fills or in the form of batts backed with foil or paper. They are installed between the interior and exterior walls and in the floor or ceiling of the attic. Windows and doors are insulated by weather stripping around the frame and by creating a dead-air space through the use of storm windows and storm doors. Many parts of the country experience large changes in temperature from season to season. So, there is a great need for building materials with insulating properties. With the emergence of new technologies, the scenario in industries of all kinds, transportation sector, entertainment sector and even in the field of medical services is much the same. The conventional engineering materials are unable to meet the requirement of these special properties like high strength, low density and low conductivity. The demand for structurally stable, cost effective and light-weight insulation materials is therefore increasing day- by- day. Foamed plastic is one of the commonly used thermal insulation materials. However, its application is limited considerably due to its poor mechanical properties [1].

Therefore, there has been a focus to fabricate a kind of light, porous material with better mechanical strength and good thermal insulation properties. Against this backdrop, emerged a class of promising engineering insulation materials – *polymer composites*.

Requirement of Thermal Conduction and Electrical Insulation

It is known that micro-electronic packaging plays an increasingly important role in the rapid progress of the electronic and electrical technologies. With the increase in integration scale of the microelectronic circuit, more and more heat is produced when the circuit works. The heat must be dissipated away in time to avoid over-heat occurrence, which requires that the packaging materials should have good thermal conductivity besides having traditional physico-mechanical properties. These packaging materials must possess low relative permittivity or low dielectric constant to reduce the signal propagation delay, which in turn

provides better device performance. They should also have a low thermal expansion coefficient.

As the demands in denser and faster circuits intensify, the heat dissipation in microelectronic packaging is becoming very crucial. Indeed, the inability to adequately conduct heat away from the chip has imposed another engineering constraint in many new product designs [2]. Traditionally, thermal problem in encapsulated devices has been addressed by the use of high cost embedded heat sinks, which are often susceptible to thermal cracking and of limited utility in thinner package configurations [3]. Polymers and ceramics have good electrical, mechanical and thermal properties, so there is a growing demand for them as packaging materials [4]. However, common polymers for packaging, such as epoxy, polyester, polyethylene (PE), polypropylene (PP), polyamide (PA), acrylonitrile-butadiene-styrene (ABS) and polyimide, etc. have low thermal conductivities. Because of this, they cannot effectively dissipate heat when used in various devices and their high thermal expansion coefficients result in thermal failure.

Under this circumstance too, emerged a class of promising packaging materials – *polymer composites*. Particulate filled polymer composites i.e. polymers filled with thermally conductive particulate matters are coming up as a cost effective way to cope with such thermal management issues [5].

Unfortunately, there is no widely accepted definition for a composite material. It can however be defined as any multiphase material that is artificially made which exhibits a significant proportion of the properties of the constituent phases. The constituent phases of a composite are usually of macro sized portions which differ in form and chemical composition and essentially insoluble in each other. The properties of composites are functions of the properties of their constituent phases, their relative amounts and size-and-shape of dispersed phase.

1.1.1 Composite Materials

Composites are combinations of two materials in which one of the materials, called the reinforcing phase, is in the form of fiber sheets or particles and are embedded in the other material called the matrix phase. The primary functions of the matrix are to transfer stresses between the reinforcing fibers/particles and to protect them from mechanical and/or environmental damage whereas the presence of fibers/particles in a composite improves its mechanical properties such as strength, stiffness etc. A composite is therefore a synergistic combination of two or more micro-constituents that differ in physical form and chemical composition and which are insoluble in each other. The objective is to take advantage of the superior properties of both materials without compromising on the weaknesses of either.

Composite materials have successfully substituted the traditional materials in several light weight and high strength applications. The reasons why composites are selected for such applications are mainly their high strength-to-weight ratio, high tensile strength at elevated temperatures, high creep resistance and toughness. Typically, in a composite, the reinforcing materials are strong with low densities while the matrix is usually a ductile or tough material. If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. The strength of the composite depends primarily on the amount, arrangement and type of fiber and /or particle reinforcement in the resin.

Types of Composite Materials

Broadly, composite materials can be classified into three groups on the basis of matrix material. They are:

a) Metal Matrix Composites (MMC)
b) Ceramic Matrix Composites (CMC)
c) Polymer Matrix Composites (PMC)

a) Metal Matrix Composites:

Metal Matrix Composites have many advantages over monolithic metals like higher specific modulus, higher specific strength, better properties at elevated temperatures and lower coefficient of thermal expansion. Because of these attributes, metal matrix composites are under consideration for wide range of applications viz. combustion chamber nozzle (in rocket, space shuttle), housings, tubing, cables, heat exchangers, structural members etc.

b) Ceramic matrix Composites:

One of the main objectives in producing ceramic matrix composites is to increase the toughness. Naturally, it is hoped and indeed often found that there is a concomitant improvement in strength and stiffness of ceramic matrix composites.

c) Polymer Matrix Composites:

Most commonly used matrix materials are polymeric. The reasons for this are two-fold. In general, the mechanical properties of polymers are inadequate for many structural purposes; particularly their strength and stiffness are low compared to metals and ceramics. These difficulties are overcome by reinforcing other materials with polymers. Secondly, the processing of polymer matrix composites need not involve high pressure and does not require high temperature. Also, equipments required for manufacturing polymer matrix composites are simpler. For this reason polymer composites were developed rapidly and soon became popular for structural applications. Polymer composites are used because overall properties of the composites are superior to those of the individual polymers. They have a greater elastic modulus than the neat polymer but are not as brittle as ceramics.

Broadly, polymer composites can be classified into two groups on the basis of reinforcing material (Figure 1.1). They are:

- Fiber reinforced polymer (FRP)
- Particle reinforced polymer (PRP)

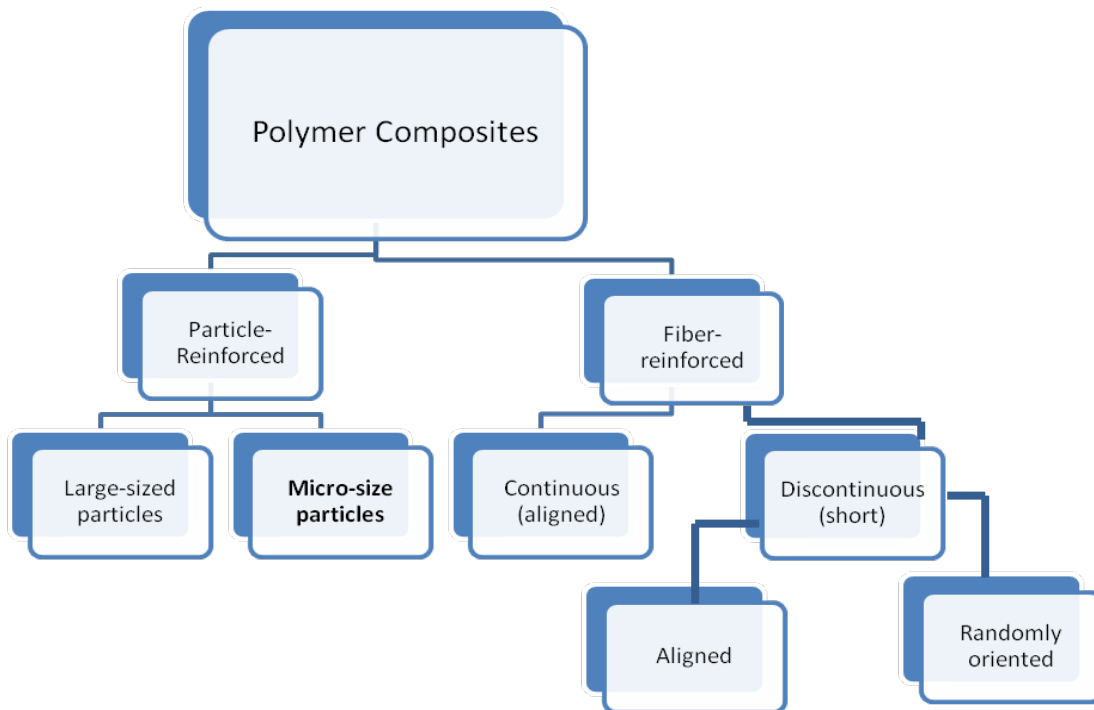

Fig. 1.1 Classification of composites based on reinforcement type

Fiber reinforced polymer

Common fiber reinforced composites are composed of fibers and a matrix. Fibers are the reinforcement and the main source of strength while matrix glues all the fibers together in shape and transfers stresses between the reinforcing fibers. The fibers carry the loads along their longitudinal directions. Sometimes, filler materials might be added to smooth the manufacturing process, impart special properties to the composites and / or reduce the product cost. Common fiber reinforcing agents include asbestos, carbon/ graphite fibers, beryllium, beryllium carbide, beryllium oxide, molybdenum, aluminium oxide, glass fibers, natural fibers etc. Similarly, common matrix materials include epoxy, phenolic resin, polyester, polyurethane, vinyl ester etc. Among these resin materials, polyester is most widely used. Epoxy, which has higher adhesion and less shrinkage than polyesters, comes in second for its high cost.

Particle reinforced polymer

Particles used for reinforcing include ceramics, small mineral particles, metal powders such as aluminium and amorphous materials including polymers and carbon black. Particles are used to increase the modulus and to decrease the ductility of the matrix. They are also used to reduce the cost of the composites. Reinforcements and matrices can be common, inexpensive materials and are easily processed. Some of the useful properties of ceramics and glasses include high melting temperature, low density, high strength, stiffness; wear resistance, and corrosion resistance. Many ceramics are good electrical and thermal insulators. Some ceramics have special properties; some ceramics are magnetic materials; some are piezoelectric materials; and a few special ceramics are even superconductors at very low temperatures. However, ceramics have one major drawback: they are brittle. An example of particle – reinforced composite is an automobile tyre, which has carbon black particles in a matrix of poly-isobutylene elastomeric polymer.

1.2 Introduction to the Research Topic

The present piece of research is basically an experimental investigation focused on the thermal and dielectric characteristics of a new class of particulate filled polymer composites. It also includes fabrication of the composites and their physical and mechanical characterization.

Miniaturization of electronic devices due to their less space and higher portability is the demand of the customer of recent times. Applications in electronic industry therefore require superior materials for packaging and encapsulation. They should also have good properties such as high thermal conductivity to dissipate the heat generated and low thermal expansion coefficient to match with that of silicon chips. Besides, they must also possess low relative permittivity and low dielectric loss to reduce the signal propagation delay, which in turn provides better device performance. Basic electronic components may be packaged discretely, as arrays or networks of like

components or integrated inside packages such as semiconductor integrated circuits, hybrid integrated circuits, or thick film devices. A modern packaging application therefore embodies a host of materials and necessitates an integrated design approach from the very outset.

Last few decades have seen a rapid advancement in electronics technology as there is a constant demand for miniaturization and hence, the sizes are gradually shrinking whereas the number of components and communication speed are increasing day-by-day which leads to generation of high amount of heat and gives rise to problems of heat dissipation. Neat polymers like epoxy or polyester are commonly used as materials for heat sink applications but they suffer from a drawback of low thermal conductivity. If these polymers are filled with metal powders like aluminum and copper, the thermal conductivity improves. But at the same time their electrical resistivity drops and there is possibility of rise in their effective dielectric constants. So, very often single filler might not satisfy both these requirements. Therefore, in order to enhance the thermal conductivity and simultaneously keep a low dielectric constant, thermally conductive fillers along with fillers having low dielectric constant of suitable volume fraction can possibly be used in polymers for such applications. This concept has been imbibed as the very basis of the present research.

Thermal conductivity is an important parameter for thermal characterization of inorganic-particulate filled polymer composites. Various complicated factors affect the thermal conductivity of such materials. In view of this, in the present research, theoretical heat transfer models for estimation of effective thermal conductivity of filled polymer (with single and multiple fillers) are developed based on the law of minimal thermal resistance and equal law of specific equivalent thermal conductivity. Effects of particulate fillers on other thermal characteristics such as glass transition temperature and coefficient of thermal expansion of the composites are also studied. Prediction of the dielectric constant or relative permittivity of composites is very important in many

relevant microelectronic applications. In view of this, a study on the effects of various fillers on the electrical resistivity and relative permittivity (dielectric constant) of these epoxy composites is also included in this research.

Epoxy is chosen as the polymer to be used as the matrix material for this work. For more than 30 years, epoxies have played a critical role in electronic assemblies. They were first introduced into the hybrid industry and enjoyed much success in bonding components, protecting devices and hermetically sealing packages. Today, nearly 80% of the world die attach market for plastic encapsulated devices is solvent-less conductive epoxies. A few reasons why epoxies are wide spread and commonplace in electronic assemblies include: low temperature cure profiles which allow for greater availability of substrates and temperature sensitive components; compliant nature of the polymer; low out-gassing and good thermal stability at elevated temperatures; very good chemical and solvent resistance; 100% solid systems are environmentally benign; and epoxies readily accept fillers.

Solid glass micro-sphere (SGM) is taken as the primary filler in the present investigation. SGMs have some advantages, such as low thermal and electrical conductivity, low dielectric constant and low density. SGM filled epoxy would be suitable mostly in insulation related applications. In addition, these micro-spheres do not generate stress concentration at the interface between the inclusions and the matrix owing to their smooth spherical surface. Boron nitride (BN) has been used as the secondary filler material along with SGM in the epoxy resin in the present research. BN has a reasonably high electrical resistivity and high thermal conductivity. These useful properties suggest that BN may be a good inorganic filler material in polymer composites for use in micro-electronics and power electronic industries.

1.3 Thesis Outline

The remainder of this thesis is organized as follows:

Chapter 2: Includes a literature review designed to provide a summary of the base of knowledge already available involving the issues of interest. It presents the research works of previous investigators on particulate reinforced polymer composites with emphasis on their thermal and dielectric behaviour.

Chapter 3: Presents the development of theoretical models for estimation of effective thermal conductivity of polymer composites with single as well as multiple fillers.

Chapter 4: Includes a description of the raw materials and the test procedures. It presents the details of fabrication and characterization of the composites under investigation.

Chapter 5: Presents the test results in regard to the physical, mechanical and micro-structural characteristics of the composites under study.

Chapter 6: Presents the results of numerical and experimental investigation on the thermal characteristics of the composites under study.

Chapter 7: Presents the test results related to the dielectric characteristics of the composites under study.

Chapter 8: Provides a summary of the findings of this research work, outlines specific conclusions drawn from both the experimental and analytical efforts and suggests ideas and directions for future research.

****

Chapter 2

LITERATURE REVIEW

The purpose of this literature review is to provide background information on the issues to be considered in this thesis and to emphasize the relevance of the present study. This treatise embraces various aspects of particulate filled polymer composites with a special reference to their thermal and dielectric characteristics. It includes reviews of available research reports:

- On particulate filled polymer composites
- On thermal characteristics of particulate filled polymer composites
- On dielectric characteristics of particulate filled polymer composites
- On polymer composites filled with glass micro-spheres
- On polymer composites filled with nitride ceramics

2.1 On particulate filled polymer composites

Fillers are used in polymers for a variety of reasons: cost reduction, improved processing, density control, optical effects, thermal conductivity, control of thermal expansion, electrical properties, magnetic properties, flame retardancy and improved mechanical properties such as hardness and wear resistance. For example, in cable applications, fillers such as metakaolinite are used to provide better electrical stability while others like alumina trihydrate are used as fire retardants. Each filler type has different properties and these in turn are influenced by the particle size, shape and surface chemistry. Moreover, most of the particulate fillers are inorganic and polar, which may give rise to poor compatibility with hydrocarbon polymers and processing problems among various other effects.

Hard particulate fillers consisting of ceramic or metal particles and fiber fillers made of glass are being used these days to dramatically improve the wear resistance even up to three orders of magnitude [6]. Various kinds of polymers and polymer matrix composites reinforced with metal particles have a wide range of industrial applications such as heaters, electrodes [7], composites with thermal durability at high temperatures [8] etc. These engineering composites are desired due to their low density, high corrosion resistance, ease of fabrication and low cost [9-11]. Similarly, ceramic filled polymer composites have been the subject of extensive research in last two decades. The inclusion of inorganic fillers into polymers for commercial applications is primarily aimed at the cost reduction and stiffness improvement [12, 13]. Along with fiber-reinforced composites, the composites made with particulate fillers have been found to perform well in many real operational conditions. It is reported by Bonner [14] that with the inclusion of micro-sized particulates into polymers, a high filler content (typically greater than 20 vol%) is generally required to bring the above stated positive effects into play. But at the same time, as already mentioned, this may also have detrimental effects on some important properties of the matrix polymers such as processability, appearance, density and aging performance.

When silica particles are added into a polymer matrix to form a composite, they play an important role in improving electrical, mechanical and thermal properties of the composites [15, 16]. Currently, particle size is being reduced rapidly and many studies have focused on how single-particle size affects mechanical properties [17–23]. The shape, size, volume fraction and specific surface area of such added particles have been found to affect mechanical properties of the composites greatly. Yamamoto et al. [24] reported that the structure and shape of silica particles have significant effects on the mechanical properties such as fatigue resistance, tensile and fracture properties. Nakamura et al. [25–27] discussed the effects of size and shape of silica particles on the strength and fracture toughness based on particle-matrix adhesion and also found an increase of the flexural and tensile strength as specific surface area of

particles increased. Moloney et al. [28–30] and Adachi et al. [31] found that the mechanical properties of epoxy composites were dependent on volume fraction of particles. Furthermore, effects of different particles of micron size magnitude and nano-particles on the properties of the composites were discussed by Yuan et al. [32] and Ng et al. [33].

The filler plays a major role in determining the properties and behaviour of particulate composites with a high content (over 60% by weight) of filler. Formulation and production of particulate composites can be based on two main principles, a filler theory and a mastic (filler matrix system) theory. As per the filler theory [34, 35], optimal composite properties are achieved when the particle size distribution permits a maximal packing of the filler particles and according to the mastic theory [34, 35], the matrix creates a coating on each filler particle with an optimal thickness. This provides a contact between the filler particles producing a rigid and stable composite mixture. Concerning these theories, two main parameters - the particle size distribution of the filler and the optimal matrix content for this distribution influence the behaviour of the composite. Other parameters affecting the mechanical behaviour of these composites are wetting of the filler by the resin and the adhesion between the two components. Physico-chemical parameters of the filler which affect the initial behaviour and durability of the composite mixture include shape, surface activity and area, size and size distribution. A detailed discussion on these parameters has been reported by Karger and Stokes et al. [36, 37].

It has also been reported that the fracture surface energies of epoxy and polyester resin and their resistance to crack propagation are relatively low [37] but if particulate filler is added to these resins, the particles inhibit crack growth. As the volume fraction of filler is varied, the fracture energy increases up to a critical volume fraction and then decreases again. Srivastava and Shembekar [38] showed that the fracture toughness of epoxy resin could be improved by addition of fly ash particles as filler. The fillers also affect the tensile properties according to their packing characteristics, size and interfacial bonding. The

maximum volumetric packing fraction of filler reflects the size distribution and shape of the particles [39].

2.2 On thermal characteristics of particulate filled polymer composites

In 1960s and 1970s, considerable work has been reported on the subject of heat transport in polymers by Hennig and Knappe [40], Hansen and Ho [41], Peng and Landel [42], Choy and Young [43] etc. Later on, Tavman [44] successfully provided a criterion for anisotropic heat conduction behaviour of polymers by changing their molecular orientation. In a recent work Griesinger et al. [45] have reported that the thermal conductivity of polyethylene increases from 0.35 to 50 W/m-K by keeping an orientation ratio of 50. However, most of these studies were confined to the thermal behaviour of neat polymers and not to their composites.

Since it is not always possible to fabricate a composite keeping the molecular orientation as per choice, a more practical method to increase the thermal conductivity of the polymer is by adding thermally conductive particles or fibers onto it. Lot of work has been reported to improve the thermal conductivity of polymers by incorporating conductive fillers. Most of them include the experimental determination of effective thermal conductivity of particulate filled polymer composites [46-50].

Metals are known for their high thermal conductivity, so they are being widely used as fillers in polymer composites. Sofian et al. [46] studied the effect of various metal powders like copper, zinc, iron and bronze on the thermal properties like conductivity, diffusivity and specific heat of high-density polyethylene matrix. Mamunya et al. [47] later reported the improvement in thermal conductivity of two different categories of polymers i.e. thermoplastic (polyvinyl chloride) and thermoset (epoxy) filled with copper and nickel particles. Though in 1990s, Tecke et al. [48] and Tavman [11] had already used copper powder as filler and measured the thermal conductivity of the composites

by hot disk method, more recently copper has again been used by Luyt et al. [49] in low density polyethylene. They have reported around 150% increase in the value of thermal conductivity for the composites filled with 24 vol% of copper. Subsequently, Tavman [50] took aluminium powders as filler and studied the thermal property of high density polyethylene whereas later Boudenne et al. [51] gave an overview on the thermal conductivity of polypropylene/aluminium composites. Silver too has high potential to be used as filler because of its high thermal conductivity. The effect of silver particulates in epoxy was studied by Bjorneklett et al. [52]. The filling of a polymer with metallic particles though resulted in increased thermal conductivity; simultaneous increase in density of the composites was also recorded, thus restricting the use of metal powders for light-weight applications.

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 [53]. Graphite with single graphene sheet shows intrinsically high thermal conductivity of about 800W/m-K [54]. Expanded graphite, an exfoliated form of graphite with layers of 20-100nm thickness, has also been used in polymer composites [55]. It was found that thermal conductivity of the chemically functionalized graphite/epoxy composite with such exfoliated graphite (20wt %) increased from 0.2 to 5.8 W/m-K. Carbon fiber, typically vapor grown carbon fiber (VGCF), is another important carbon-based filler [56]. Studies conducted on modified thermal conductivity of polymer composites filled with carbon nanotubes have recently been reviewed by Han and Fina [57].

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. In that case a balance is required

that maximizes the thermal dissipation effect of the electrically insulating molding compound as well as which prevents the leakage of current across the conductors due to very low resistivity. 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 [58], Si_3N_4 [59], $Sr_2Ce_2Ti_5O_{16}$ [60], CeO_2 [61] AlN [62, 63], Al_2O_3 [64, 65] and ZnO [66, 67] are in use to improve thermal conductivity of various polymers. It is observed from the above literature on ceramic particle filled polymers that there is an appreciable increase in thermal conductivity of the composite with increase in filler concentration whereas no significant changes are observed in electrical conductivity of such composites. Incorporation of multiple fillers into the polymer matrix for the improvement of thermal conductivity has also been reported [68- 70].

Factors other than the intrinsic thermal conductivity of the fillers such as shape, size, distribution and interconnectivity between the particles also decide the composite thermal conductivity. Boudenne et al. [51] studied the effect of two different particle sizes of aluminium filler and found that the composite filled with larger particle size shows significantly high thermal conductivity. It is due to the formation of more stable thermally conductive pathways in the matrix material. Similar behaviour was observed by Zhou et al. [71]. On the contrary, some authors have highlighted the higher heat transport ability of the composites filled with smaller particles [46, 72]. Boudenne et al. [73] too experimented with copper powders instead of aluminum and found better thermal conductivity with particles of smaller size. Weidenfeller et al. [74] studied the effect of the interconnectivity of the filler particles and its important role in improving the thermal conductivity of the composites. Tekce et al. [48] noticed the strong influence of the shape factor of fillers on thermal conductivity of the composite. Effects of interfacial thermal barrier resistance together with particle shape and size on the thermal conductivity was shown by Jiajun et al. [75].

Most of the research works to predict the thermal conductivity of polymer composites is on experimental basis, though some numerical studies have also been done to predict the effective thermal conductivity [76, 77]. A numerical approach to evaluate the effective thermal conductivity of granular or fibrous reinforced composite materials was proposed by Veyret et al. [78], whereas Kumlutas and Tavman [79] have developed a numerical model for particulate filled polymers which shows good agreement with the experimental values.

Apart from heat dissipation problem, high coefficient of thermal expansion (CTE) of matrix material is also a major source of thermal failure in many applications where material is subjected to periodic heating and cooling due to thermal cycling. Iyer et al. [80] have recently reported significant reduction in CTE as the content of boron nitride is increased in the composite. Dey et al. [81] have studied the dependence of CTE on volume fraction of filler at ambient temperature. Yasmin et al. [82] have reported that, as the graphite concentration in epoxy increases to about 2.5 wt %, glass transition temperature increases and CTE of the composite decreases, however on further addition of graphite i.e. 5 wt%, the CTE of the composite starts increasing. Thomas et al. [83] studied about the effect of $Sm_2Si_2O_7$ particles as reinforcement in two different matrix materials (polyethylene and polystyrene) on CTE.

2.3 On dielectric characteristics of particulate filled polymer composites

Dielectric constant of a composite is a measure of the degree to which an electromagnetic wave slows down as it travels through the material [84, 85]. In general, materials with lower dielectric constant are preferred in certain electronic applications as they have lower impedance on signal propagation.

The dielectric permittivity of composite materials is very important in many relevant technological applications. So, in this regard several theoretical models have been developed for two-phase composites (a substrate with particles) [86-88]. Some of the well known models are series model, parallel model, Litcheneker's model and Maxwell-Wagner's equation [89]. The series and

parallel models represent the extreme cases where material is composed of alternate layers of different phases located normal or parallel to the applied field respectively. On the other hand, Maxwell's equation deals with the dielectric constant of composites with spherical inclusions in a continuous matrix and Litcheneker's model represents widely used empirical relationship that does not consider any physical geometry characteristic of the composite material.

Although, these models are currently used, they often fail to get a fitting in the whole particle-concentration range. For this reason, many researchers have started developing novel models based on numerical methods [2, 3, 86-91]. The aim of these methods is to obtain an estimation of the electric field distribution inside the composite material and to get the overall dielectric properties by post - processing. A variety of methods have been employed to find the field problem in two and three dimensional domains. Examples of these are the boundary integral method [89], the finite element method (FEM) [90], and the finite difference time-domain method [91]. Some advantages of FEM over the other methods are its potential to handle complex geometries by using unstructured meshes, its capability to consider non-homogeneous and non-linear material properties and the feasibility to incorporate a large number of components. For these reasons, FEM seems to be a suitable way to obtain accurate descriptions of the electric field inside composites. Thereby, the main composite characteristics such as the dielectric properties of the phases and their concentrations and the size and distribution of particles play a crucial role in modeling composite materials by FEM. It is clear that the most accurate numerical approach will be obtained by considering a computational domain size equal to the real sample and also taking into account the real particle-size distribution along with a random spatial distribution for particles. Nevertheless, such numerical 'random' models require higher computational resources. Also, the subtleties of the proper treatment of anisotropic and non-homogeneous properties are still not comprehensively understood and simulation of random hetero-structures is a field still in its infancy.

There are reports on experimental investigations as well as on the dielectric characteristics of composites with an objective to develop low dielectric constant materials. It is specially pointed out that low-dielectric-constant composites are very important for application in the microelectronic industries in order to increase the velocity of signal propagation and reduce signal attenuation, especially as the working frequency of electronic appliances increases [89, 90]. Yung et al. [91, 92] have studied the effects of hollow glass micro-spheres on the dielectric behaviour of brominated epoxy-matrix composites and found out that the dielectric constant and the dissipation factor vary substantially with increase in filler content. Zhu et al. [93] gave an insight to the thermal, dielectric as well as mechanical properties of hollow glass micro-sphere filled epoxy matrix composites and found that with the increase in temperature, the dielectric constant of the composites decreased. Ansermet and Baeriswyl [94] also investigated about the development of thermally insulating materials and low dielectric-constant materials. While Gupta et al. [95] studied the characterization of mechanical and dielectric properties of epoxy-glass micro-balloon syntactic composites, Todd and Shi [96, 97] conducted a detailed study on the molecular basis of the inter-phase dielectric properties of microelectronic and optoelectronic packaging materials. Some of the authors studied the ceramic matrices as possible alternatives for use in microelectronic packaging due to their good dielectric properties [98-102] while some studied about the possibility of epoxy composites for capacitor and for high microwave frequency applications [103-105]. Lu and Xu [4] studied the thermal and dielectric properties under humid environment. They used carbon and alumina fillers and found that their thermal conductivities can increase up to 50 times that of pure polyurethane keeping the electrical conductivity well below 10^{-8} S cm^{-1} which is good for certain applications.

2.4 On polymer composites filled with glass micro-spheres

Compared to the investigations carried out on polymer composites filled with metal and ceramic powders, behaviour of glass micro-sphere filled composites

has remained a relatively less studied area. Spherical glass beads are being used in industry, due to certain advantages such as strong filling ability, smooth spherical surface, small and well distributed internal stress in the products and good processibility of the filled materials. Studies on the structure-property correlation of glass bead filled polymers have been made by several researchers over the past 20 years [106-113]. Glass beads (micro-spheres) are being used commercially with various resin matrices, both thermoplastics and thermosets, to improve the physical and mechanical properties of the resins [114]. Among the mechanical properties, hardness, modulus of elasticity and fracture toughness are known to be improved with the incorporation of glass beads in brittle resin matrices [115-117]. The tensile strength and ductility (elongation to break), on the other hand, decreases with the increase in filler volume fraction [118, 119]. Glass beads are preferred as fillers especially when composite properties such as isotropy or low melt viscosity are important. They are considered to be a reinforcement which does not create a source of stress concentration in the matrix unlike other long fibers which have sharp edges leading to stress generation in the matrix and in turn early failure of the composites. The creep and fracture properties also play an important role in deciding the failure of a composite material. In this regard, Sahu and Broutman [108] studied in considerable detail the mechanical and fracture properties of glass sphere filled epoxy and polyester resins with various particle matrix interface conditions. Mallick and Broutman [112] presented a possible explanation for the strength behaviour of glass micro-sphere filled brittle resin composites and described the flexural, compressive and fracture properties of brittle epoxy matrix composite containing glass beads of 15 micron average particle size.

Few research works have been reported recently on glass micro-spheres with thermoplastics and concept of linear elastic fracture mechanics (LEFM) has been widely employed to study the fracture toughness of such thermoplastic composites [113-117]. Sánchez-Soto et al. [118] have analyzed the fracture behaviour of a material model composed of polysterene and solid glass beads

and found out that small quantities of glass beads are enough to modify polystyrene fracture behaviour changing the propagation mode, which tends to stabilize as more quantity of beads are added to the matrix. Lim [119] researched on melt viscoelastic behaviour such as die-swell, melt fracture and wall-slip of glass bead filled high density polyethylene (HDPE) composites. Faulkner and Schmid [120] studied the rheological and mechanical properties of glass bead filled polypropylene (PP) composites and noted that the relative tensile modulus and relative flexural modulus were both linear functions of bead fraction over the entire range of filler concentration i.e. 0-29 vol%. Lepez et al. [121] carried out thermo-rheological analysis of glass micro-sphere filled HDPE and polystyrene (PS) melts and proposed a new empirical model that allowed the prediction of complex viscosity of the composite melts. Zhang and Berglund [122] observed the deformation and fracture of glass-bead-rubber-epoxy composites. Qu and Yu [123] investigated the effects of the interfacial adhesion on the micro-damage and the rheological behaviour of glass bead filled nylon and found that the interfacial adhesion strength significantly affected the tensile strength and the rheological behaviour of the composites. Lu and his co-workers [124] analyzed the role of creep damage in glass bead filled HDPE and pointed out that the creep behaviour of rigid particle filled plastics could be influenced to a remarkable degree by creep damage, especially at high stress levels. Hashemi et al. [125] found that the fracture toughness of glass bead filled poly-oxy-methylene decreased sharply with increasing bead content. Li et al. [126] analyzed the dynamic and mechanical properties of glass bead filled low density polyethylene composites using a dynamic mechanical analyzer and found that when the volume fraction of the glass beads is increased, the relative storage modulus and the loss modulus, including flexural and shear, for the filled LDPE composites increases non-linearly at 25°C. Lee et al. [127] investigated the major energy dissipation mechanisms of glass micro-sphere filled epoxies based on the previously established knowledge about the micro-mechanical deformations occurring during the fracture.

Liang and Li [128, 129] gave an insight about the tensile and flexural properties of hollow glass bead-filled ABS composites and later on tensile and impact properties of hollow glass bead filled PVC composites. Gupta et al. [130,131] compared the tensile and compressive characteristics of vinyl ester/glass micro-balloon syntactic foams and also did a microscopic examination of their compressive fracture features. Gupta et al. [132] also analyzed the flexural and compressive properties of hollow-particle filled composites and found a similar kind of observation. Yung et al. [91] investigated thermal, mechanical as well as dielectric properties of the composites and concluded that the properties of composites are mainly dependent on the characteristics of hollow glass micro-sphere (HGM). With increase in the content or decrease in the density of hollow glass micro-sphere, there is a decreasing trend for thermal conductivity, dielectric constant, dielectric loss as well as compressive modulus and strength of the composites and the compressive strength increases with increase in HGM density. Later on, Zhu et al. [93] reported on thermal, dielectric as well as compressive properties of hollow glass micro-spheres where in addition to mechanical properties, the thermal conductivity and dielectric properties of HGM filled polymer-matrix composites were also investigated as a function of testing temperature to develop thermally-insulating and low-dielectric constant materials respectively. They specially pointed out that composites having low-dielectric constant are very important for application in the microelectronic industries in order to increase the velocity of signal propagation and reduce signal attenuation, especially when the working frequency of electronic appliances increases. Ferreira et al. [133] investigated the effects of hollow glass micro-sphere filled hybrid composites and studied about the addition of short fiber reinforcements on the mechanical behaviour of epoxy binding matrix composites. It was observed that in terms of specific values, both flexural and compressive stiffness increase with increase in micro-sphere content but the addition of glass fibers produces a slight improvement in the flexural stiffness and fracture toughness in comparison to hybrid composites with 0.9% carbon fiber.

Hollow glass micro-spheres have low density and so they reduce the weight of the composites to a great extent, but according to Kim et al. [134], their addition tends to reduce the Young's modulus and ultimate strength of the composites. Even specific values of flexural stiffness are only marginally increased for high volume fractions of spheres but this difficulty can be overcome by using rigid inorganic particles, so solid glass spheres might serve as a good alternative.

Though, there is an extensive research in the area of mechanical properties of glass micro-sphere filled polymer composites, not much work has been done on their thermal behaviour. There are only a few published papers on evaluation of effective thermal conductivity of polymer composites filled with glass beads. Park et al. [135] in 2005 prepared hollow glass micro-sphere filled epoxy composites and studied their surface properties, cure behaviour, coefficient of thermal expansion, glass transition temperature, dielectric constant and fracture toughness. It was found that hollow glass micro-sphere filled composites showed higher surface free energy, lower coefficient of thermal expansion and lower dielectric constant than those of neat epoxy matrix and the glass transition temperature and mechanical interfacial properties of hollow glass micro-sphere reinforced composites studied were significantly higher than those of neat epoxy resin. The improvements in the dynamic - mechanical and interfacial properties were also observed. In 2006, Liang and Li [136] reported on measurement of thermal conductivity of hollow glass-bead-filled polypropylene composites. They also carried out finite element analysis for two-dimensional and three-dimensional heat transfer and simulated the variation of effective thermal conductivity of hollow glass micro-sphere filled polymer composites. Liang and Li [137] further proposed a theoretical model to predict the thermal conductivity of such composite systems. Yung et al. [91] have also reported the preparation and properties of hollow glass micro-sphere filled epoxy matrix composites but all these studies are for polymer composites filled with hollow glass spheres and surprisingly, there is no report available on evaluation of effective thermal conductivity of solid glass micro-sphere filled polymer composites.

2.5 On polymer composites filled with nitride ceramics

Materials for electronic packaging or printed circuit board substrates are required to have high thermal conductivity, low electrical conductivity and low dielectric constant. Polymers with high electrical resistivity and low dielectric constant are therefore suitable for these applications provided their poor thermal conductivity is taken care of by reinforcing them with thermally conductive and electrically insulative fillers. Nitride ceramics such as aluminum nitride (AlN) and boron nitride (BN) having high electrical resistivity and high thermal conductivity can be gainfully used for this purpose [93, 138]. Xu et al. [139] have reported on the effect of aluminium nitride whiskers on thermal properties of polymer composites using epoxy resin or polyvinylidene fluoride (PVDF) as matrix material. It was ascertained that effective thermal conductivity of AlN particle (size ~ 115µm) filled epoxy matrix increased by nearly 97%. In addition to this, it enhanced the dielectric property of the composites as well.

Boron nitride has a reasonably high electrical resistivity (10^{14} Ω cm) and breakdown strength (53 kV/mm) and a small relative permittivity of about 4.88, which is close to that of many polymer matrices and much smaller than other ceramics. It also has good heat transfer characteristics. These useful properties suggest that boron nitride may be a good inorganic filler material in microelectronic and power electronic industries. However, there is little in the published literature about the dielectric properties of boron nitride filled composites [140-142].

Important roles in lowering the electrical properties and amelioration of thermal properties of composites are brought about by intromission of aluminum nitride (AlN) and boron nitride (BN) into polymer matrix to form composites of desired applications [84,142,143]. These engineering composites are also desired due to low density, high corrosion resistance, ease of fabrication and low cost [9-11]. Zhou et al. [143] have reported an extensive research on the thermal conductivity of boron nitride reinforced high density polyethylene (HDPE) composites under special dispersion state of filler particles surrounding HDPE

particles. The effects of BN content and particle size of HDPE and the temperature on thermal conductivity of the composites are discussed. The results indicated that the special dispersion of BN in the matrix provides the composites with higher thermal conductivity. The conductivity increases with increasing filler content but significantly deviates from the predictions obtained from the theoretical models. It is further reported that the combined use of BN particles and alumina short fibers gives higher thermal conductivity of composites compared to the use of BN particles alone [143]. Wattanakul et al. [144] studied the thermal conductivity as well as the mechanical properties of BN-filled epoxy composite as a function of filler content, mixing conditions and BN agglomerate size and found that mechanical properties of the composite increases with increase in filler content, mixing speed, mixing time and mixing temperature but with decrease in BN agglomerate size. Wattanakul et al. [145] further developed a new hybrid organic-inorganic thermally conductive thermoset composite composed of an epoxy resin cross-linked with a flexible diamine hardener and boron nitride particles. Hill and Supancic [146] studied on the thermal conductivity of nitride ceramic platelet filled polymer composites. The approach is to produce a new material which involves addition of ceramic fillers of intrinsically high thermal conductivity to polymers, providing heat-conducting paths through the composite and increasing the mean thermal conductivity. Empirically, it appears that fillers with a high aspect ratio may be particularly effective in providing good particle-to-particle contact to efficiently transfer heat. In particular, platelet-shaped particles offer a high degree of contact and can be prepared with low surface area to facilitate high filler loading in a polymer matrix. Soft filler platelets, such as BN, are shown to deform under stress, making it possible to achieve higher density and greater surface contact between particles than is observed for harder and more rigid fillers. The higher density and improved contact appears to result in the formation of conductive clusters of particles in the composite with improved capability to transfer heat. This deformation and surface contact clearly explain the improved thermal performance of BN-filled composites over that of composites filled with rigid particles.

2.6 Knowledge Gap in Earlier Investigations

In spite of a number of research works reported in the past, there is a huge knowledge gap that demands a well planned and systematic research in this area of particulate filled polymer composites. An exhaustive review of the published literature reveals that:

- Most of the investigations are aimed at enhancing the thermal conductivity of the polymer by adding conductive fillers rather than attempting to improve its insulation capability.
- Most of the studies are for single filler composites and only very few papers have reported on the synergistic effects of two different kinds of fillers on the thermal/dielectric properties.
- Reports are available in the literature on studies carried out on thermal and electrical behaviour of hollow glass micro-spheres (HGM), but surprisingly, there is no report available on effective thermal and dielectric properties of solid glass micro-sphere (SGM) filled polymer composites.
- Some investigators have developed numerical and analytical models for estimation of effective thermal conductivity of particulate filled composites but there is no model available for composites filled with hybrid i.e. more than one type of fillers.
- Though a few papers have been reported on thermal and dielectric behaviour of boron nitride filled polymer composites, a possibility that the incorporation of both solid glass micro-spheres and BN in epoxy could provide a synergism in terms of improved thermal conductivity and modified dielectric properties has not been addressed so far.

In view of the above, the present work is undertaken to investigate on the thermal characteristics such as effective thermal conductivity, glass transition temperature, coefficient of thermal expansion etc. along with the dielectric properties of epoxy matrix composites filled with solid glass micro-spheres (SGM) with additional ceramic fillers such as BN.

2.7 Objectives of the Present Work

The objectives of this work are outlined as follows:

- Development of theoretical models for estimation of effective thermal conductivity of polymer composites with single and hybrid i.e. more than one type of fillers.
- Estimation of effective thermal conductivity of particulate filled polymer composites using finite element method (FEM).
- Fabrication of different sets of epoxy composites filled with SGM, with micro-sized BN and with both SGM and BN respectively and measurement of their thermal conductivities.
- Validation of proposed theoretical models and FEM results by comparing the theoretical values with the measured values of effective thermal conductivity of the composites.
- Physical, mechanical and micro-structural characterization of the composites.
- Study of the effects of fillers on properties like glass transition temperature, coefficient of thermal expansion, electrical resistivity and dielectric constant of these composites and exploring the possibility of their use in micro-electronic applications.

Chapter Summary

This chapter has provided

- An exhaustive review of research works on various aspects of particulate filled polymer composites reported by previous investigators
- The knowledge gap in earlier investigations
- The objectives of the present work

The next chapter presents the development of two theoretical models to estimate the effective thermal conductivity of polymer composites filled with single and multiple particulate fillers.

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MATERIALS AND METHODS

This chapter describes the materials and methods used for processing and characterizing the composites under investigation. It presents the details of the tests related to the physical, mechanical, micro-structural, thermal and dielectric characterization of the prepared particulate filled polymer composite specimens.

4.1 MATERIALS

4.1.1 Matrix Material

Matrix materials are of different types like metals, ceramics and polymers. Polymer matrices are most commonly used because of cost efficiency, ease of fabricating complex parts with less tooling cost and they also have excellent room temperature properties when compared to metals and ceramic matrices. Polymer matrices can be either thermoplastic or thermoset. Thermoset matrices are formed due to an irreversible chemical transformation of the resin into an amorphous cross-linked polymer matrix. Due to huge molecular structures, thermoset resins provide good electrical and thermal insulation. They have low viscosity, which allow proper fiber wet out, excellent thermal stability and better creep resistance [163].

The most commonly used thermoset resins are epoxy, polyester, vinyl ester and phenolics. Among them, the epoxy resins are being widely used for many advanced composites due to their excellent adhesion to a wide variety of fibers, superior mechanical and electrical properties and good performance at elevated temperatures. In addition to that they have low shrinkage upon curing and good chemical resistance. Due to several advantages over other thermoset polymers as mentioned above, epoxy (LY 556) is chosen as the matrix material for the present research work. It chemically belongs to the 'epoxide' family. Its

common name is Bisphenol-A-Diglycidyl-Ether (commonly abbreviated to DGEBA or BADGE) and its molecular chain structure is shown in Figure 4.1. 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 (Figure 4.2). The LY 556 epoxy resin (Figure 4.3) and the corresponding hardener HY-951 are procured from Ciba Geigy India Ltd. Table 4.1 provides some of the important properties of epoxy.

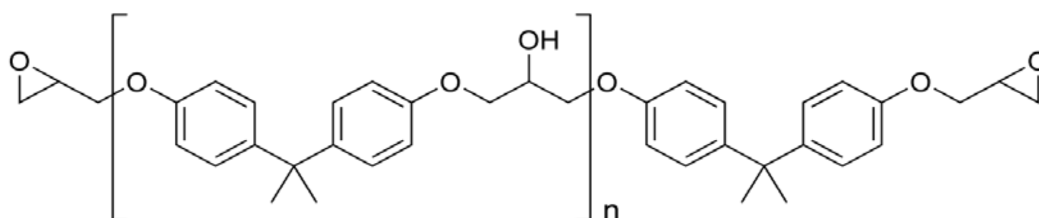


Fig. 4.1 Unmodified epoxy resin chain ('**n**' denotes number of polymerized unit)

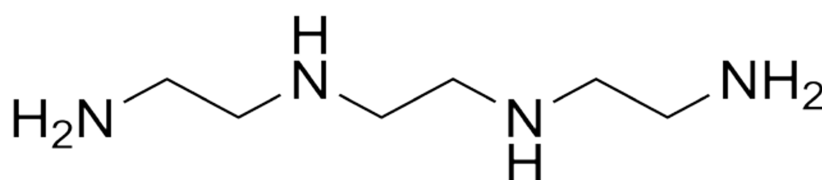


Fig. 4.2: Tri-ethylene-tetramine (hardener used for epoxy matrix)

Table 4.1 Some important properties of epoxy

Characteristic Property	Inferences
Density	1.1 gm/cc
Compressive strength	90 MPa
Tensile strength	58 MPa
Micro-hardness	0.085 GPa
Thermal conductivity	0.363 W/m-K
Glass transition temperature	104°C
Coefficient of Thermal expansion	62.83 ppm /°C
Electrical conductivity	0.105×10^{-16} S/cm
Volume Resistivity	10^{15} ohm-cm
Dielectric constant	3.98 at 1MHz

Fig. 4.3 Epoxy resin and hardener

Fig. 4.4 Solid glass microspheres used as filler in the present work

Fig. 4.5 Micro-sized boron nitride (BN) particles used as filler in epoxy

4.1.2 Filler Material - 1 :(Solid Glass Micro-spheres)

Micro-sized solid glass microspheres (SGMs) of three different average sizes (100 µm, 200µm and 300µm) procured from NICE Ltd. were used as the filler material in the present research. These microspheres are normally obtained by heating tiny droplets of dissolved sodium meta-silicate (Na_2SiO_3, commonly referred to as water glass or liquid glass) during ultrasonic spray pyrolysis process. These are made of high grade *soda lime silica glass* containing around 70% of SiO_2. These are usually free from lead and iron. A pictorial view of glass microspheres (100µm) used in the present work as the particulate filler is given in Figure 4.4. Table 4.2 provides some of its important properties.

Table 4.2 Some important properties of glass microspheres

Characteristic Property	Inferences
Density	1.5 gm/cc
Compressive strength	248 MPa
Tensile strength	56 MPa
Micro-hardness	6.845GPa
Thermal conductivity	0.04 W/m-K
Coefficient of Thermal expansion	32 ppm/°C
Electrical conductivity	0.109×10^{-16}S/cm
Volume Resistivity	10^{8}-10^{13} ohm-cm
Dielectric constant	3.67 at 1MHz

4.1.3 Filler Material **-** 2**:** (Boron Nitride)

Micro-sized boron nitride (BN) powder (procured from Hi-Media Laboratories Pvt. Ltd., Mumbai) has been used as the second filler material in the present investigation. BN particles are normally acquired synthetically from boric acid (H_3BO_3) and boron trioxide (B_2O_3). The hexagonal form of boron nitride (h-BN or α-BN) is the most stable crystalline form with a melting point as high as 2973°C. It has a layered structure like graphite where each layer is covalently bonded together making it electrically insulating and thermally conductive. The pictorial view of micro-sized boron nitride (BN) powder used in this work is given in Figure 4.5. Table 4.3 provides some of its important properties.

Table 4.3 Some important properties of boron nitride

Sl.No.	Characteristic Property	Inferences
1	Density	2.3 gm/cc
2	Compressive strength	30-120 MPa
3	Tensile strength	52MPa
4	Micro-hardness	0.107Gpa
5	Thermal conductivity	110 W/m-K
6	Coefficient of thermal expansion	36 ppm/°C
7	Electrical conductivity	0.112×10^{-16}S/cm
8	Volume resistivity	10^{11}-10^{14}ohm-cm
9	Dielectric constant	4.88 at 1MHz

4.2 EXPERIMENTAL DETAILS

4.2.1 Composite Fabrication

Set 1 Epoxy Composites filled with solid glass micro-spheres (100 µm)

Low temperature curing epoxy resin (LY 556) and corresponding hardener (HY951) are mixed in a ratio of 10:1 by weight as recommended. Solid glass micro-spheres (SGM) of average particle size 100 µm were reinforced in the resin to prepare the composites in different proportions according to the experimental requirement. The uniformly mixed dough (epoxy filled with SGM) is then slowly decanted into the glass molds, coated beforehand with wax and a uniform thin film of silicone-releasing agent. The composites were cast in these molds so as to get disc type specimens (diameter 20 mm, thickness 5 mm).

Composites of 8 different compositions with varying SGM content (Table 4.4) are made. The castings were left to cure at room temperature for about 24 hours after which the glass moulds are broken and samples are released.

A schematic diagram of the fabrication process using hand-layup technique for particulate filled epoxy composites is given in Figure 4.6. Figure 4.7 shows some of these composite samples prepared through this hand-layup technique.

Set 2 Epoxy Composites filled with solid glass micro-spheres

In a similar manner, epoxy composites of 8 more different compositions (Table 4.5) were made for each of the three microsphere sizes (100, 200 and 300 μm). For each composition, the composites were cast in glass moulds so as to get both disc type specimens (diameter 10, 20 mm and thickness 5, 10 mm) and rectangular specimens (length 150 mm, width 20 mm, thickness 4 mm).

Set 3 Epoxy Composites filled with micro-sized boron nitride

Using the same hand lay-up technique, BN particles of average particle size 100 μm were reinforced in the resin to prepare the composites in different proportions (Table 4.6) according to the experimental need. The composites were cast onto glass moulds so as to get disc type specimens (Figure 4.8) of different dimensions (diameter 10, 20 mm and thickness 5, 10 mm).

Set 4 Epoxy Composites filled with micro-sized boron nitride

In a similar manner, epoxy/BN composites of 8 more different compositions (Table 4.7) were made and for each of these compositions, the composites were cast in glass moulds so as to get both disc type specimens (dia 20 mm, thickness 5 mm) and rectangular specimens (length 150 mm, width 20 mm, thickness 4 mm).

Set 5 Epoxy Composites filled with hybrid fillers (SGM and BN)

Further, a set of hybrid composites (more than one type of fillers reinforced in the polymeric resin) was fabricated. Composites of 60 different compositions

with varying SGM and BN contents were included in this set of hybrid specimens. The SGM content was varied between 0 to 20 vol% (0, 5, 10, 15 and 20 vol%) and the BN content was varied from 0 to 27.5 vol%.

Table 4.4 Epoxy composites filled with glass microspheres (**Set 1**)

Composition
Epoxy + 0 vol % SGM
Epoxy + 1.4 vol % SGM
Epoxy + 3.35 vol % SGM
Epoxy + 6.5 vol % SGM
Epoxy + 11.3 vol % SGM
Epoxy + 17.9 vol % SGM

Table 4.5 Epoxy composites filled with glass microspheres (**Set 2**)

Composition
Epoxy + 0 vol % SGM
Epoxy + 5 vol % SGM
Epoxy + 10 vol % SGM
Epoxy + 15vol % SGM
Epoxy + 20vol % SGM
Epoxy + 25vol % SGM
Epoxy + 30vol % SGM
Epoxy + 35vol % SGM

Table 4.6 Epoxy composites filled with micro-sized boron nitride (**Set 3**)

Composition
Epoxy + 0 vol % boron nitride
Epoxy + 1.40 vol % boron nitride
Epoxy + 3.35 vol % boron nitride
Epoxy + 5.23 vol % boron nitride
Epoxy + 7.85 vol % boron nitride
Epoxy + 9.04 vol % boron nitride
Epoxy + 11.3 vol % boron nitride
Epoxy + 17.9 vol % boron nitride

Table 4.7 Epoxy composites filled with micro-sized boron nitride (**Set 4**)

Composition
Epoxy + 0 vol % boron nitride
Epoxy + 5 vol % boron nitride
Epoxy + 10 vol % boron nitride
Epoxy + 15vol % boron nitride
Epoxy + 20vol % boron nitride
Epoxy + 25vol % boron nitride
Epoxy + 30vol % boron nitride
Epoxy + 35vol % boron nitride

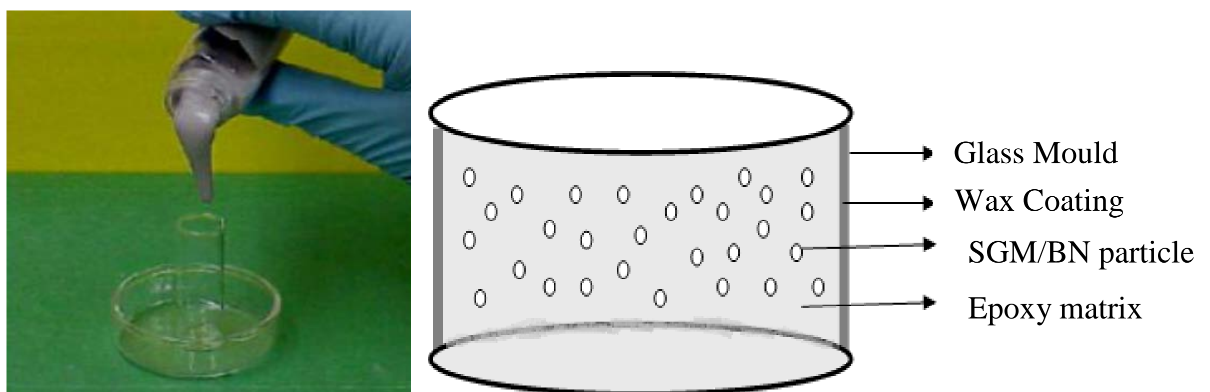


Fig. 4.6 Particulate filled epoxy composite fabrication by hand lay-up process

Fig. 4.7 Solid glass micro-spheres filled epoxy composites

Fig. 4.8 Boron Nitride filled epoxy composites

4.3 Physical Characterization

4.3.1 Density and volume fraction of voids

Density of a composite depends on the relative proportion of matrix and reinforcing materials and it is one of the most important factors for determining the properties of the composites. The theoretical density (ρ_{ct}) of composite materials in terms of weight fractions of different constituents can easily be obtained using the following equation given by Agarwal and Broutman [164].

$$\rho_{ct} = 1 \Big/ \left\{ \left(\frac{w_f}{\rho_f} \right) + \left(\frac{w_m}{\rho_m} \right) \right\} \qquad \textbf{(4.1)}$$

where, w and ρ represent the weight fraction and density respectively. The suffixes f and m stand for the filler and matrix respectively in a composite with single filler. In the present work, since some of the composites are hybrid type i.e. filled with double fillers (SGM and BN), the above expression for density has been modified for them as:

$$\rho_{ct} = 1 \Big/ \left\{ \left(\frac{w_{f_1}}{\rho_{f_1}} \right) + \left(\frac{w_{f_2}}{\rho_{f_2}} \right) + \left(\frac{w_m}{\rho_m} \right) \right\} \qquad \textbf{(4.2)}$$

where, the suffix f_1 and f_2 stand for the first and second filler and m stands for the matrix respectively. The actual density (ρ_{ce}) of the composite can be

determined experimentally by the Archimedes principle or water displacement technique (ASTM D 792-91).

The volume fraction of voids (v_v) in the composites is calculated by using the following equation:

$$v_v = (\rho_{ct} - \rho_{ce}) / \rho_{ct} \quad \textbf{(4.3)}$$

4.3.2 Scanning Electron Microscopy

The micro-structural features of the various particulate filled composite specimens were examined by Scanning Electron Microscope JEOL JSM-6480 LV (Figure 4.9). The specimens were mounted on stubs with silver paste. To improve the penetration of light and for better surface micrographs, a thin film of platinum is vacuum-evaporated onto the samples before the pictures were taken.

4.4 Mechanical Characterization

4.4.1 Micro-hardness

Micro-hardness measurement was done using a Leitz micro-hardness tester (Figure 3.10). A diamond indenter, in the form of a right pyramid with a square base and an angle 136° between opposite faces, was forced into the material under a load *F*. The two diagonals *X* and *Y* of the indentation left on the surface of the material after removal of the load were measured and their arithmetic mean was calculated. In the present study, the load considered *F*= 0.2454 N and Vickers hardness number is calculated using the following equation.

$$H_v = 0.1889 \frac{F}{L^2}$$

where, $$L = \frac{X+Y}{2} \quad \textbf{(4.4)}$$

where, *F* is the applied load (N), *L* is the diagonal of square impression (mm), *X* is the horizontal length (mm) and *Y* is the vertical length (mm).

4.4.2 Compressive strength

The cured composite samples of required dimension (length 10 mm, diameter 10 mm), shown in Figure 4.11 were used for the uni-axial compression test as per ASTM D 695 standard [165]. This helps to avoid buckling, reduce friction due to small cross-sectional area, avoid premature failure due to sharp corners and prevent self-reaction of the epoxy resin during curing. Static uni-axial compression tests were carried out on these specimens using Universal Testing Machine *Instron 1195* (Figure 4.12a). The loading arrangement is shown in Figure 4.12b. Four identical specimens were tested for each composition and the average result was recorded as the compressive strength of the composite. The crosshead speed was maintained constant at 1 mm/min and the compression was stopped when the specimen showed signs of failure or when densification was complete.

4.4.3 Tensile strength

The cured dog bone shaped composite samples (prepared from the rectangular slabs) of required dimension (length 150mm, end width 20mm and mid width 12 mm) shown in Figure 3.13 were used for the tensile test as per ASTM E 1309 standard. A uni-axial load is applied through both the ends. In the present work, this test is performed in the same universal testing machine Instron 1195 at a cross head speed of 10 mm/minute and the results were used to calculate the tensile strength of the composite samples. The machine and the loading arrangement are shown in Figure 4.14. In this case also, the test was repeated four times on each composite type and the mean value was reported as the tensile strength of that composite.

Fig. 4.9 Scanning Electron Microscope (JEOL JSM-6480LV)

Fig. 4.10 Leitz micro-hardness tester

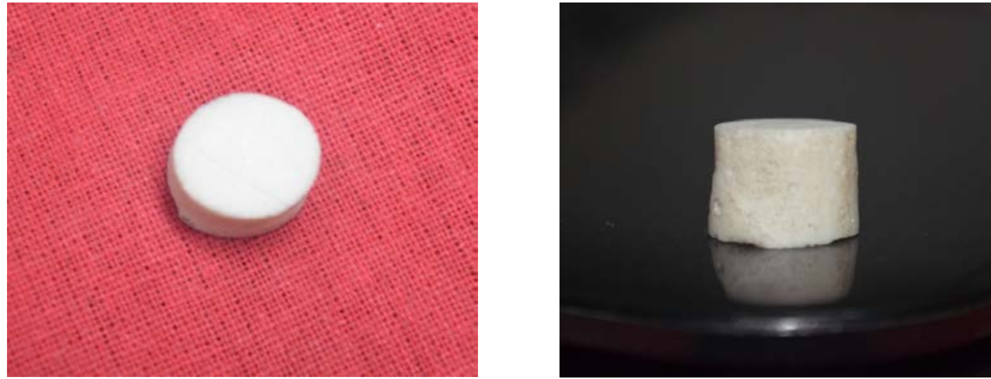


Fig. 4.11 A typical composite specimen for compression test

(a) (b)

Fig. 4.12 (a) Universal testing machine *Instron 1195* and
(b) Loading arrangement for compression test

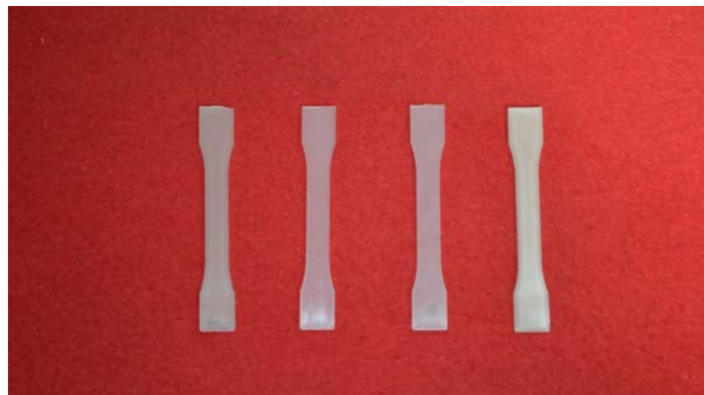
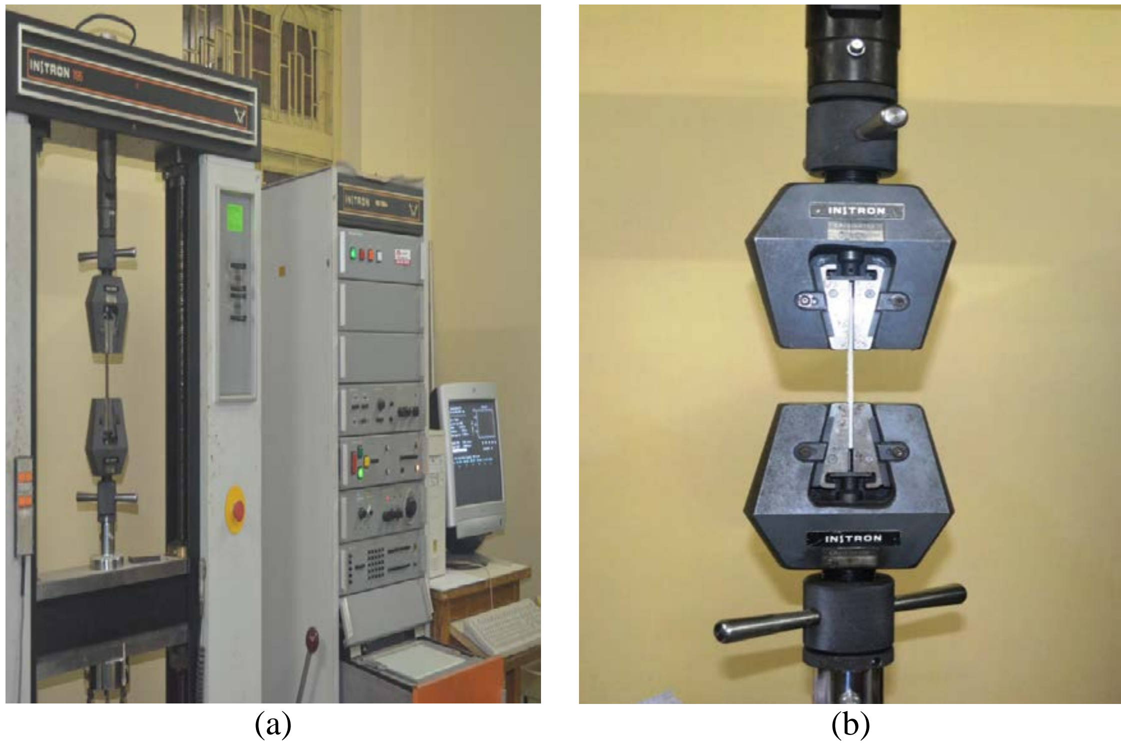


Fig. 4.13 Typical composite specimens for tensile test



(a) (b)

Fig. 4.14 (a) Universal testing machine *Instron 1195* and (b) Loading arrangement for tensile test

Fig. 4.15 Thermal Conductivity Tester *Unitherm^{TM} 2022*

4.5 Thermal Characterization

4.5.1 Thermal Conductivity: Experimental Determination

Unitherm^{TM}Model 2022 Thermal Conductivity Tester was used to measure the thermal conductivity of various materials, which include polymers, glasses, ceramics, rubbers, composites, few metals and other materials with medium to low thermal conductivity. Fluid or semi-fluids like paste etc. can be tested using a special container. In the present work, this instrument is used to measure the room temperature effective thermal conductivity of the composite specimens. Disc type specimens are used for this purpose. This test is conducted in accordance with ASTM E-1530 standards. The pictorial view of the Unitherm^{TM}Model 2022 tester is given in Figure 4.15.

Operating Principle of UnithermTM Model 2022

The material was held under uniform compressive load between two polished surfaces, each controlled at a different temperature. The lower surface is part of a calibrated heat flow transducer. The heat flows from the upper surface, through the sample, to the lower surface, establishing an axial temperature gradient in the stack. After reaching thermal equilibrium, the temperature difference across the sample was measured along with the output from the heat flow transducer. These values and the sample thickness were then used to calculate the thermal conductivity. The temperature drop through the sample was measured with temperature sensors in the highly conductive metal surface layers on either side of the sample.

By definition "Thermal conductivity is the exchange of energy between adjacent molecules and electrons in a conducting medium, it is a material property that describes heat flow within a body for a given temperature difference per unit area."

For one-dimension heat flow, the equation is given as:

$$Q = \kappa A \frac{T_1 - T_2}{x} \qquad \textbf{(4.5)}$$

where, Q is the heat flux (W), A is the cross-sectional area (m^2), k is thermal conductivity (W/m-K), x is the sample thickness (m), $T_1 - T_2$ is the temperature difference between surfaces (°C or K).

The thermal resistance of the sample is given as:

$$R = \frac{T_1 - T_2}{QA} \quad \textbf{(4.6)}$$

where, R is sample resistance between hot and cold surfaces. (m^2-K / W)
From the former equation, we can write

$$k = \frac{x}{R} \quad \textbf{(4.7)}$$

In Unitherm™ 2022, transducers measure the value of heat flux Q and temperature difference between upper and lower plate. Thus, thermal resistance between surfaces can be evaluated. Providing different thickness and known cross-sectional area as input parameters, the sample thermal conductivity can be calculated.

4.5.2 Thermal Mechanical Analyzer

Glass transition temperature (T_g) is the temperature at which the mechanical properties of amorphous polymer changes from the brittle state of glass to a rubbery state. The most important property change at the glass transition temperature of the printed circuit board (PCB) materials is the thermal expansion, which is a swift from a relative low value to a very high value. This kind of change is not desirable as it imposes stress on the PCBs when they experience high-temperatures during manufacturing, assembly or during their service-life. Similarly, coefficient of thermal expansion (CTE) is the rate of change of the thermal expansion of a material. A material with high CTE will induce stress within the component. A low CTE is therefore preferable. In the present work, T_g and CTE of the composites were measured with a *Perkin Elmer DSC-7 Thermal Mechanical Analyzer* (TMA) in expansion mode (Figure 4.16).

At first, the TMA sample stage was purged with nitrogen gas. The sample length is set between 6-8 mm and the width as well as thickness was about 2-3 mm. During the TMA measurement, the specimen was heated from 30 to 150°C at a heating rate of 5°C/min. For each measurement, two heating scans were used. The first heating scan was 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 was used to determine the T_g and CTE of the material.

4.6 Electrical Characterization

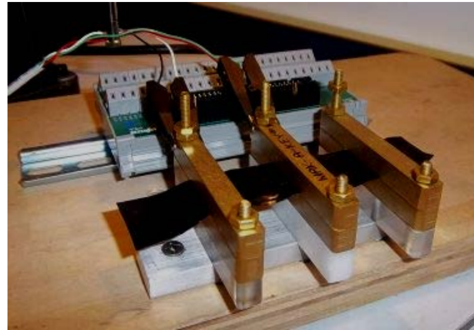
4.6.1 Electrical Resistivity

Bulk resistivity or Volume resistivity 'ρ' is the measurement of resistance (R) multiplied by the cross-section of a specimen (width × thickness) divided by the length of the material between the electrodes. Its units are typically Ohm-cm (Ω-cm) and it is expressed by the equation:

$$\rho = R\left(\frac{W \times T}{L}\right) \quad \textbf{(4.8)}$$

where 'ρ' is the resistivity, R= Resistance, W= width of the specimen, T=thickness of the sample and L =Length of the sample.

Fig. 4.16 Perkin Elmer DSC-7 Thermal Mechanical Analyzer



Arrangement of the sample between the pair of strip electrodes

Fig. 4.17 High resistance meter (type ZC36)

Fig. 4.18 Hioki 3532-50 LCR Hi tester

Fig. 4.19 Aluminium foil wrapped test samples for dielectric test

Resistivities of the samples were measured by using *High Resistance Meter (Type ZC36)* at a voltage of DC 1 kV. The tests were carried out at ambient temperature and pressure as per ASTM D 257. The pictorial view of the high resistance meter (ZC 36) is given in Figure 4.17. In this case, the electrodes were in contact with both sides of the material at each end.

4.6.2 Dielectric Measurement

A dielectric is an electrical insulator that can be polarized by an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material as they do in a conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced towards the field and

negative charges shift in the opposite direction. This creates an internal electric field which reduces the overall field within the dielectric itself. While the term "insulator" implies low electrical conduction, "dielectric" is typically used to describe materials with a high polarizability. The latter is expressed by a number called the relative permittivity, also known as dielectric constant. The term insulator is generally used to indicate electrical obstruction while the term dielectric is used to indicate the energy storing capacity of the material (by means of polarization). A common example of a dielectric is the electrically insulating material between the metallic plates of a capacitor.

Using *Hioki 3532-50 Hi - Tester LCR Analyzer* with applied voltage of 500 mV and in frequency range 1 kHz – 1 MHz, the dielectric constant (D_k) can be calculated from capacitance by:

$$D_k = Ct/\varepsilon_0 A \quad \textbf{(4.9)}$$

where, C is the capacitance, t is the thickness of disc, ε_0 is the electrical permittivity of free space and A is the disc area.

Figure 4.18 gives the photograph of *Hioki 3532-50 Hi - Tester LCR Analyzer* used in the present work for the measurement of dielectric constant. Disc type samples (Figure 4.19) with both surfaces wrapped with aluminium foil were used for this purpose.

Chapter Summary

This chapter has provided:

- The descriptions of materials (matrix and particulates) used in this research
- The details of fabrication and characterization of the composites
- The details of thermal and dielectric property measurement

The next chapter presents the test results related to the physical and mechanical properties of the polymer composites under this study.

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Chapter 5

Results and Discussion – I

PHYSICAL AND MECHANICAL CHARACTERISTICS OF COMPOSITES

This chapter presents the measured values of the physical and mechanical properties of the epoxy composites filled with solid glass micro-spheres (SGM) and/or micro-sized boron nitride (BN) particles. The relative effects of different filler materials on various physico-mechanical properties of the composites have also been discussed. It also presents scanning electron micrographs showing some typical micro-structural features of the composites under this study.

5.1 PHYSICAL CHARACTERISTICS

5.1.1 Density and volume fraction of voids

The theoretical and measured densities along with the corresponding volume fraction of voids in the epoxy-SGM and epoxy-BN composites are presented in Tables 5.1 and 5.2 respectively. It may be noted that the composite density values calculated theoretically from weight fractions using Eqn.4.1 are not equal to the experimentally measured values. This difference is a measure of voids and pores present in the composites. It was found that with the increase in solid glass microsphere content in epoxy resin from 0 to 35 vol%, there was a rise in density of the composite by about 11% although there was a simultaneous increase in the void fraction or porosity from 0.727 % to 2.258% (Table 5.1). Similarly, a substantial rise in composite density by about 28% was observed as the micro-sized boron nitride content in epoxy increased from 0 to 35 vol%. For the epoxy-BN composite with BN content of 35 vol%, the volume fraction of voids was estimated to be as high as 7.763% (Table 5.2).

Table 5.1 Measured and Theoretical densities of the composites (Epoxy filled with SGM)

Composites	Measured density (gm/cc)	Theoretical density (gm/cc)	Void fraction (%)
Neat Epoxy (hardened)	1.092	1.100	0.727
Epoxy + SGM (5 vol%)	1.107	1.119	1.072
Epoxy + SGM (10 vol%)	1.126	1.140	1.228
Epoxy + SGM (15 vol%)	1.142	1.160	1.551
Epoxy + SGM (20 vol%)	1.158	1.179	1.781
Epoxy + SGM (25 vol%)	1.174	1.200	2.167
Epoxy + SGM (30vol%)	1.193	1.220	2.213
Epoxy + SGM (35 vol%)	1.212	1.240	2.258

Table 5.2 Measured and Theoretical densities of the composites (Epoxy filled with BN)

Composites	Measured density (gm/cc)	Theoretical density (gm/cc)	Void fraction (%)
Neat Epoxy (hardened)	1.092	1.100	0.727
Epoxy + BN (5 vol%)	1.142	1.159	1.466
Epoxy + BN (10 vol%)	1.198	1.220	1.803
Epoxy + BN (15 vol%)	1.241	1.279	2.971
Epoxy + BN (20 vo %)	1.288	1.340	3.880
Epoxy + BN (25 vol%)	1.324	1.400	5.428
Epoxy + BN (30vol%)	1.369	1.460	6.232
Epoxy + BN (35 vol%)	1.402	1.520	7.763

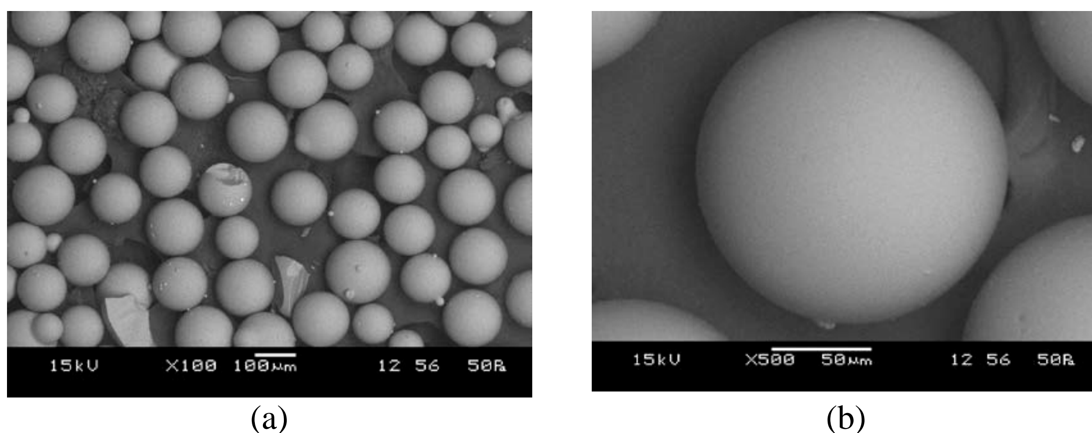
Density of a composite depends on the relative proportion of matrix and reinforcing materials and this is one of the most important factors determining the properties of the composites. The void content is the cause for the difference between the values of true density and the theoretically calculated ones. The voids significantly affect some of the mechanical properties and even the performance of composites in the workplace. Higher void content usually mean

lower fatigue resistance, greater susceptibility to water penetration and weathering [164]. The knowledge of void content is desirable for better estimation of quality of the composites. It is understandable that a good composite should have fewer voids. However, presence of void is unavoidable particularly in composites made through hand-lay-up route.

5.1.2 Micro-structural characterization

It is well known that the properties of the composites are strongly dependent on the interaction of the filler and the matrix. In order to evaluate this interaction, the microstructure of the composites, including the dispersion of the SGM and BN particles in the epoxy matrix were observed under scanning electron microscope.

Figure 5.1a shows a typical SEM image of solid glass micro-spheres used as the primary filler in the present work. A single microsphere at a higher magnification is shown in Figure 5.1b. These micrographs confirm the spherical shape of these glass beads used as reinforcement in the epoxy resin.



(a) (b)

Fig. 5.1 SEM images of glass micro-spheres used as particulate filler

The surface morphologies of SGM filled epoxy composites are shown in Figures 5.2a and 5.2b. It is seen from these micrographs that SGMs are exposed on the fracture surface or peeled from the matrix to form holes or embedded in the matrix and the dispersion of SGMs in the epoxy matrix is uniform.

Beside dispersion, the interface between the SGM and the epoxy matrix can also be observed as in Figure 5.2c. When the magnification of the images was improved, an interlayer between the SGM and the epoxy matrix is clearly observed, as indicated by arrow marks in Figures 5.2d and 5.2e. Furthermore, the inter-layers are more clearly shown as in Figure 5.2f, indicating that the epoxy molecules are strongly bonded at the surface of the SGM.

From the observed interface between the SGM and the epoxy-matrix, it is inferred that the interaction between them is strong and is enhanced with increasing SGM content due to the increase in the interface. The strong interaction can markedly modify the properties of the composite, as described above. The interlayer between the filler and polymer-matrix can be regarded as a new phase, i.e., an inter-phase. In the past, some researchers considered the existence of inter-phase regions at polymer-filler interfaces when they studied the physical and electrical characteristics of particulate-filled polymer composites [96,166-171].

In this study, inter-phase regions were observed directly. As mentioned above, an inter-phase region is comprised of polymer molecules that are bonded at the filler particle surface, which will result in an inter-phase, exhibiting unique physical and electrical properties. Obviously, the influence of the inter-phase becomes dominant when its volume fraction increases to a certain extent. Generally, the high volume fraction of the inter-phase is obtained at small filler size, for example, at sub-micrometer and nanometer ranges, and suitable filler content considering the overlapping of the inter-phase regions of adjacent filler particles.

Figure 5.2g presents the surface morphology of BN filled epoxy composites which exhibits uniform dispersion of micro-sized boron nitride particles in the epoxy matrix although no filler-polymer interlayer is seen. Figure 5.2h illustrates a typical image of the surface of the hybrid composite containing both SGM as well as BN particles as fillers.

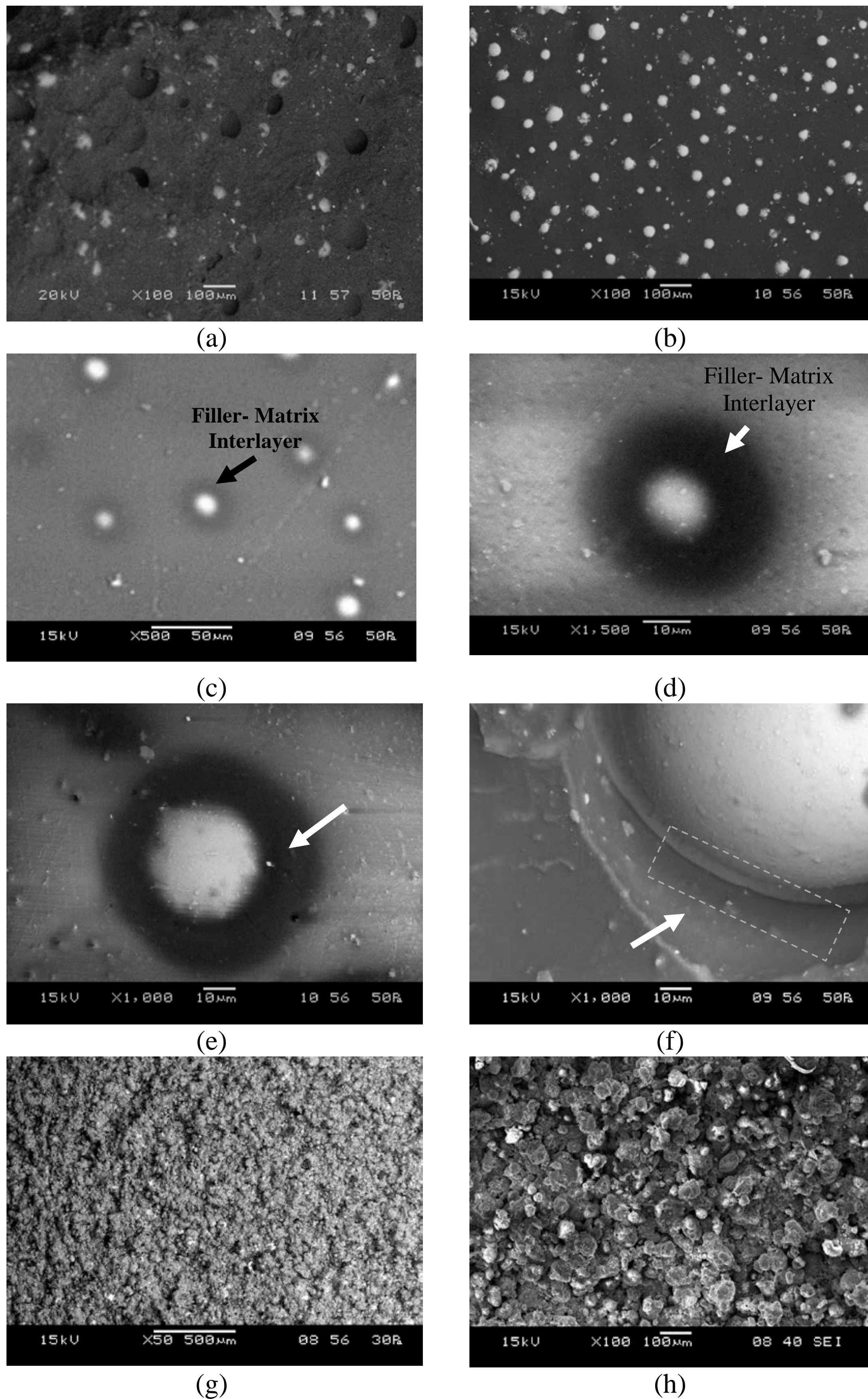


Fig. 5.2 Some typical SEM images of particulate-filled epoxy composites

5.2 MECHANICAL CHARACTERIZATION

5.2.1 Composite Micro-hardness

Hardness is considered as one of the most important characteristic features of a multi-component composite system as it indicates the ability of the composite to resist indentation. In the present work, micro-hardness values were measured and the test results for the epoxy-SGM and epoxy-BN composites are presented in Tables 5.3 and 5.4 respectively. It is evident that with addition of SGMs, micro-hardness of the composites is improved and this improvement is a function of the SGM content. With 35 vol% of SGM addition, the hardness is improved by about 7.5 times. Similarly, for epoxy-BN composites also, with the increase in BN content, the composite micro-hardness is found to be increasing although the rate of improvement is not as high as in the case of epoxy-SGM composites. While the hardness of neat epoxy is 0.085 GPa, that of the epoxy-BN composite with 35 vol% of BN comes out to be only 0.255 GPa indicating an improvement of about 3 times. This difference in hardness is obvious as the glass microspheres are much harder than boron nitride.

Mean micro-hardness values of the hybrid composites filled with both SGM and BN in different proportions are also illustrated in Figure 5.3 which shows a gradual increase in hardness values with increase in filler content.

5.2.2 Compressive Strength

Compressive strengths of the composite specimens were evaluated by conducting uni-axial compression test and the test results for the epoxy-SGM and epoxy-BN composites are presented in Tables 5.3 and 5.4 respectively. It is noticed that with addition of SGMs, compressive strength of the composite is improved and this improvement is a function of the SGM content. While the compressive strength of neat epoxy is 90 MPa, it increases by about 28% to 115.8 MPa with the incorporation of 35 vol% of SGMs in it. But in case of epoxy-BN composites, although the compressive strength is found to be increasing with BN content, the improvement is not as high as in the case of

epoxy-SGM composites. Here, an enhancement of only about 13% in compressive strength is recorded with a BN content of 35 vol%.

Measured compressive strength values of the hybrid composites filled with both SGM and BN in different proportions are also illustrated in Figure 5.4 which shows a gradual increase in compressive strength values with increase in filler content.

Table 5.3 Mechanical properties of the composites (Epoxy filled with SGM)

Composites	Tensile strength (MPa)	Compressive strength (MPa)	Micro-hardness (GPa)
Neat Epoxy (hardened)	58.00	90.00	0.085
Epoxy + SGM (5 vol%)	57.34	92.34	0.117
Epoxy + SGM (10 vol%)	57.14	93.76	0.232
Epoxy + SGM (15 vol%)	56.92	97.00	0.387
Epoxy + SGM (20 vol%)	56.59	102.23	0.445
Epoxy + SGM (25 vol%)	56.18	107.78	0.523
Epoxy + SGM (30vol%)	55.65	111.45	0.586
Epoxy + SGM (35 vol%)	55.06	115.80	0.634

Table 5.4 Mechanical properties of the composites (Epoxy filled with BN)

Composites	Tensile strength (MPa)	Compressive strength (MPa)	Micro-hardness (GPa)
Neat Epoxy (hardened)	58.00	90.00	0.085
Epoxy + BN (5 vol%)	57.16	91.43	0.092
Epoxy + BN (10 vol%)	55.98	92.76	0.105
Epoxy + BN (15 vol%)	54.12	94.08	0.139
Epoxy + BN (20 vol%)	53.54	96.27	0.182
Epoxy + BN (25 vol%)	52.09	99.03	0.198
Epoxy + BN (30vol%)	50.65	100.44	0.234
Epoxy + BN (35 vol%)	48.24	102.05	0.255

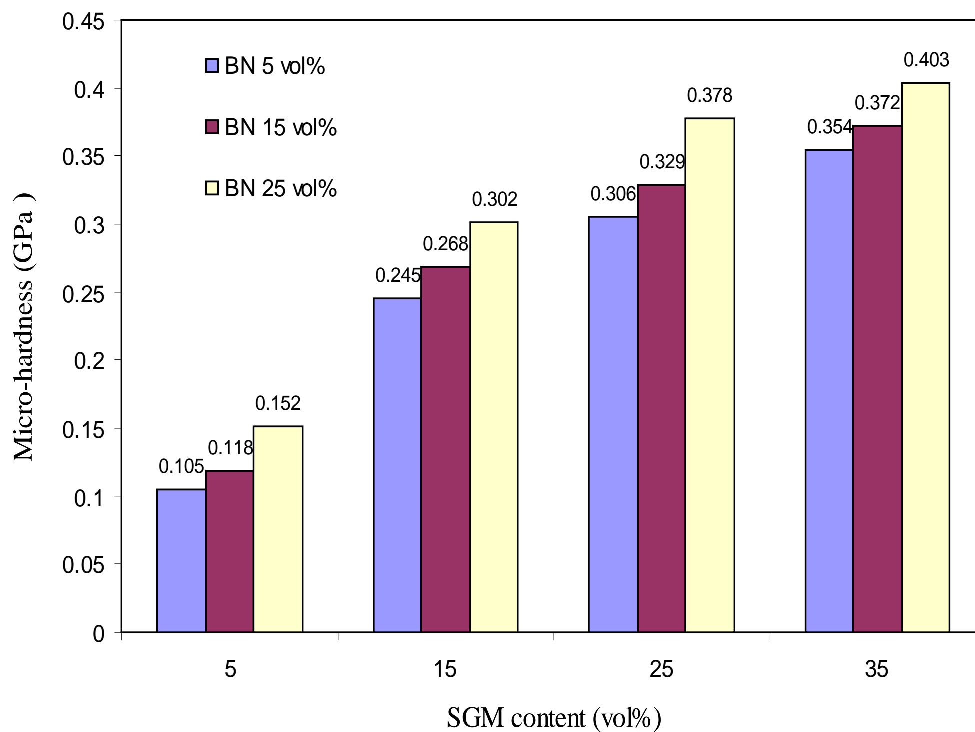


Fig. 5.3 Micro-hardness values of epoxy composites with hybrid filler

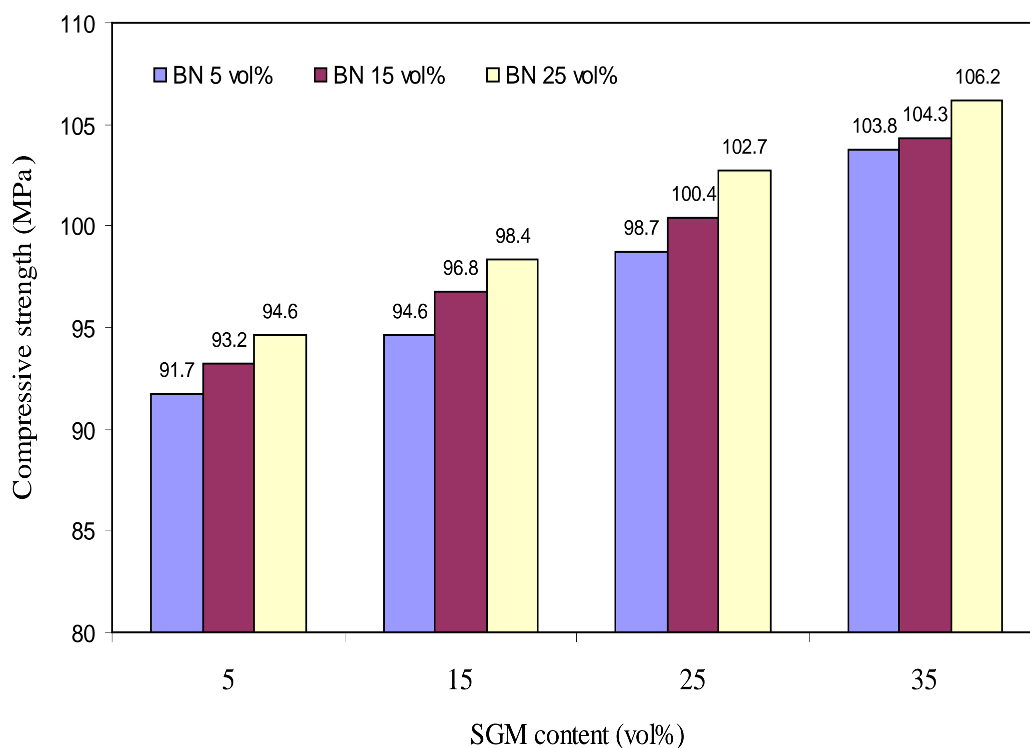


Fig. 5.4 Variation of compressive strength of hybrid filler composites

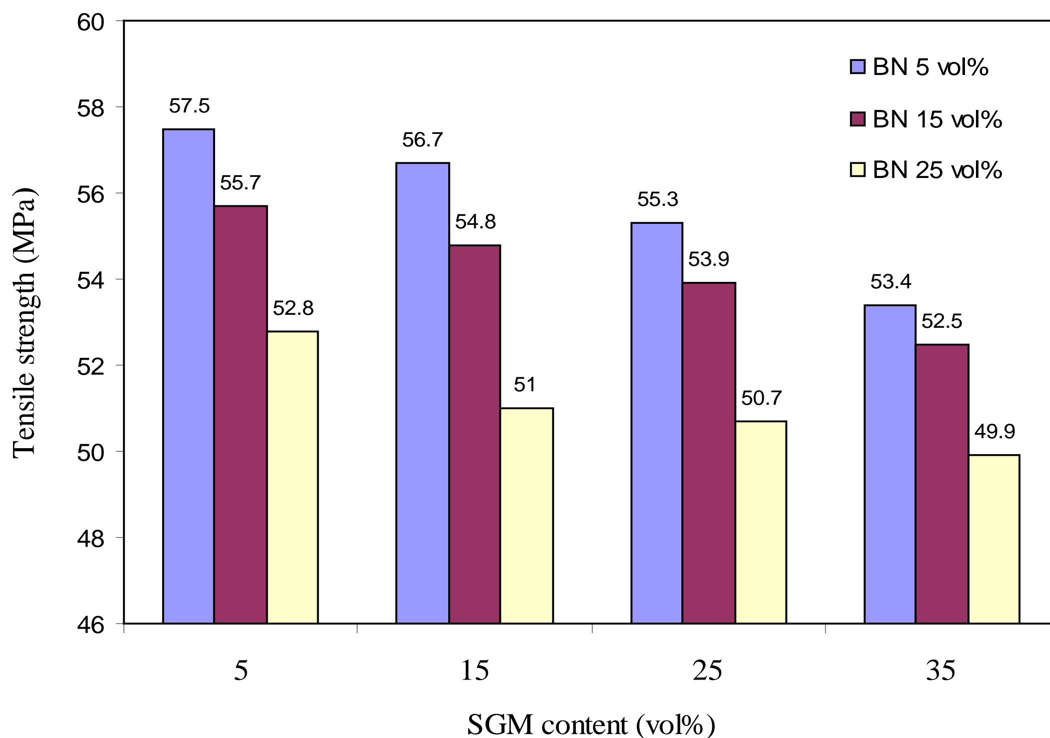


Fig. 5.5 Variation of tensile strength of hybrid filler composites

5.2.3 Tensile Strength

Tensile strengths of the composite specimens were evaluated and the test results for the epoxy-SGM and epoxy-BN composites are presented in Tables 5.3 and 5.4 respectively. It is noticed that with addition of SGMs, tensile strength of the composite decreases and this decrement is a function of the SGM content. While the tensile strength of neat epoxy is 58 MPa, it decreases by about 5 % to 55.06 MPa with the incorporation of 35 vol% of SGMs in it. In case of epoxy-BN composites too, the tensile strength is found to be decreasing with BN content and the reduction is more as compared to the epoxy-SGM composites. Here, a reduction of about 17% in the tensile strength is recorded with a BN content of 35 vol%.

Measured tensile strength values of the hybrid composites filled with both SGM and BN in different proportions are also illustrated in Figure 5.5 which shows a gradual drop in tensile strength values with increase in filler content.

Discussion

Density of the particulate filled composites is always higher than that of the polymer since both SGM and BN are denser than epoxy. Similarly, incorporation of SGM and/or BN leads to the improvement of mean composite hardness. Mechanical characterization of the composites under this investigation reveals that the trends observed in respect to the compressive strengths are quite different from those obtained in the case of tensile strength variations with the filler loading (Tables 5.3 and 5.4). The increase in compressive strength with increased filler content is due to the favourable deformation processes facilitated by the presence of fillers (either SGM or BN or both) in the matrix. Under a compressive loading situation, the fillers apparently aid the load bearing capability of a composite, rather than acting as stress raiser as is the case in tensile loading. Further, the fact that in a compression test, any cracks or flaws introduced by dispersion of the filler will, if at all, get healed (closed) and made ineffective, contrary to the crack opening mechanism occurring in a tensile loading situation.

Chapter Summary

Several important conclusions emerge from the extensive results obtained in these studies carried out on epoxy composites with single and hybrid filler systems with regard to their physical, mechanical and micro-structural behaviour. The results presented in this chapter clearly indicate a trendy characterization in the behaviour of different particulate composites studied and they provide a very important criterion for the choice of the composites for specific needs.

The next chapter presents the test results related to the thermal characteristics of the composites filled with solid glass micro-spheres and/or boron nitride with emphasis on their heat conduction / insulation capabilities.

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Chapter 6

Results and Discussion – II

THERMAL CHARACTERISTICS OF THE COMPOSITES

This chapter presents the test results for thermal properties such as effective thermal conductivity (k_{eff}), glass transition temperature (T_g) and coefficient of thermal expansion (CTE) of all the single and multi-filler composites under this investigation. The results of the numerical analysis and validation of the proposed theoretical models in regard to the determination of effective thermal conductivity are presented in this part of the thesis. This chapter also explores promotion of inter-connectivity among the fillers in the epoxy matrix, leading to higher $k_{eff,}$ by the use of hybrid fillers. The effects of particulate fillers on T_g and CTE of the composites are discussed.

6.1 EFFECTIVE THERMAL CONDUCTIVITY (k_{eff})

Effective thermal conductivities of epoxy composites filled with single and hybrid fillers are evaluated theoretically and experimentally. The interpretation and comparison of results obtained from different methods for composites with different filler concentrations are presented.

6.1.1 Epoxy Composites filled with Solid Glass Microspheres (SGM)

Numerical Method: *Concept of Finite Element Method and ANSYS*

The basic idea in the finite element method (FEM) is to find the solution of a complex engineering problem by replacing it with a simpler one. Since the actual problem is replaced by a simpler one in finding the solution, one is able to find only an approximate solution rather than an exact solution. The finite element method was first developed in 1956 by Turner et al. [172] for the

analysis of structural problems in aviation industry. Thereafter, the method was recognized for potential application in different types of applied sciences and engineering problems. Today, it is considered as one of the best methods for solving a wide variety of real world engineering problems.

In FEM, the actual continuum of matter is represented as an assemblage of subdivisions called finite elements. These elements are considered to be interconnected at specific points called nodes. The nodes generally lie on the element boundaries where adjacent elements are considered to be connected. Since the actual variation of field variables such as displacement, temperature, stress, pressure, velocity etc. inside the continuum is not known, it is assumed as the variation of field variables inside a finite element can be approximated by a simple function. These approximating functions called interpolation models are defined in terms of the values of the field variable at the nodes. When the equilibrium equation for the whole continuum is written, the new unknowns will be the nodal values of the field variable. By solving the field equations, which are generally in matrix form, the nodal values of the field variable will be known. Once these are known, the approximating functions define the field variable throughout the assemblage of elements. A general purpose finite element modeling package called ANSYS is used for solving a wide variety of mechanical problems which entails to static/dynamic, structural analysis (both linear and non-linear), heat transfer and fluid flow problems as well as acoustic and electromagnetic problems.

Basic Steps in Finite Element Method

Solving a general engineering problem in FEM involves the following steps:

- The first step in the finite element method is to divide the structure or continuum into subdivisions or elements. Then the structure is to be modeled with suitable finite elements. The size, shape, arrangement and number of elements are to be decided in the first step.

- In the second step, a proper interpolation model is to be selected. Since the solution of a complex structure under any specified conditions cannot be predicted exactly, a suitable solution within an element is assumed to approximate the unknown solution. The assumed solution must be simple from a computational standpoint, but it should satisfy certain convergence requirements.
- In the third step, element characteristic matrices and input data are to be derived from the assumed interpolation model by using either equilibrium conditions or a suitable variational principle.
- In the next step, the element equations are assembled to obtain overall equilibrium equations. Since the structure is composed of several finite elements, the individual element characteristic matrices and input data are to be assembled in a suitable manner.
- The last step is to obtain the solution for the unknown nodal variables. The overall equilibrium equations have to be modified incorporating the boundary conditions of the problem.

Advantages of finite element method over several other numerical methods:

- Irregular shaped domain with different boundary conditions can be analyzed.
- Multiple numbers of domains can be easily analyzed.
- Domains consisting of more than one material can be analyzed.
- Solution accuracy can be improved either by choosing approximation of higher degree polynomial or by proper refinement of mesh.

In the present work, using the finite-element program ANSYS, thermal analysis is carried out for the conductive heat transfer through the epoxy-SGM composite body. In order to make this analysis, three-dimensional physical models with spheres-in-cube (SGM in epoxy) lattice arrays have been used to simulate the microstructure of composite materials for five different filler concentrations. Furthermore, the effective thermal conductivities of these composites filled with SGM up to about 17.9 % by volume are numerically determined.

Description of the problem:

The estimation of effective properties of composites is of vital importance for proper design and application of composite materials. The micro-structural characteristics are essential criteria which influence the effective properties of the composite. Micro-structure means the shape, size, spatial distribution and orientation of the embedment in the matrix. Despite the fact that most composite systems have inclusions of random distribution and orientation, a great insight of the effect of microstructure on the effective properties can be achieved from the analysis of composites with periodic structure. A system with high degree of symmetry in its structure is preferred as it can be easily analyzed. Based on micro-structure, composites can generally be classified as laminate composite, i.e. with multi-layered structure and dispersion composite, i.e. including a matrix phase and one or more dispersion phases. In this work, models of dispersion composite are generated. The factors affecting the effective thermal conductivity of dispersion composite are structural features of the composite and thermal conductivity of each component material. The structural features include shape and size of matrix, and volume fraction, shape, size and orientation of dispersion. The structure of dispersion composite is considered to be composed of some very simplified basic models. In a basic model, the shape of composite is assumed to be cubical.

A schematic representation of solid glass micro-spheres embedded in an epoxy body having a periodic arrangement is shown in Figure 6.1. The prescribed boundary conditions with the direction of heat flow for the conduction problem is shown in Figure 6.2 in which the temperature at the nodes along the surface ABCD is T_1 (=100^0C), the ambient convective heat transfer coefficient is assumed to be 25 W/m^2-K and the analysis of the problem is done at a room temperature of 27°C. The other surfaces parallel to the direction of the heat flow are assumed to be adiabatic. The temperatures at the inside domain and on the other boundaries are not apprehended.

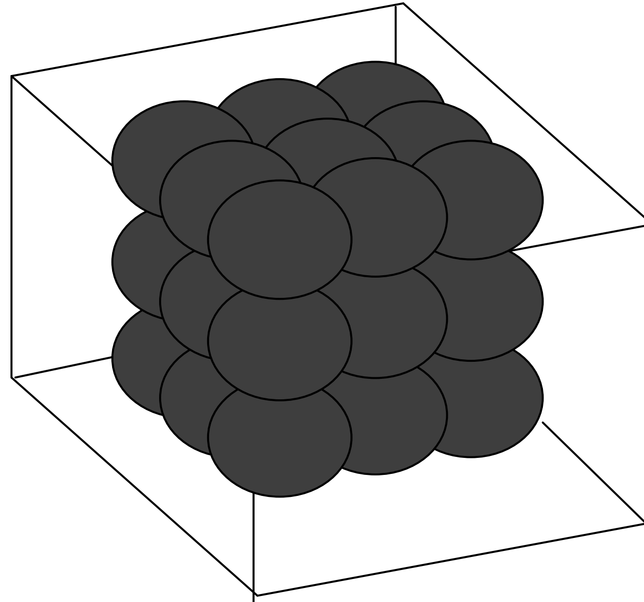


Fig. 6.1 Schematic diagram showing a typical arrangement of SGM in epoxy

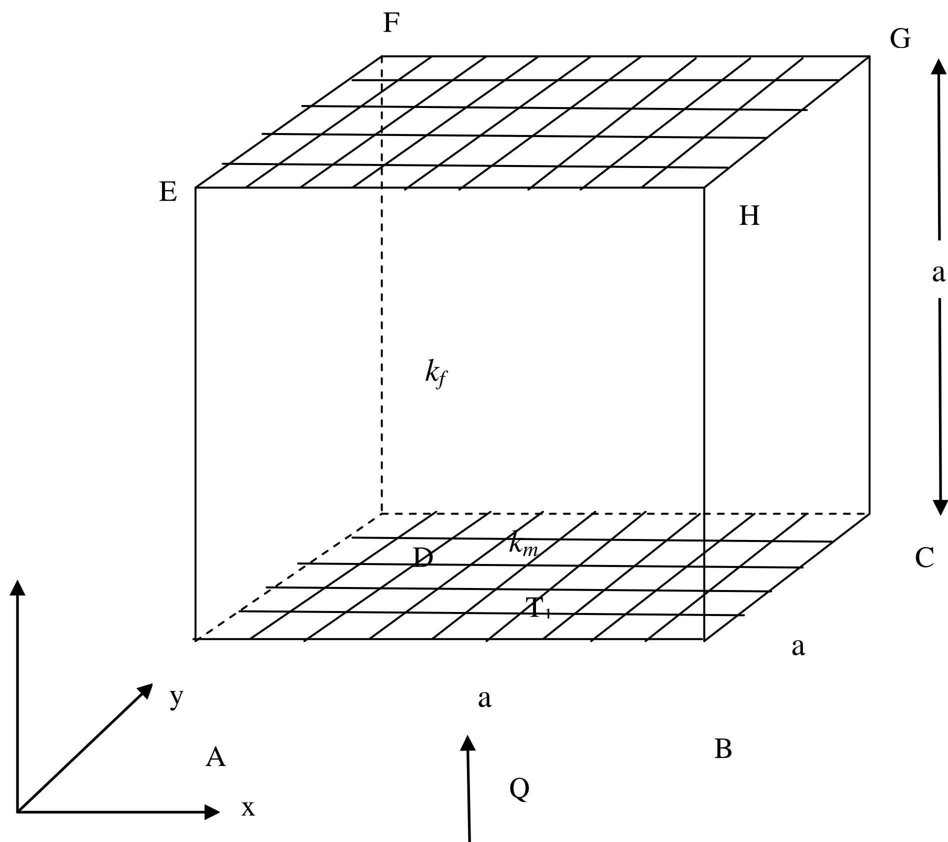


Fig. 6.2 The heat flow direction and boundary conditions for the particulate-polymer composite system

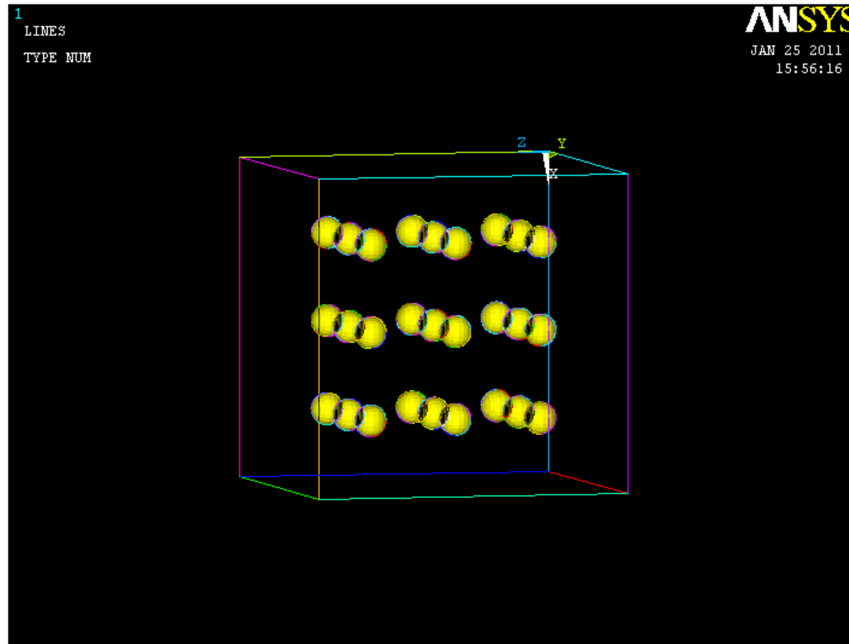
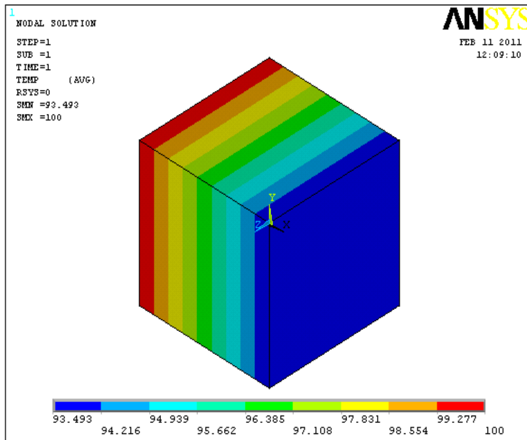


Fig. 6.3 A typical 3-D sphere-in-cube model with 1.4 vol % filler concentration

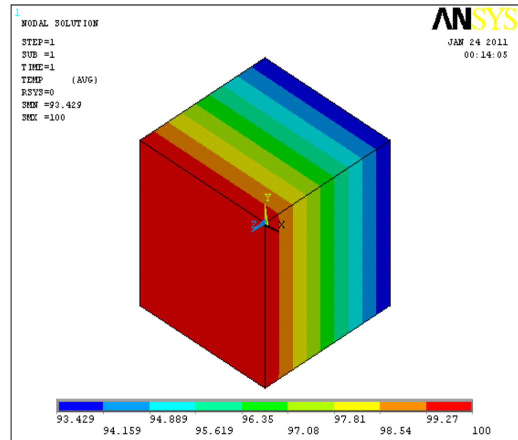
Thereafter, the finite-element program package ANSYS is used to obtain the temperature plots. A few presumptions involved in this analysis are:

- 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 from voids.
- The fillers are assumed to be uniformly distributed in the matrix in a square periodic array.

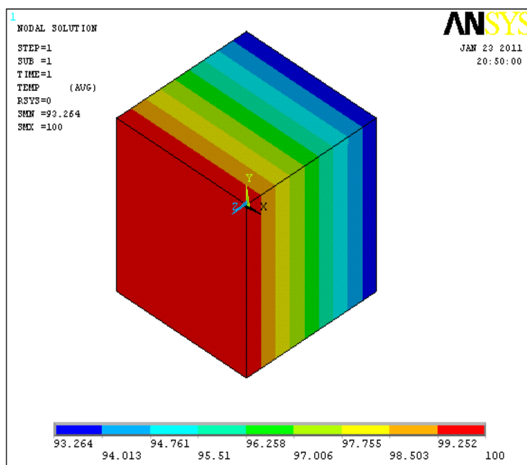
Thermal conductivities of the SGM-epoxy composites are numerically estimated by using the sphere-in-cube model. A typical 3-D model showing arrangement of solid glass micro-spheres (1.4 vol%) within the cube shaped matrix body is illustrated in Figure 6.3. Temperature profiles obtained from FEM analysis for these composites with SGM (100 μm size) concentrations of 1.4, 3.35, 6.5, 11.3 and 17.9 vol% are presented in Figures 6.4a, 6.4b, 6.4c, 6.4d and 6.4e respectively.



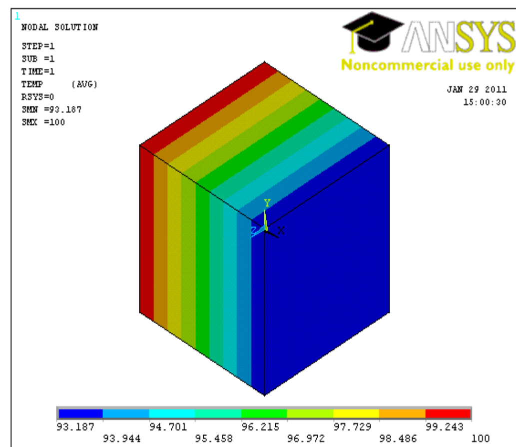
(a) Filler concentration 1.4 vol %



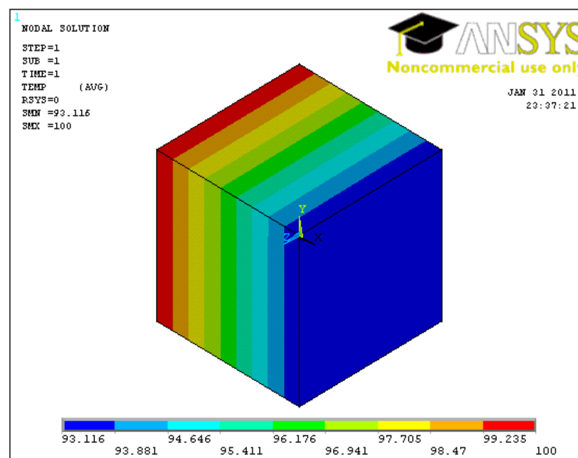
(b) Filler concentration 3.35 vol %



(c) Filler concentration 6.5 vol %



(d) Filler concentration 11.3 vol %



(e) Filler concentration 17.9 vol %

Fig. 6.4 Temperature profiles for epoxy-SGM composites with different filler concentrations

Table 6.1. k_{eff} values for composites obtained from FEM

SGM content (vol %)	k_{eff} (W/mK)
0	0.3630
1.4	0.2862
3.35	0.2568
6.5	0.2283
11.3	0.2195
17.9	0.2145

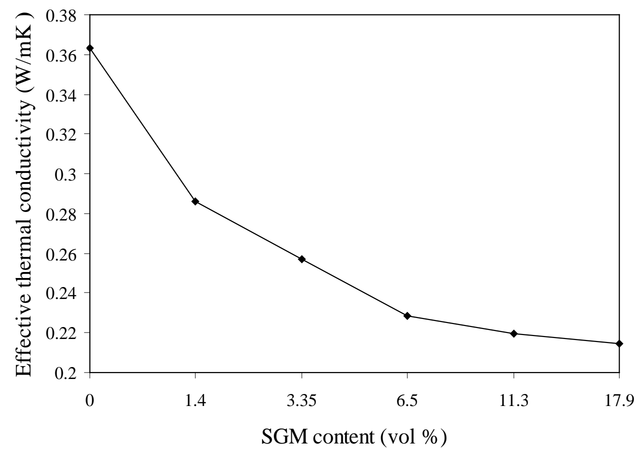


Fig. 6.5 Variation of k_{eff} with SGM content

It is observed in Figure 6.4 that the temperature difference between the opposite faces of the modeled cube increases with the increase in volume percentage of SGM particle. It is possibly due to the obstruction in heat flow by the micro-sized glass particles along the heat conduction path.

Table 6.1 and Figure 6.5 presents the variation of effective thermal conductivity (k_{eff}) obtained by FEM with the SGM content in the composites. It is clearly observed that with the increase in filler concentration in the composites, the value of k_{eff} gradually decreases. With the addition of 1.4 vol% of SGM, the thermal conductivity of epoxy decreases by about 21% and with addition of 17.9 vol% of SGM, the effective conductivity of the composite decreases by about 41% compared to neat epoxy resin.

<u>Experimental Determination of Effective Thermal Conductivity:</u>

Unitherm™ Model 2022 Thermal Conductivity Tester is used to measure conductivity of the composites fabricated for this investigation in accordance with ASTM E-1530 test standards. Figure 6.6 presents the values of effective thermal conductivity (both FEM as well as measured) as a function of the SGM content in the composites. The variation of k_{eff} with filler concentration suggests

that the incorporation of SGM imparts insulative characteristics to the epoxy matrix due to its insulative nature. The comparison graph in Figure 6.6 also indicates that there is a discrepancy between the FEM simulated results and the measured values of conductivity. This is attributed to certain assumptions that are made for the numerical analysis for simplification of the problem. In the numerical analysis, the distribution of SGM in the matrix body is supposed to be in an arranged manner, whereas the glass micro-spheres dispersed in the resin are actually randomly distributed in the composite sample. Further, the composites are not free from voids as assumed.

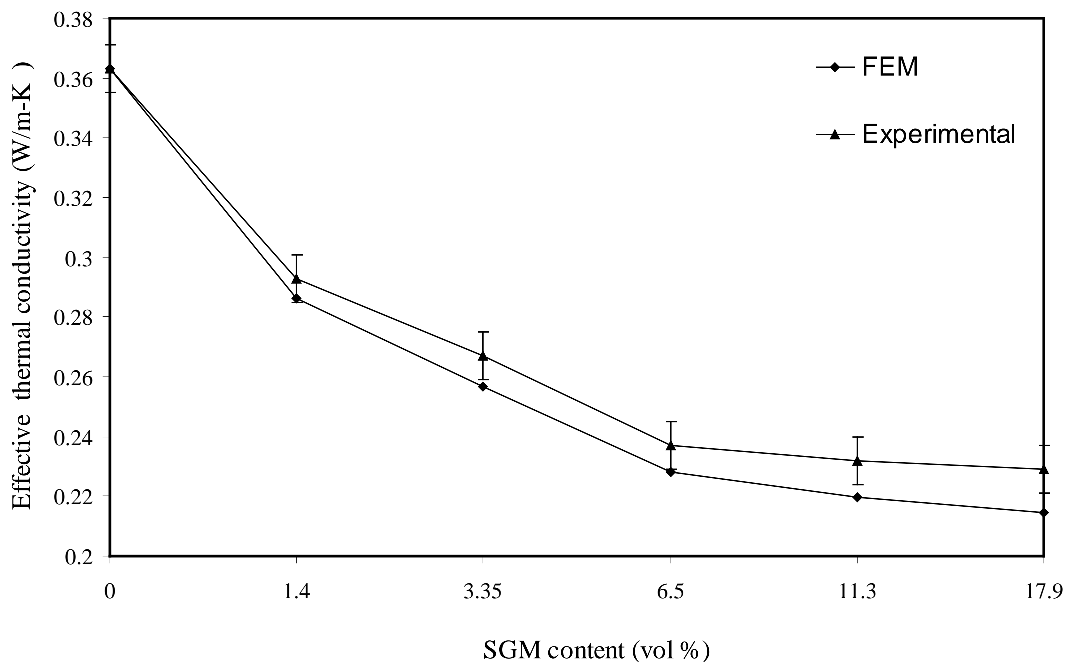


Fig. 6.6 Comparison of k_{eff} values obtained from FEM with measured values

Figure 6.7 delineates a comparison of measured values of k_{eff} of the SGM filled epoxy composites with the values determined using some of the already existing theoretical models and correlations like Maxwell's equation [79], Lewis and Nielsen's equation [79] and Russell's model [79]. It is seen in the figure that all these theoretical models overestimate the value of k_{eff} *as* the measured values are much lower for composites irrespective of SGM content. Table 6.2 provides the percentage errors associated with k_{eff} values obtained from different

models/correlations with respect to the corresponding measured values. It may be noted that the errors associated with the theoretical models are quite high whereas those associated with FEM simulations, with respect to the measured values lie within a nominal acceptable range of just 0-2 %.

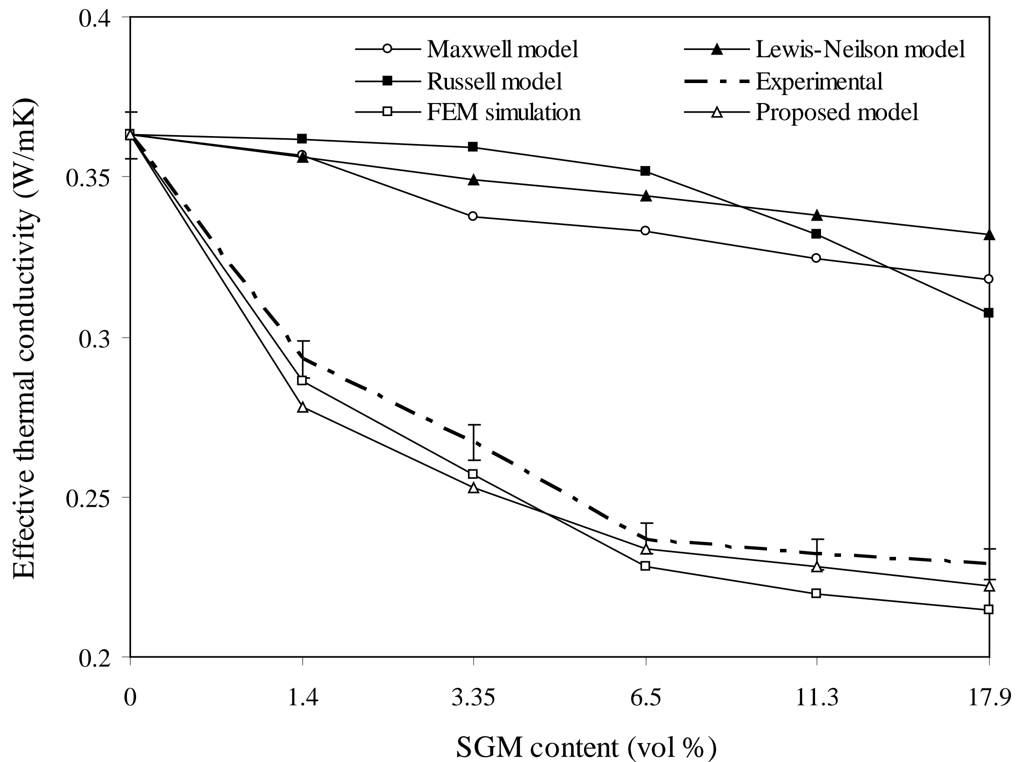


Fig. 6.7 Comparison of k_{eff} of composites obtained from different models

Table 6.2 Percentage errors (with respect to the measured values) associated with k_{eff} values obtained using different methods

SGM content in composite (vol %)	Measured value of k_{eff} (W/m-K)	Percentage errors associated with k_{eff} values obtained from different models/correlations with respect to the corresponding measured values			
		Maxwell's equation	Lewis Nielsen's equation	Russell's model	FEM model
0	0.363	0	0	0	0
1.4	0.293	1.763	1.928	0.33	0.7
3.35	0.267	6.969	3.856	1.074	1.1
6.5	0.237	8.319	5.234	3.168	0.9
11.3	0.232	10.606	6.887	8.539	1.3
17.9	0.229	12.396	8.539	15.289	1.5

Thus, it is propitious that the incorporation of SGM results in significant drop in thermal conductivity of epoxy resin. It is seen that with the addition of 1.4 vol% of SGM, the effective thermal conductivity of the composite decreases by about 19% and with 17.9 vol% of SGM the thermal conductivity decreases by about 37% compared to neat epoxy resin.

Determination of k_{eff} by using Proposed Theoretical Model:

Effective thermal conductivity values of the above composites have also been estimated theoretically by using the correlation given in Eqn. 3.29 derived on the basis of the one-dimensional heat conduction model proposed in this work. The details of model development have already been described in Chapter 3. The proposed correlation is as follows:

$$k_{eff} = \left[1 \Big/ k_p \left(1 - \frac{6v_f}{\pi}\right)^{1/3} + 2\left(k_p \left(\frac{4\pi}{3v_f}\right)^{1/3} + \pi \left(\frac{2v_f}{9\pi}\right)^{1/3} \times \left(k_g \frac{\rho_c}{\rho_g} - k_p \right)\right)^{-1} \right]^{-1}$$

Here, k_p and k_g are the respective heat conductivities of the polymer and the micro-sphere phase, ρ_p and ρ_g are the effective densities of the polymer and the micro-sphere phase respectively, and v_f is the volume fraction of the filler i.e. the SGM in the composite.

Table 6.3 presents the values of k_{eff} obtained from the proposed correlation for epoxy composites with different SGM concentrations. The corresponding measured and the FEM simulated values are also presented in this table for the purpose of comparison.

Table 6.3 Thermal conductivity values obtained from different methods

SGM content (vol %)	Thermal Conductivity (k_{eff}) obtained from different methods (W/m-K)		
	Proposed Model	Measured Value	FEM Model
0	0.3630	0.363	0.3630
1.4	0.2783	0.293	0.2862
3.35	0.2527	0.267	0.2568
6.5	0.2340	0.237	0.2283
11.3	0.2283	0.232	0.2195
17.9	0.2220	0.229	0.2145

Figure 6.8 presents a comparison of k_{eff} values obtained from the proposed correlation with the corresponding FEM simulated and experimentally measured values for the composites with different SGM concentrations. It is seen that the theoretical values are in fairly good agreement with the experimental ones. This agreement therefore validates the proposed model for composites with a filler concentration up to 17.9 vol %.

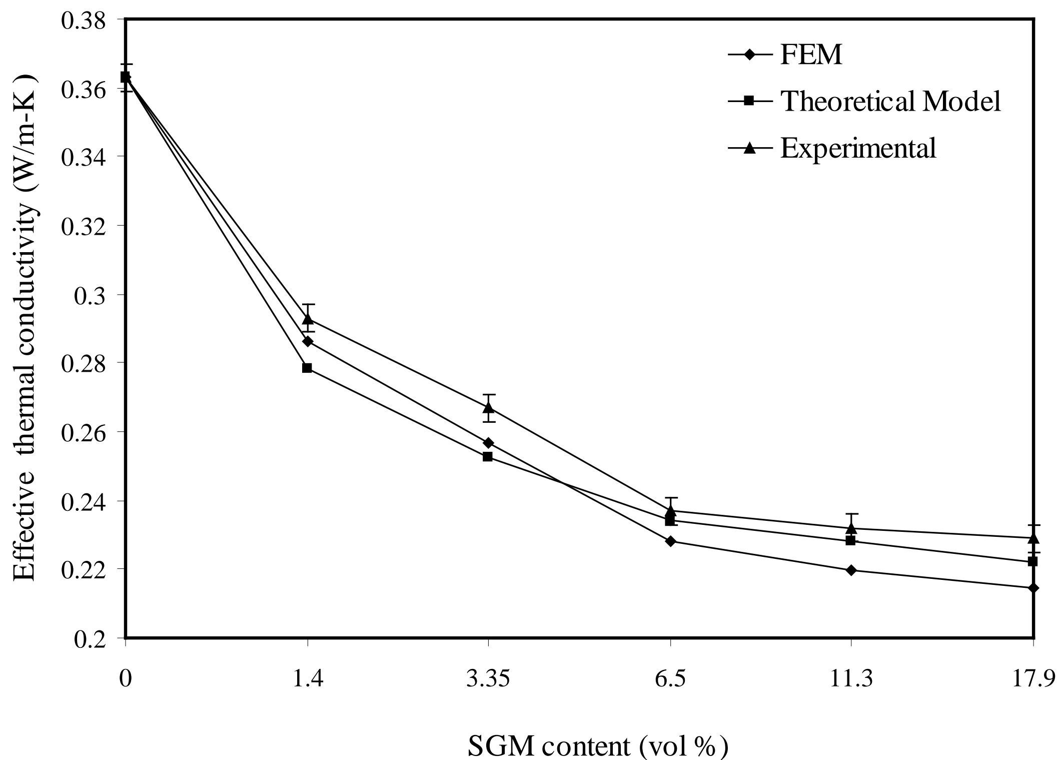


Fig. 6.8 Comparison of k_{eff} values obtained from FEM model and proposed theoretical correlation with the measured values

Effective thermal conductivity (k_{eff}) of epoxy based composites (Set-2) with SGM content ranging from 0 to 35 vol% are estimated by using some of the existing theoretical models and the proposed correlation. These values are compared with the corresponding measured values of conductivity (Table 6.4). The k_{eff} values obtained from the proposed theoretical model are in good agreement with the experimentally measured values as is seen in Figure 6.9. It is thus observed that the analytical model serves as a very good empirical model for the estimation of effective thermal conductivity for spherical inclusions and

that the proposed correlation (Eqn.3.29) can very well be used to estimate k_{eff} of composites for a broad range of SGM concentrations.

Table 6.4 Comparison of k_{eff} of composites obtained from different models.

SGM content (vol %)	Effective Thermal Conductivity (W/m-K)				
	Maxwell's equation	Lewis Nielsen's equation	Russell's model	Proposed model	Measured Values
0	0.363	0.363	0.363	0.3630	0.363
5	0.2663	0.3390	0.345	0.275	0.298
10	0.3189	0.3163	0.327	0.234	0.287
15	0.2982	0.2947	0.237	0.215	0.258
20	0.2783	0.2741	0.221	0.182	0.231
25	0.2591	0.2545	0.201	0.156	0.189
30	0.2407	0.2358	0.187	0.132	0.159
35	0.2229	0.2179	0.172	0.112	0.136

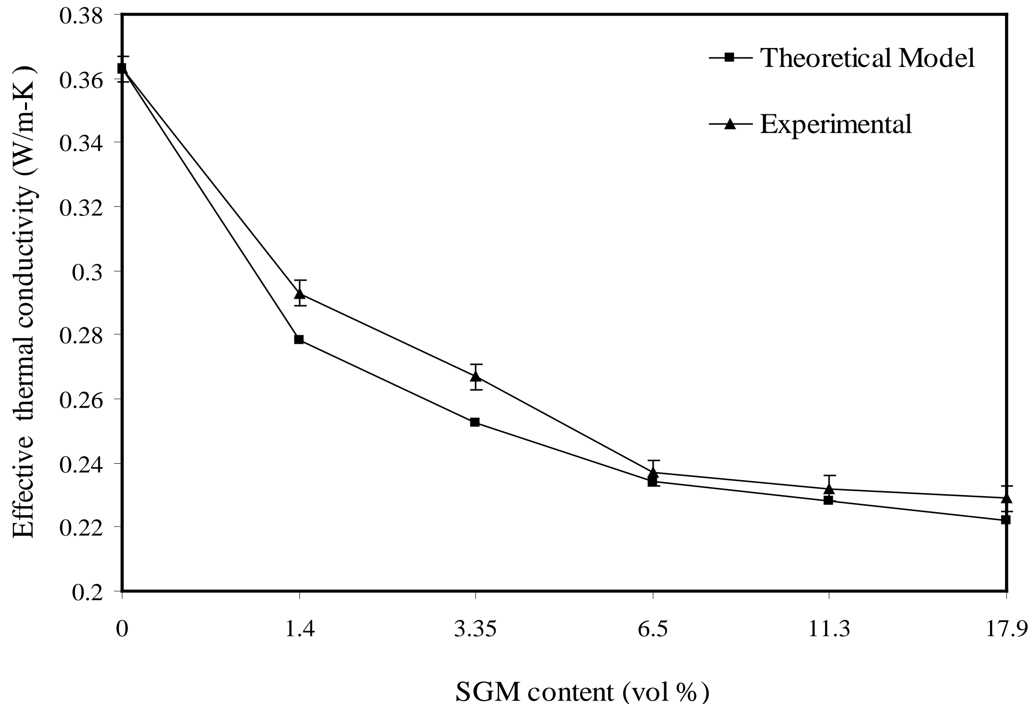


Fig. 6.9 Comparison of k_{eff} values obtained from proposed theoretical model with the experimentally measured values

Effect of micro-sphere size on effective thermal conductivity:

Thermal conductivities of composites filled with SGMs of three different sizes (100, 200 and 300 μm) are measured to study the effect of micro-sphere size on k_{eff}. The variation of k_{eff} with micro-sphere size is presented in Figure 6.10.

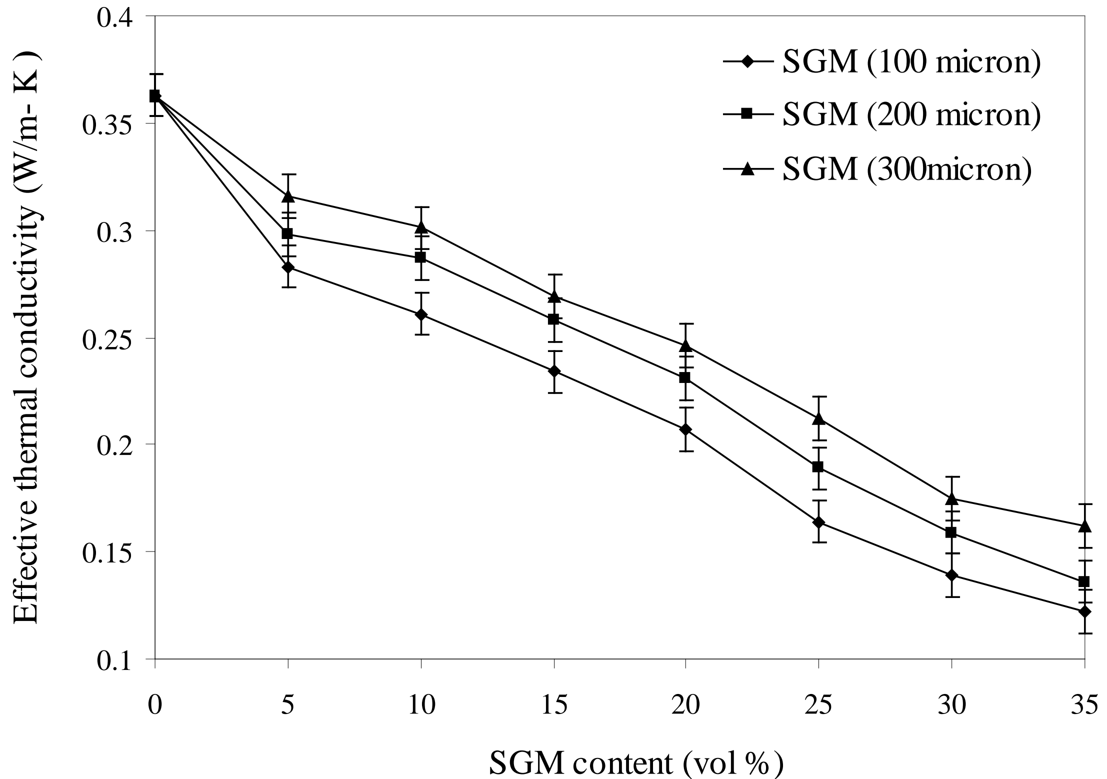


Fig. 6.10 Variation of k_{eff} with size and content of SGM

It is evident from the figure that with addition of SGMs, irrespective of the micro-sphere size, there is always a reduction in the heat conduction capability of the composites. However, it is found that this reduction is maximum in case of SGMs of smallest size i.e. 100 μm. In other words, smaller the size of solid glass micro-spheres, higher is the drop in conductivity of the composites. With addition of 35 vol% of SGM (100 μm), the thermal conductivity decreases by about 66% as compared to that of neat epoxy. At the same time, with the incorporation of same 35 vol% of SGM (300 μm), the drop in thermal conductivity is only about 53%.

6.1.2 Epoxy Composites filled with Micro-Sized Boron Nitride (BN)

This part presents the values of k_{eff} obtained from different methods (numerical, experimental and theoretical) for epoxy composites filled with different proportion of micro-sized boron nitride (BN) particles.

Numerical Method:

Using the finite-element program ANSYS, thermal analysis is carried out for the conductive heat transfer through the epoxy-BN composite body. In order to make this analysis, three-dimensional physical models with sphere-in-cube (BN in epoxy) lattice arrays have been used to simulate the microstructure of composite materials for seven different filler concentrations. Temperature profiles obtained from FEM analysis for these composites with BN concentrations of 1.4, 3.35, 5.23, 7.85, 9.04, 11.3 and 17.9 vol% are presented in Figures 6.11a, 6.11b, 6.11c, 6.11d, 6.11e, 6.11f and 6.11g respectively. It is observed in Figure 6.11 that the temperature difference between the opposite faces of the modeled cube decreases with the increase in volume percentage of BN particles. Effective thermal conductivities of the SGM-epoxy composites are then numerically estimated. It is noticed that the results obtained from FEM analysis gives an increasing trend with increase in BN concentration from 0 to 17.9 vol% as shown in Table 6.5 and Figure 6.12. It is seen that as per FEM simulation, for addition of 1.4 vol% of BN, the increase in thermal conductivity of epoxy is about 1.37% and similarly for 17.9 vol% of BN addition, the increase in thermal conductivity is about 29%.

Experimental Determination of Effective Thermal Conductivity:

Unitherm™ Model 2022 Thermal Conductivity Tester is used to measure conductivity of the composites fabricated for this investigation in accordance with ASTM E-1530 test standards. Figure 6.13 presents the values of effective thermal conductivity (both FEM as well as measured) as a function of BN content in the composites. The variation of k_{eff} with filler concentration suggests that the incorporation of BN enhances the conductivity of the composites and this enhancement is a function of the BN content in the composites.

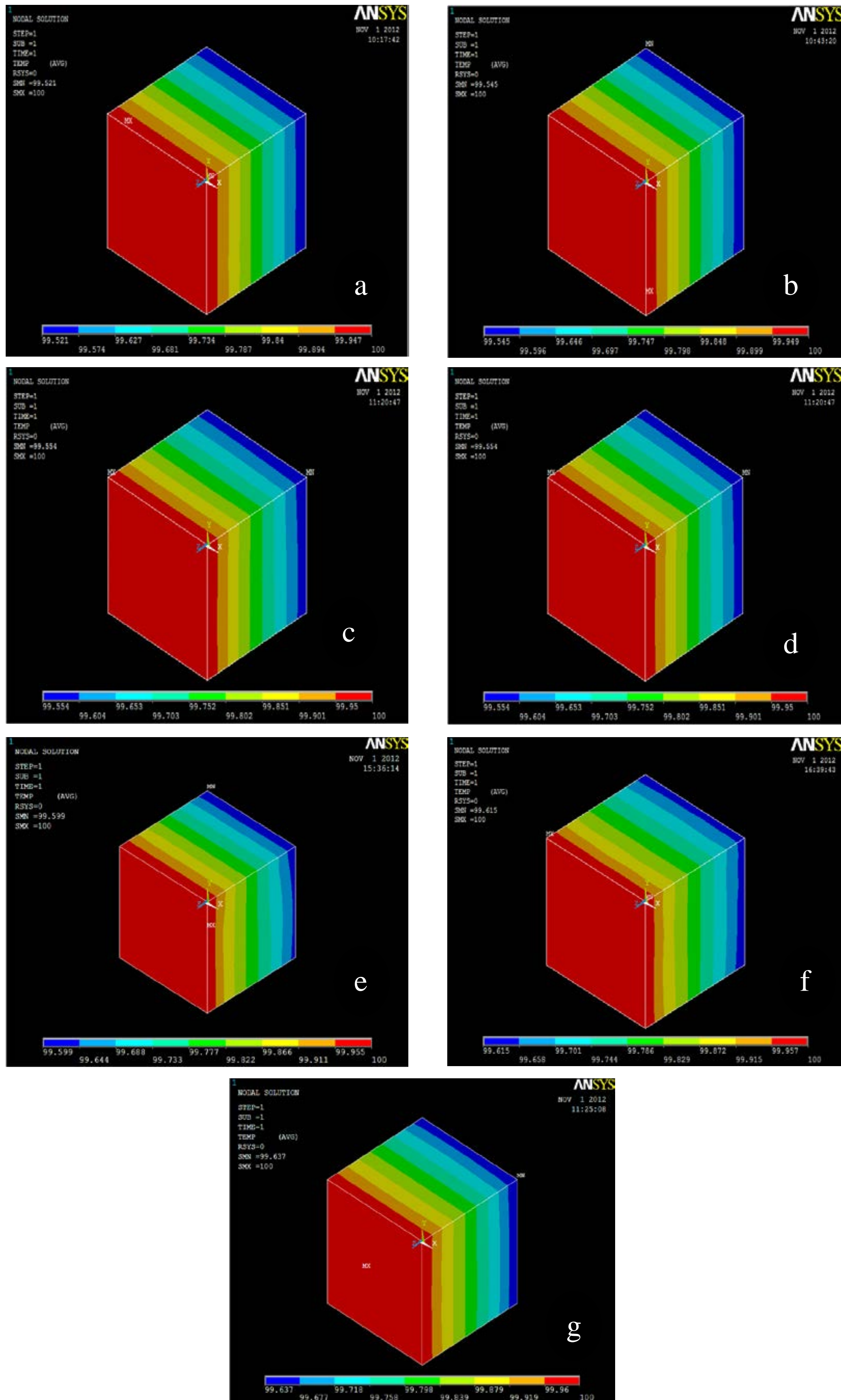


Fig. 6.11 Temperature profiles for epoxy-BN composites with different filler concentrations

Table 6.5 k_{eff} values for composites obtained from FEM

BN content (vol %)	k_{eff} (W/mK)
0	0.363
1.4	0.368
3.35	0.369
5.23	0.4025
7.85	0.424
9.04	0.4335
11.3	0.4545
17.9	0.4682

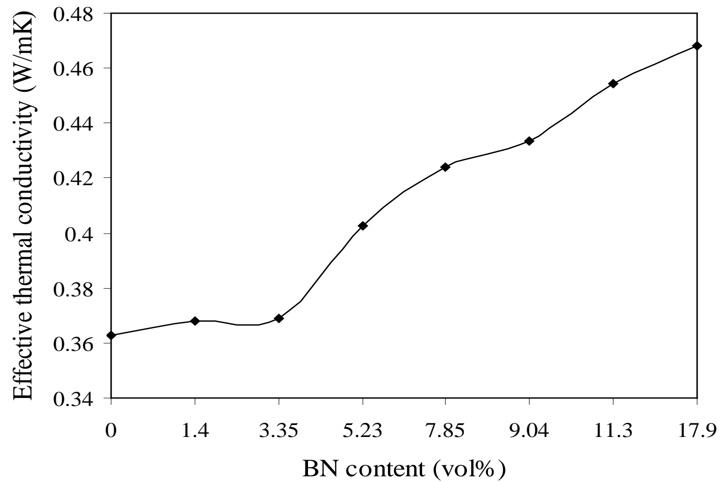


Fig.6.12 Variation of k_{eff} with BN content

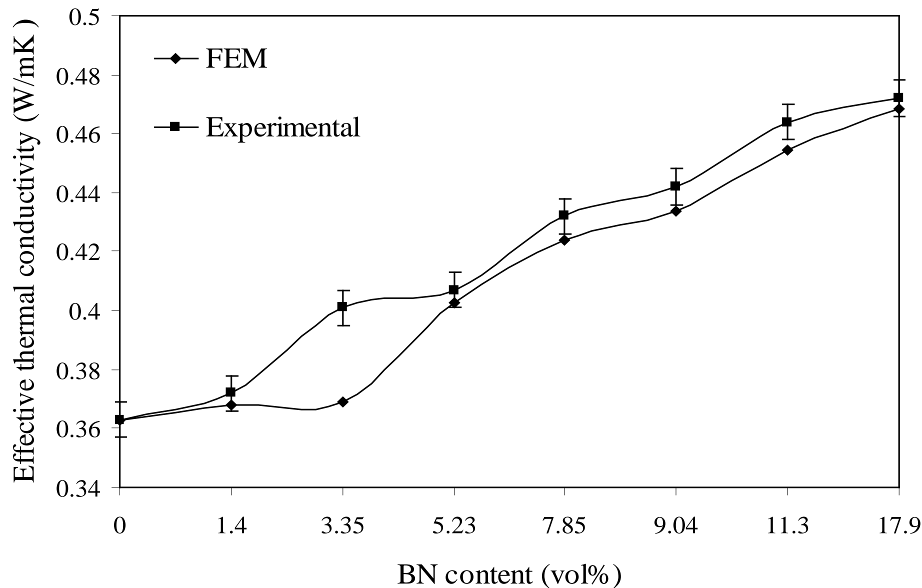


Fig. 6.13 Comparison of k_{eff} values obtained from FEM model with the experimentally measured values

It is noted in Figure 6.13 that there is an anomaly in the conductivity of measured and the simulated values because some of the premonitions are not real like the shape of BN is assumed to be spherical whereas the actual shape of BN particles is not perfectly spherical. Moreover, in the FEM analysis, the distribution of BN in the matrix body is supposed to be in an arranged manner, whereas they are actually randomly distributed in the composite sample.

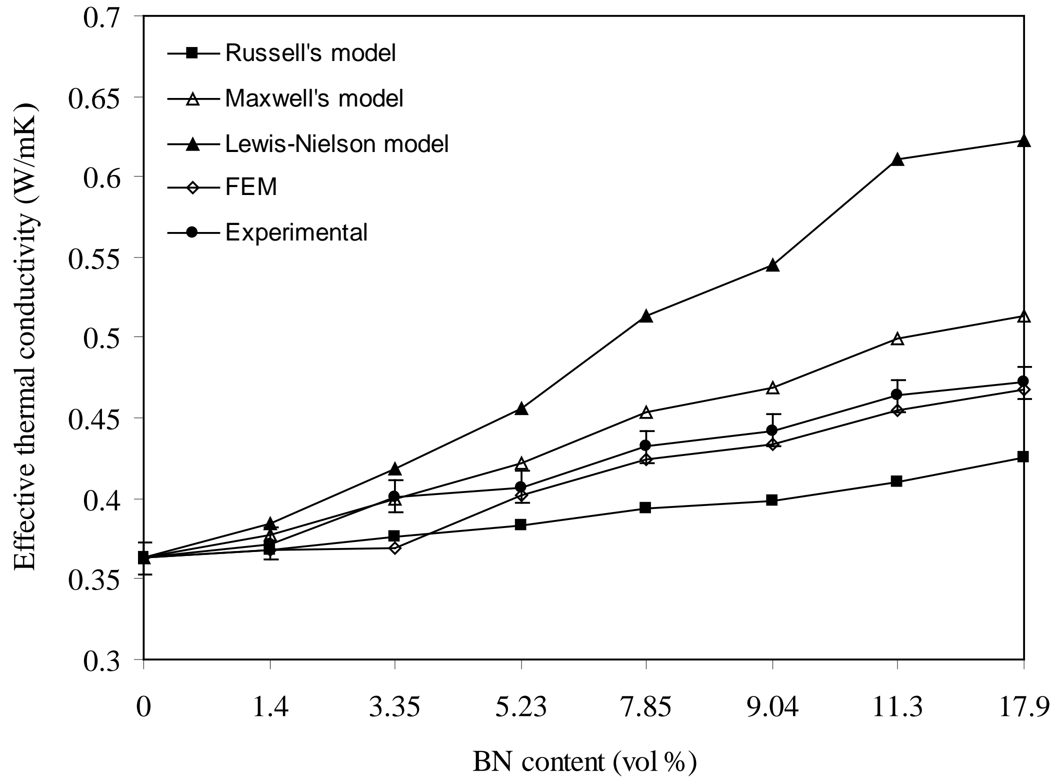


Fig. 6.14 Comparison of k_{eff} values of epoxy-BN composites obtained from different models

Figure 6.14 delineates a comparison of measured values of k_{eff} of the epoxy-BN composites with the values estimated using some of the already existing theoretical models and correlations like Maxwell's equation [79], Lewis and Nielsen's equation [79], Russell's model [79] etc. It is seen in the figure that the values obtained from Russell's model and Maxwell's equation are much higher than the measured values while those obtained from Lewis and Nielsen's equation are found to be much less. On the contrary, the values estimated by the numerical method based on FEM are comparatively in good agreement with the experimentally measured ones.

Determination of k_{eff} using Proposed Theoretical Model:

Effective thermal conductivity values of the above composites have also been estimated theoretically by using the correlation given in Eqn. 3.29 derived on the basis of one-dimensional heat conduction model proposed in this work. Figure

6.15 presents the values of k_{eff} obtained from the proposed correlation for epoxy composites with different BN concentrations. A comparison with the corresponding measured values is also presented in this figure. Figure 6.16 compares the k_{eff} values obtained from different models with the measured values.

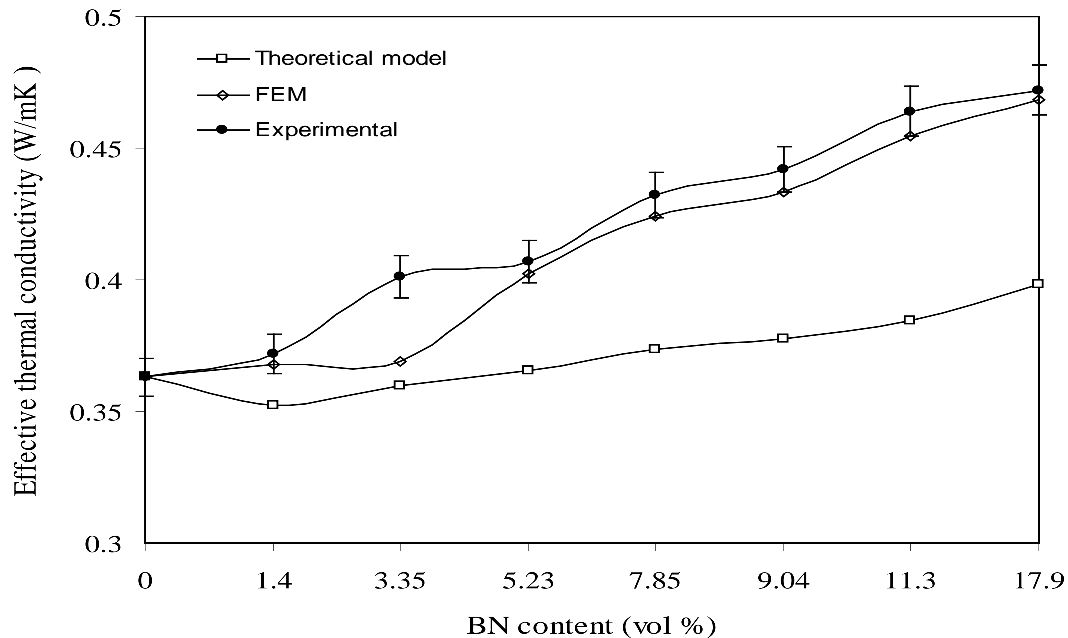


Fig. 6.15 Comparison of k_{eff} values obtained from the proposed theoretical model with the measured values for different BN concentrations

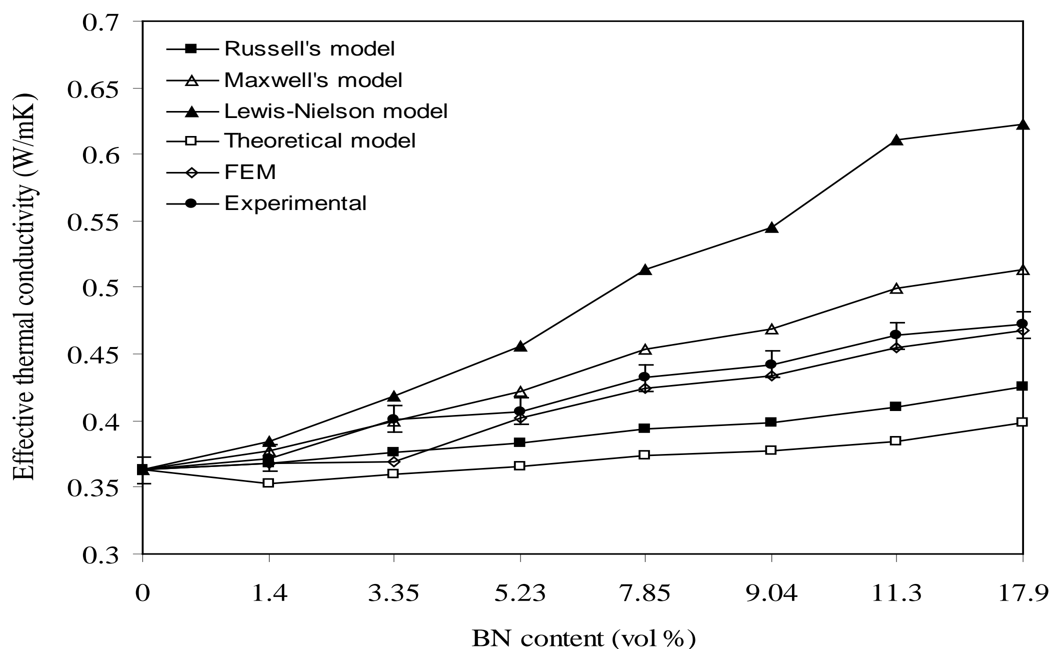


Fig. 6.16 Comparison of k_{eff} values obtained from the proposed theoretical model with other theoretical models and measured values

With increasing BN content in the composite, the value of k_{eff} keeps on increasing. Boron nitride is a solid lubricant that improves the rheological properties of the polymer system. This increases the mobility of the hexagonal BN particulates which, in turn, promotes their natural tendency to attach themselves to each other by their basal planes. Thermal bridges are formed across these planes throughout the system resulting in a rise in conductivity.

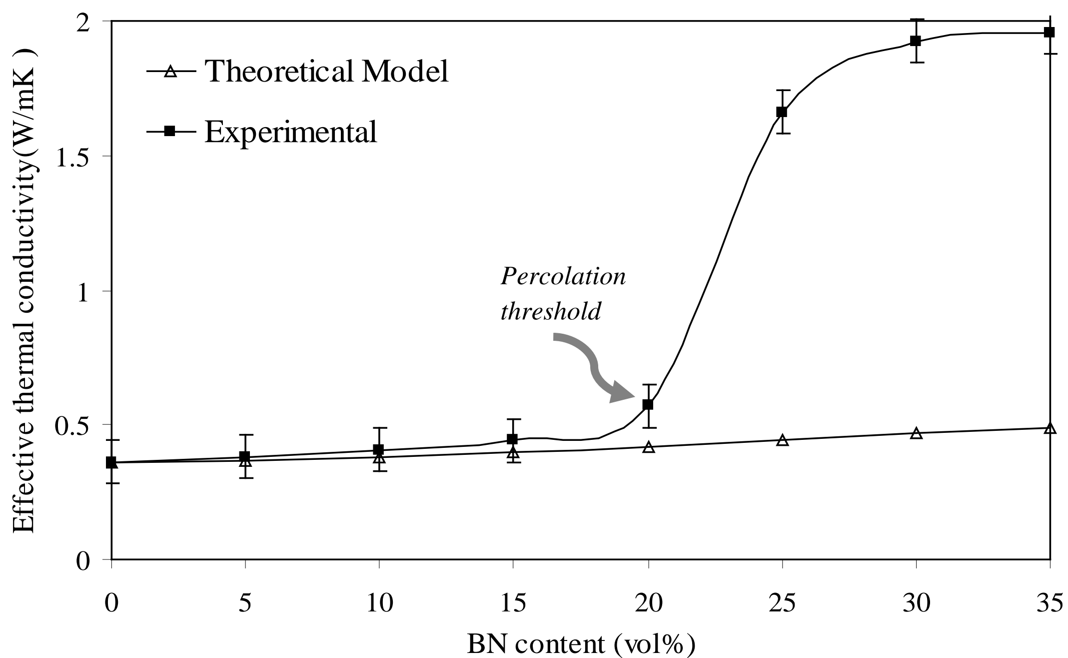


Fig. 6.17 Comparison of k_{eff} values obtained from the proposed theoretical model with the measured values for composites with different BN concentrations

Effective thermal conductivity (k_{eff}) of epoxy based composites (Set-4) with BN content ranging from 0 to 35 vol% are estimated by using the proposed correlation. These values are compared with the corresponding measured values of conductivities (Figure 6.17). It is seen that the results obtained from the proposed correlation are in good agreement with experimental results up to a filler concentration of about 20 vol %. The BN particles show percolation behaviour at this volume fraction (20 %) at which a sudden jump in the thermal conductivity is noticed. This is the critical concentration, called the percolation threshold, at which BN particles start contacting with each other and hence the

actual size of the agglomerates becomes larger. Consequently, the heat conduction performance of epoxy composites incorporating BN exceeds expectations. It is thus concluded that the analytical model serves as a very good empirical model for the estimation of effective thermal conductivity for spherical inclusions and that the proposed correlation (Eqn. 3.29) can very well be used to estimate k_{eff} for composites within the percolation limit.

6.1.3 Epoxy Composites with hybrid filler (SGM and BN)

Determination of k_{eff} by using Proposed Theoretical Model:

Effective thermal conductivity values of the above composites have also been estimated theoretically by using the correlation given in Eqn. 3.40 derived on the basis of one-dimensional heat conduction model for composites with two different filler materials proposed in this work. The details of model development have already been described in Chapter 3. The proposed correlation that is used to find out the k_{eff} of the epoxy based hybrid composites (Set-5) with SGM and BN in different proportions for the present investigation is as follows:

$$k_{eff} = 2\times\left[\left[\frac{1}{k_p}-\frac{1}{k_p}\left(\frac{12v_{f_a}}{\pi}\right)^{1/3}+\frac{2}{\left\{k_p\frac{\rho_a}{\rho_c}\left(\frac{2\pi}{3v_{f_a}}\right)^{2/3}+\left(\frac{4v_{f_a}}{9\pi}\right)^{1/3}\pi\left(k_a-\frac{k_p\rho_a}{\rho_c}\right)\right\}}\right]+\left[\frac{1}{k_p}-\frac{1}{k_p}\left(\frac{12v_{f_b}}{\pi}\right)^{1/3}+\frac{2}{\left\{k_p\frac{\rho_b}{\rho_c}\left(\frac{2\pi}{3v_{f_b}}\right)^{2/3}+\left(\frac{4v_{f_b}}{9\pi}\right)^{1/3}\pi\left(k_b-\frac{k_p\rho_b}{\rho_c}\right)\right\}}\right]\right]^{-1}$$

Here,

k_p , k_a , k_b are the heat conductivities of epoxy, SGM and BN respectively;

ρ_c, ρ_a ,ρ_b are the effective densities of the composite, SGM and BN respectively;

v_{fa} , v_{fb} are the volume fractions of SGM and BN in the composite respectively.

Figure 6.18 presents the variation in the theoretically estimated values of k_{eff} with SGM and BN content in the composites. It is seen that for fixed SGM content, k_{eff} values of the composites improve with increase in the BN content and for

fixed BN content in the composites, k_{eff} decreases with increase in the SGM content. This variation is obvious as the thermal conductivity of BN is higher than that of epoxy and the thermal conductivity of glass micro-sphere is much less.

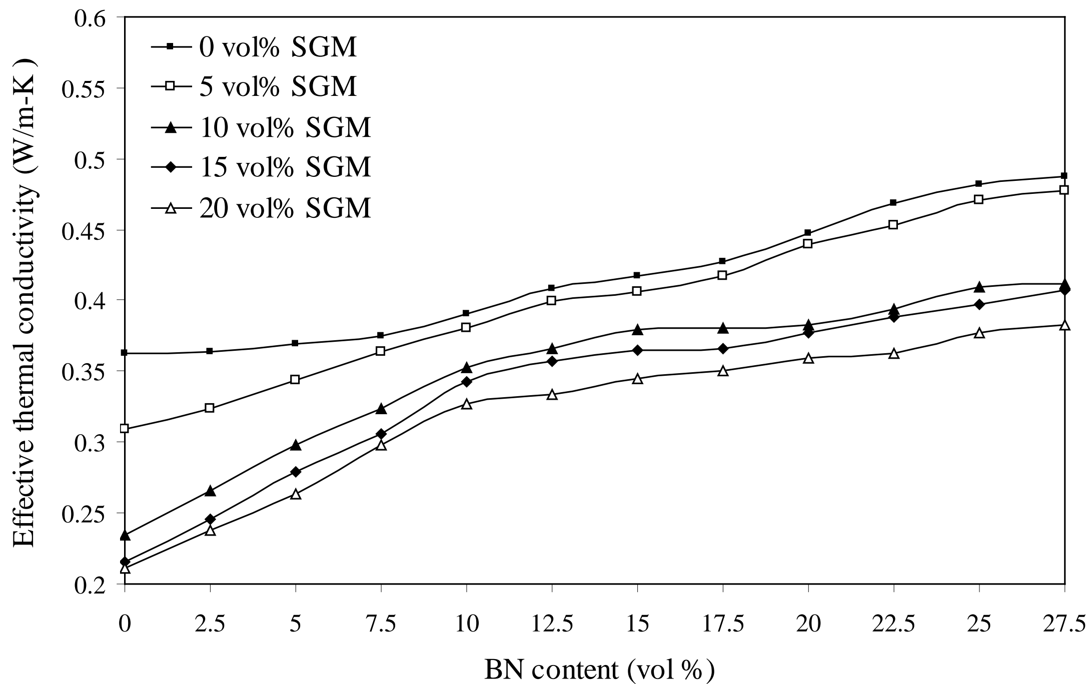


Fig. 6.18 Variation of k_{eff} (estimated using the proposed theoretical correlation) of hybrid filler composites filled with SGM and BN in different proportions

Experimental Determination of k_{eff} for hybrid composites

Unitherm™ Model 2022 Thermal Conductivity Tester is used to measure conductivity of all the hybrid composites (filled with SGM and BN in different proportions) under this investigation. Variation of effective thermal conductivity k_{eff} with BN content for composites with 0 vol% of SGM content is shown in Figure 6.19. This figure also presents the comparison of the measured k_{eff} values with the corresponding theoretical values obtained from the proposed theoretical correlation (Eqn. 3.40). The variations in theoretical and measured values of k_{eff} with BN content for composites with fixed SGM content of 5, 10 and 15 vol% are subsequently shown in Figures 6.20, 6.21 and 6.22 respectively.

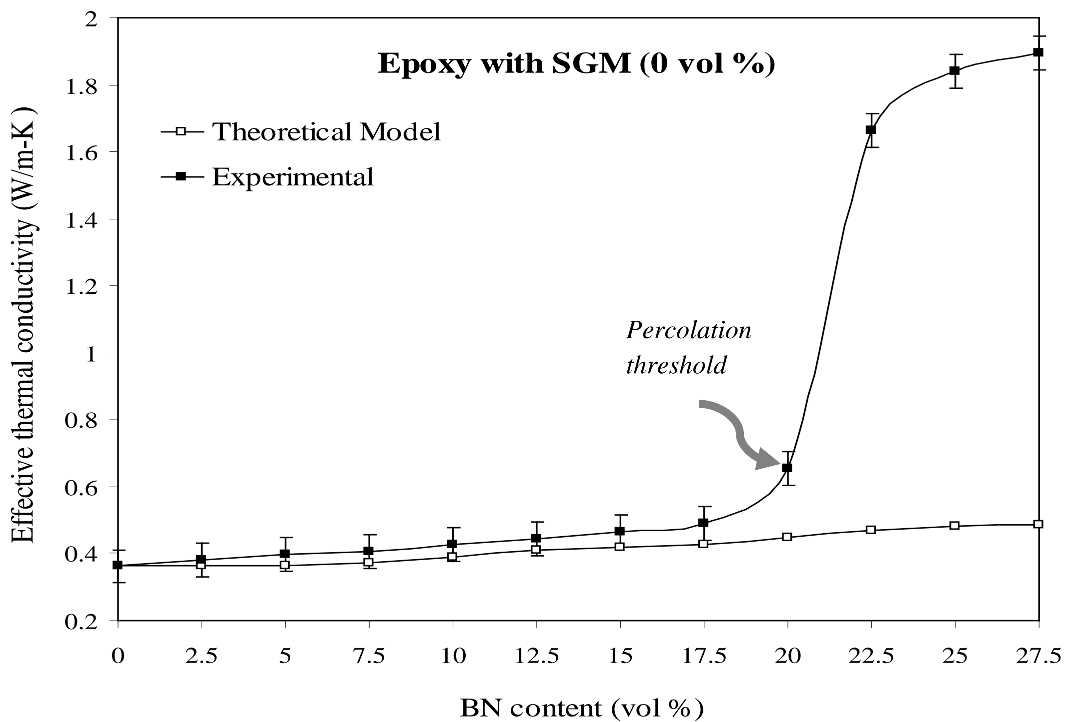


Fig. 6.19 Comparison of k_{eff} (theoretical model and experimental) for composites with different BN content and fixed SGM content (0 vol%)

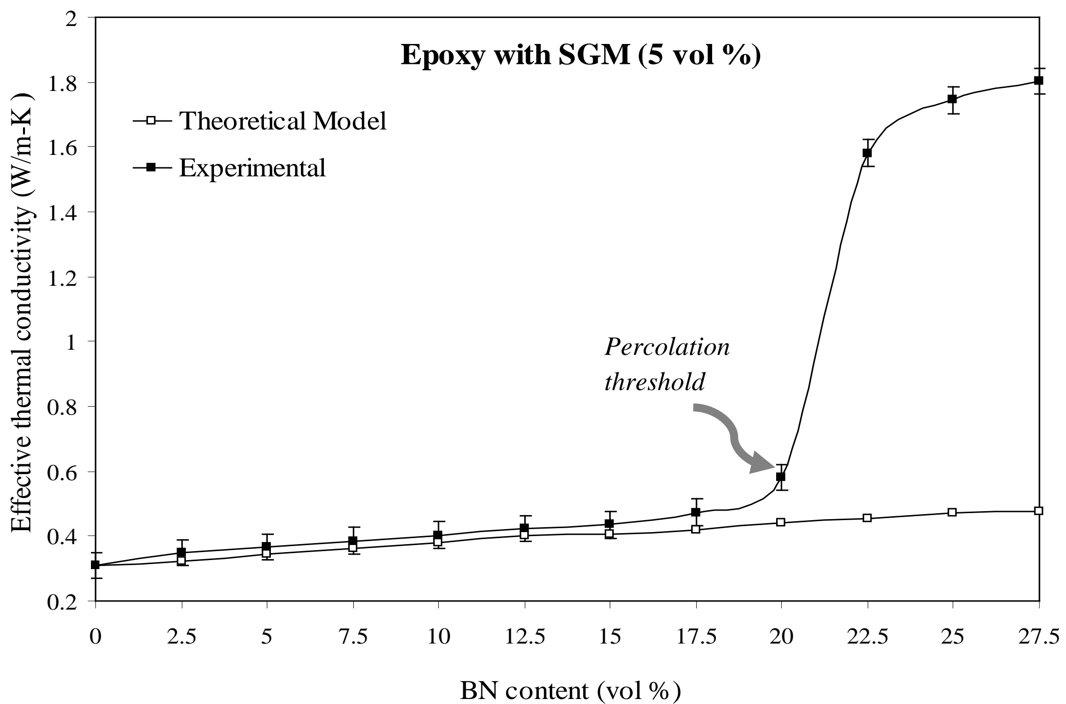


Fig. 6.20 Comparison of k_{eff} (theoretical model and experimental) for composites with different BN content and fixed SGM content (5 vol%)

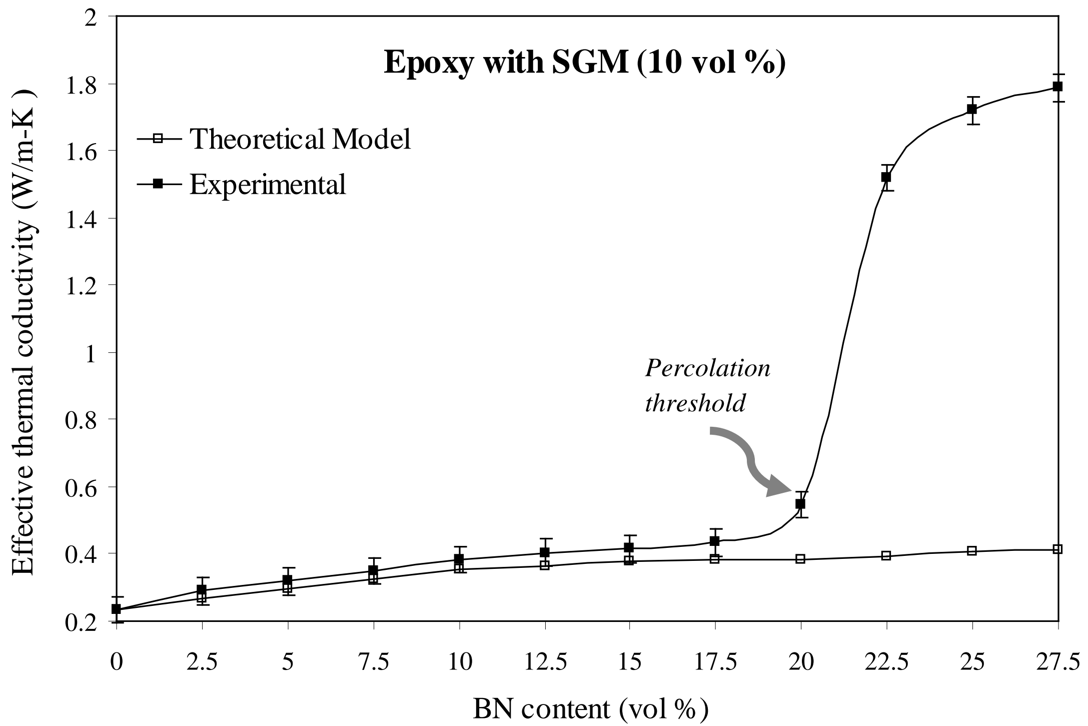


Fig. 6.21 Comparison of k_{eff} (theoretical model and experimental) for composites with different BN content and fixed SGM content (10 vol%)

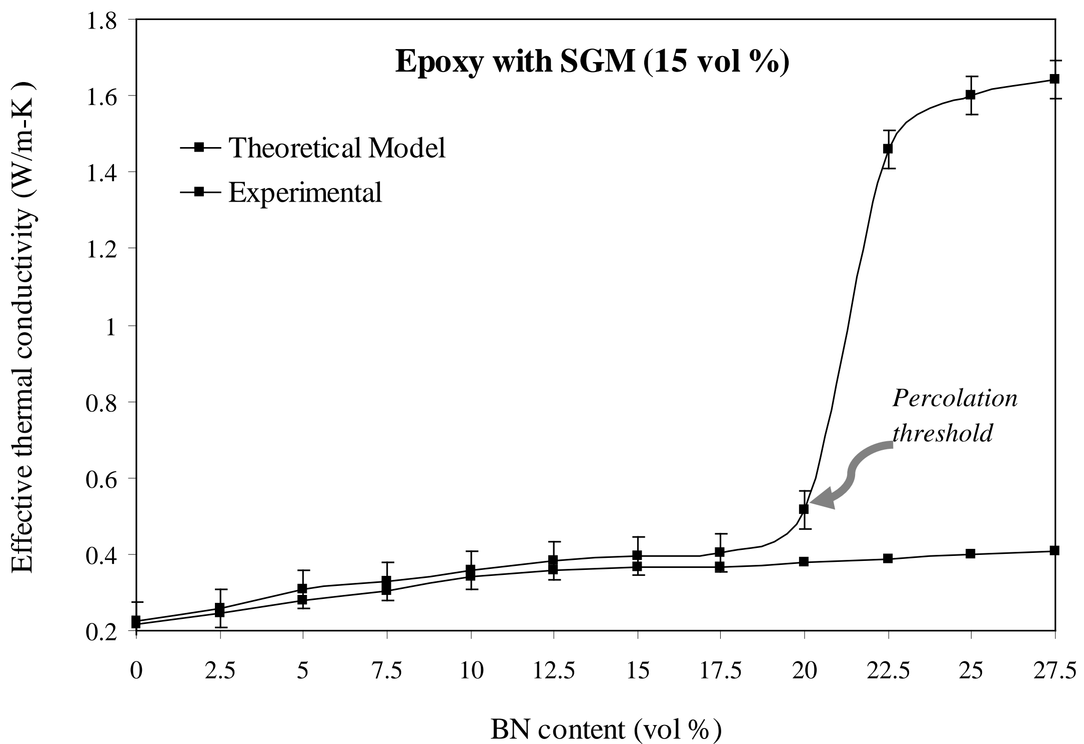


Fig. 6.22 Comparison of k_{eff} (theoretical model and experimental) for composites with different BN content and fixed SGM content (15 vol%)

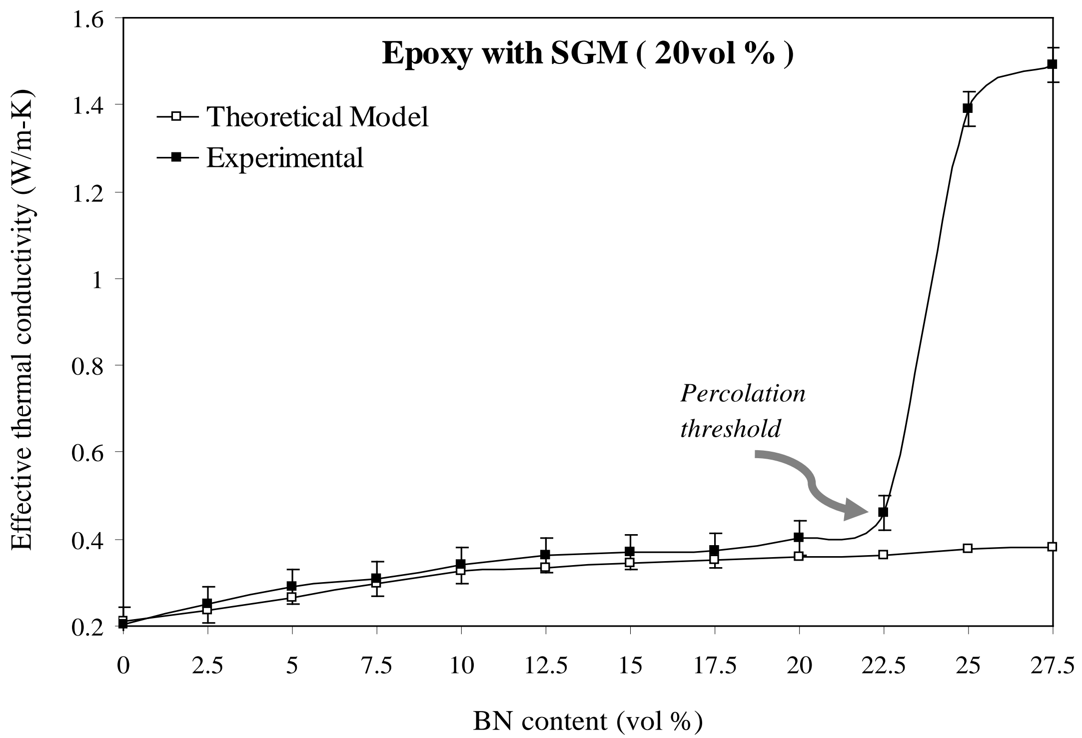


Fig. 6.23 Comparison of k_{eff} (theoretical model and experimental) for composites with different BN content and fixed SGM content (20 vol%)

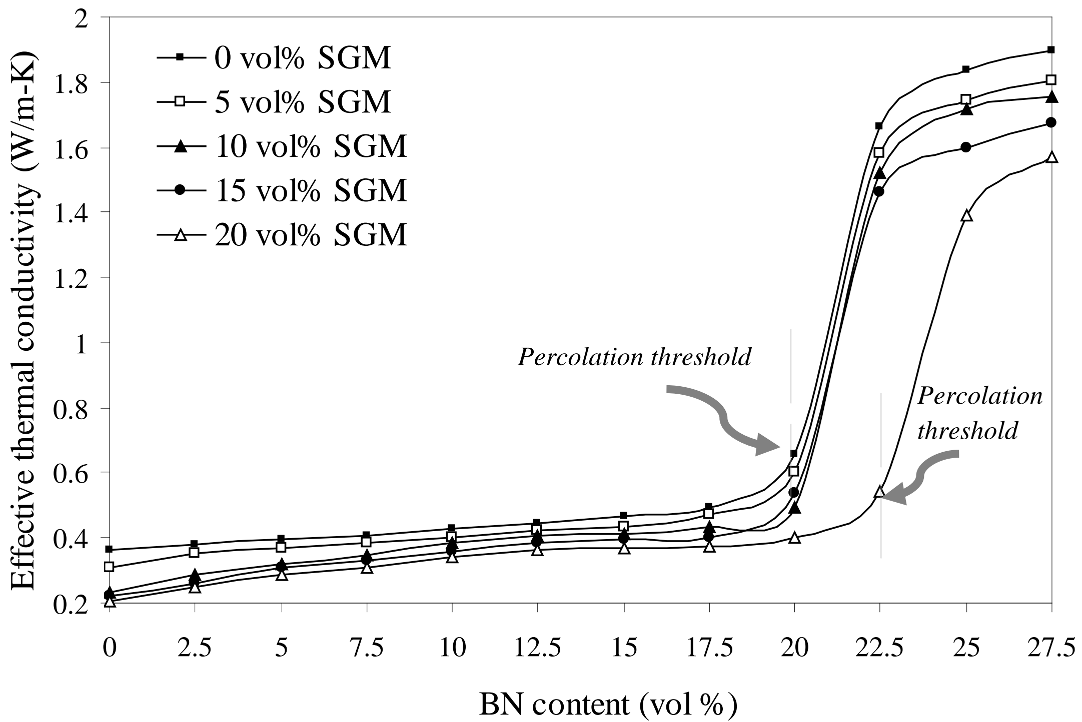


Fig.6.24 Variation of thermal conductivity with BN volume fraction for hybrid composites (measured values)

It is further seen in Figure 6.19 that the theoretical and measured values are in good agreement for composites with BN content up to 20 vol%. But for composites with BN content more than 20 vol%, the difference between the theoretically estimated and experimentally measured values of thermal conductivity becomes suddenly huge. It is interesting to note that for the hybrid composites with fixed SGM content of 5, 10 and 15 vol% also, the theoretical and measured values of k_{eff} are in good agreement with each other till the volume fraction of BN reaches 20 vol%, as shown in Figures 6.20, 6.21 and 6.22 respectively. So, it is concluded on the basis of the experimental findings that the BN particles in epoxy matrix show percolation behaviour at this volume fraction (20 %) at which a sudden jump in the thermal conductivity is noticed. However, for the hybrid composites with SGM content of 20 vol%, the percolation behaviour is exhibited by the BN particles at a slightly higher volume fraction i.e. 22.5 % (Figure 6.23). This shift is possibly due to the higher concentration of non-conductive glass micro-spheres in the matrix body. The critical concentration, at which a sudden jump in the effective thermal conductivity is noticed, is called the percolation threshold. At the percolation threshold, BN particles start contacting with each other and hence the actual size of the agglomerates becomes larger.

Figure 6.24 shows the variations of effective thermal conductivity and the percolation threshold of all the hybrid composites under this investigation.

Discussion

Thermal conductivity of the composite is usually the same as that of the insulating polymer as long as the filler concentration is zero or little higher than zero. When the polymer is filled with any non-conductive filler (having conductivity lower than that of polymer) like SGM, the effective conductivity of the composite reduces making it even more insulative. This trend is observed in case of all the epoxy-SGM composites considered in this study. It is found that with increase in the SGM content, the value of k_{eff} decreases irrespective of the

particle size and a reduction as high as 66% is recorded for epoxy filled with 35 vol% of SGM (100 μm).

When a thermally insulating polymer like epoxy is filled with any conductive filler (having conductivity higher than that of polymer) like boron nitride, the effective thermal conductivity of the composite starts improving and at higher filler concentrations, the composite becomes conductive in nature. Initially, at low filler concentration, since the number of the conductive particles is insufficient to form a continuous conducting path, the conductive domains are insulated from each other by the polymer medium and the heat conducting behaviour cannot be observed. As the filler (BN) volume increases, the conductive particles appear to contact each other forming a continuous network for the transfer of heat. In the present work, at a volume fraction of 20 %, the BN particles show percolation behaviour and at that point the thermal conductivity increases swiftly.

The hybrid systems considered in the present investigation are composites of epoxy filled with non-conductive SGMs and conductive BN particles in different proportions. Due to the presence of these two fillers, synergistic effects are exhibited by the composites as far as their heat conduction behaviour is concerned. When BN is added along with SGM fillers in epoxy matrix, the effective thermal conductivity is ameliorated as BN is conductive in nature. It is seen that there is a sudden jump in the composite thermal conductivity at the percolation threshold (BN content of 20 vol%) despite the presence of non-conducting SGM. However, for composites with higher SGM concentration, percolation threshold shifts to BN content of 22.5 vol%.

Percolation theory deals with the effects of varying the connectivity of elements (e.g, particles, sites, or bonds) on a random system. The percolation transition point is the point at which a network first spans the system. This is the first appearance of long-range connectivity**.** According to experimentally determined k_{eff} of the composites,the effective thermal conductivity of the composites increases rapidly when the filler volume fraction reaches the percolation

threshold. Furthermore, the effective thermal conductivity increases non-linearly with the increase in filler content due to the gradual development of density of the network. The precise location of the percolation threshold is affected by many factors, including the size, aspect ratio and size/spatial distributions of the conductive particles [47,173,174].

Immediately after the percolation threshold, a slight increase in the concentration of conductive BN particles is found to greatly increase the bridges in the conducting network leading to substantial improvement in effective thermal conductivity of the hybrid composites. The insulating composite (epoxy-SGM) is thus transformed into a conducting material in a jump wise fashion. Further increase (25 to 27.5 vol%) in the concentration of the BN particles, however, only causes the volume of the conducting domains to increase without any significant increase in the pathways for heat, leading to a monotonic and marginal rise in conductivity.

The experimental findings suggest that the effective thermal conductivity of the hybrid composites is always higher than that of neat epoxy. For the composite with fixed SGM content of 10 vol%, the k_{eff} is about 1.65 W/m-K when the BN content is 25 vol%. This enhancement in k_{eff} is about 354% with respect to the thermal conductivity of neat epoxy (0.363 W/m-K). Similarly, the k_{eff} of the hybrid composite with 20 vol% SGM and 27.5 vol% BN is found out to be 1.47 W/m-K, which is about four times the conductivity of epoxy. These data indicate that the effective thermal conductivities of hybrid composites are always higher than that of neat epoxy despite the presence of SGM in them. As already mentioned earlier in this thesis, higher thermal conductivity is very important for electronic packaging materials. The thermal conductivity values recorded for the hybrid composites under this study are higher than that of some common commercial product, e.g., 0.36 W/m-K for PCL-FR-226 laminate/PCL-FRP-226 prepreg and PCL-FR-240 laminate/PCL-FRP-240 prepreg [91].

6.2 GLASS TRANSITION TEMPERATURE (T_g)

The glass transition temperature (T_g) of the composites are measured with a Perkin Elmer DSC-7 thermal mechanical analyzer (TMA). Figure 6.25 shows the glass transition temperature (T_g) of the epoxy-SGM composites. It is observed that the T_g of neat epoxy is about 104^0C and it gradually increases to 124°C as the SGM content increases from 0 to 35 vol%. The increase in T_g of the composites can be attributed to strong interaction between the SGMs and the epoxy-matrix. The interaction between the micro-spheres and the polymer restricts the mobility of the polymer chain, which results in an increase in the glass transition temperature. Similar observations have also been reported by previous investigators [175, 176].

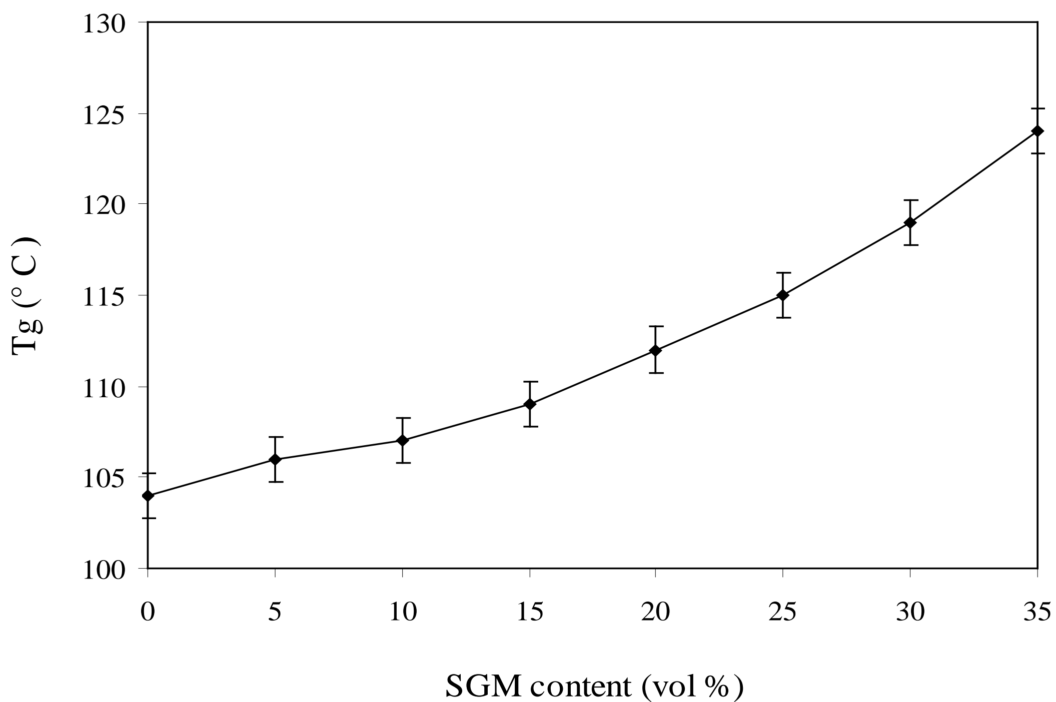


Fig. 6.25 Variation of T_g with filler content for epoxy-SGM composites

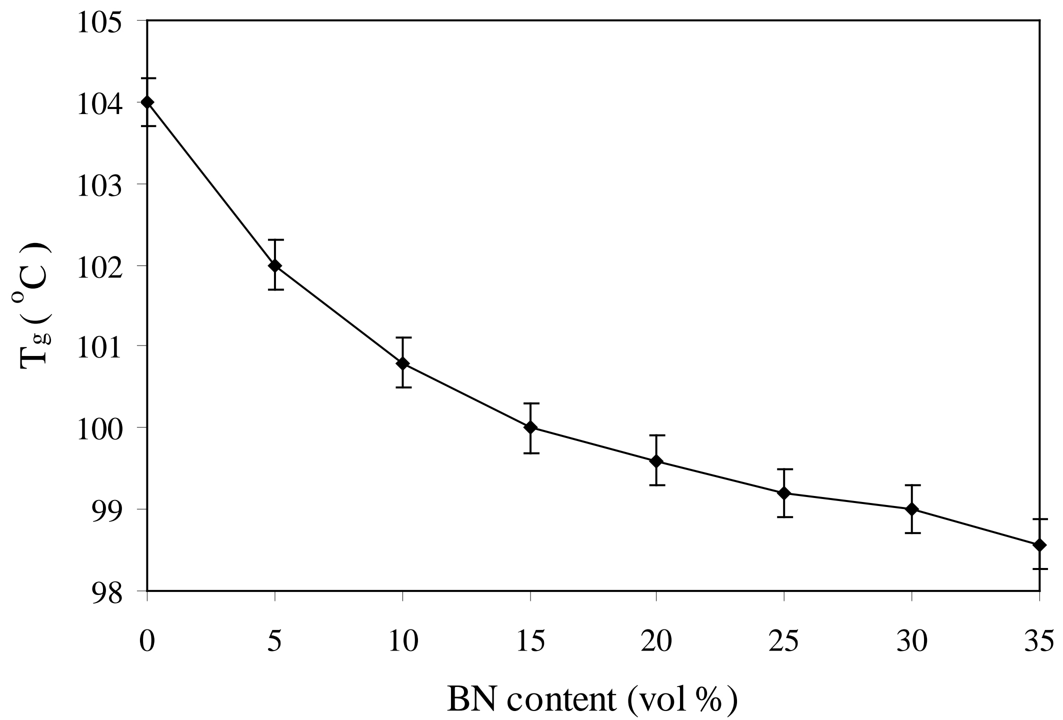


Fig. 6.26 Variation of T_g with filler content for epoxy-BN composites

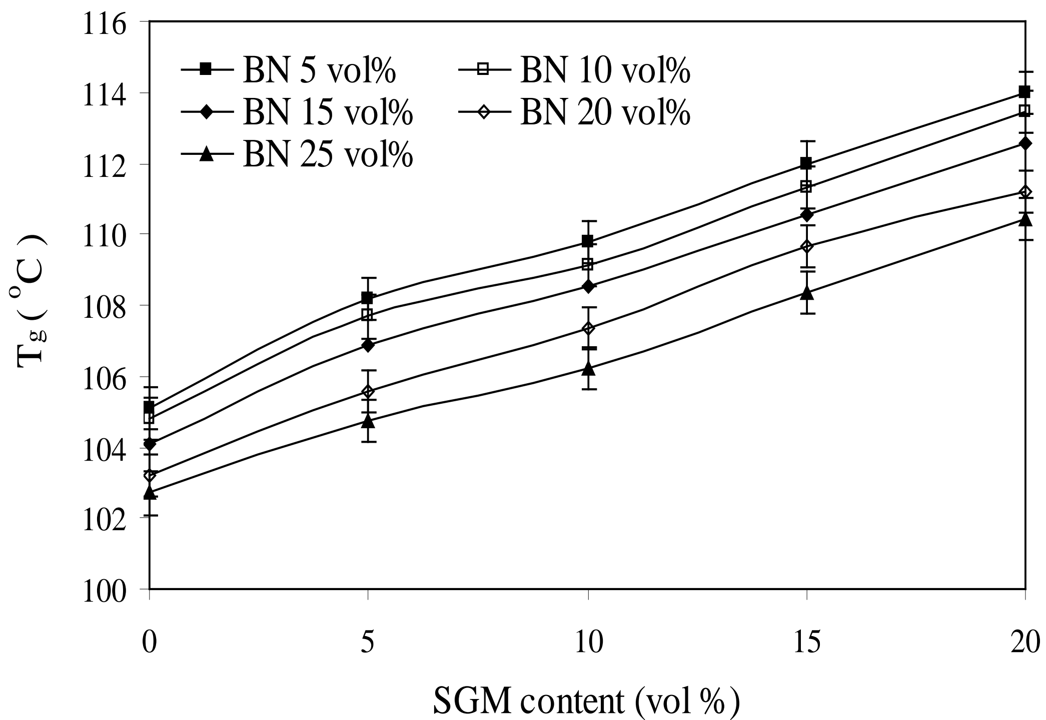


Fig. 6.27 Variation of T_g with filler content (BN + SGM) for hybrid composites

On the contrary, with the addition of boron nitride, glass transition temperature of epoxy is found to be decreasing. Figure 6.26 shows the variation of glass transition temperature (T_g) of the epoxy-BN composites. It is observed that the T_g of neat epoxy is about 104^0C and it gradually drops to about 98.5 ^{0}C as the BN content increases from 0 to 35 vol%. Similar observation has been reported by Couderc et al. [177] for polymer filled with BN and this drop in T_g has been attributed to possible impediment of reticulation by boron nitride particles, acting as obstacles to the reaction. This results from a more mobile molecular structure produced by less complete reticulation.

Figure 6.27 shows the variation of T_g of the hybrid composites with different SGM and BN concentrations. It is encouraging to note that the hybrid composites under this investigation, exhibit improved T_g, as compared to that of neat epoxy, confirming a more reticulated and less mobile structure. This means that the presence of only solid glass micro-spheres does not modify the reticulation reaction, whereas in presence of boron nitride the reaction is more effective.

6.3 COEFFICIENT OF THERMAL EXPANSION (CTE)

The variation of coefficient of thermal expansion of epoxy-SGM composites with filler content is illustrated in Figure 6.28. It shows that the CTE of the composite decreases with the increase in SGM content. While the CTE of the neat epoxy is about 62.83 ppm/ °C, it gradually decreases to 40.19 ppm/°C with an increase in the SGM content and a maximum decrease of about 34% in CTE is obtained for the composite with SGM content of 35 vol%. The low CTE of SGM (about 32 ppm/ °C) and the constraint of deformation of the epoxy-matrix due to the interaction of SGM and epoxy are responsible for the reduced CTE of the composites.

As far as the variation of CTE of the epoxy-BN composites is concerned, similar observations as reported by Couderc et al. [117] are noticed in the present work as well. Figure 6.29 clearly shows that incorporation of BN substantially reduces

the CTE of epoxy-BN composites. There is a drop of 12.71 ppm/°C in the CTE for epoxy-BN composites with BN content of 35 vol%. Here too, low CTE of BN (36 ppm / °C) and the constraint of deformation of the epoxy-matrix due to the filler-matrix interaction are responsible for the reduced CTE of the composites.

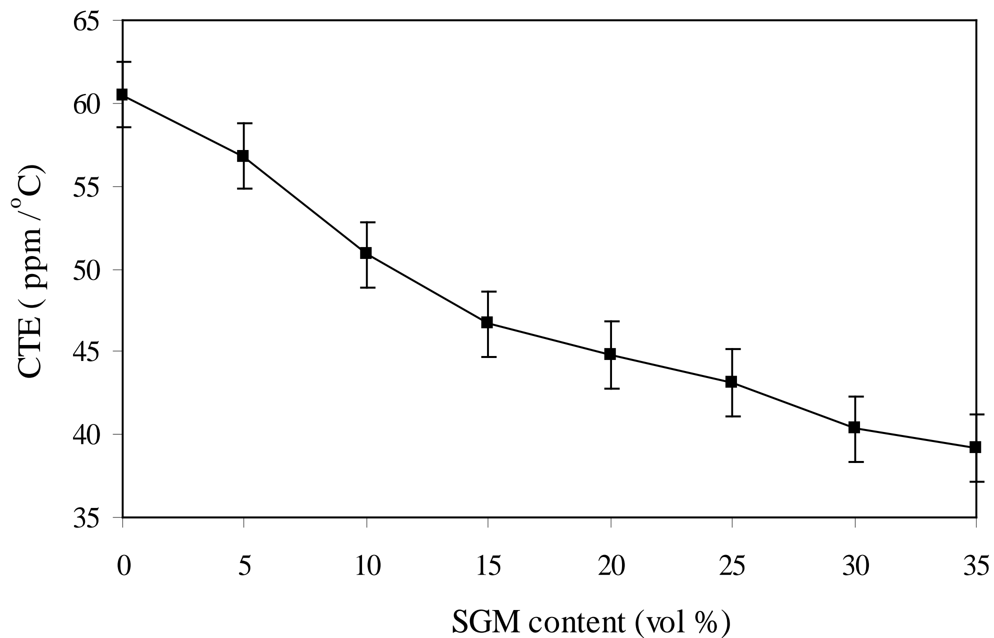


Fig. 6.28 Variation of CTE with filler content for epoxy-SGM composites

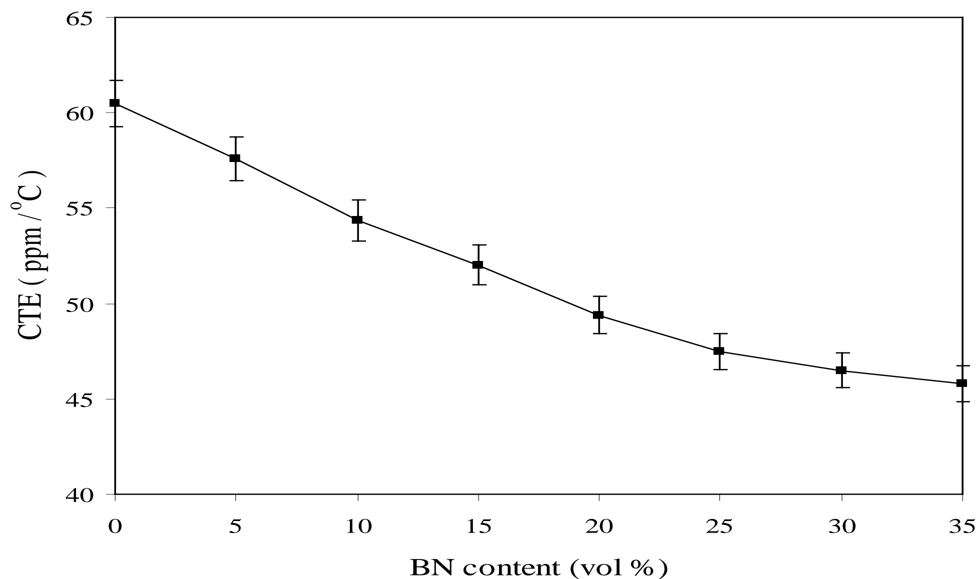


Fig. 6.29 Variation of CTE with filler content for epoxy-BN composites

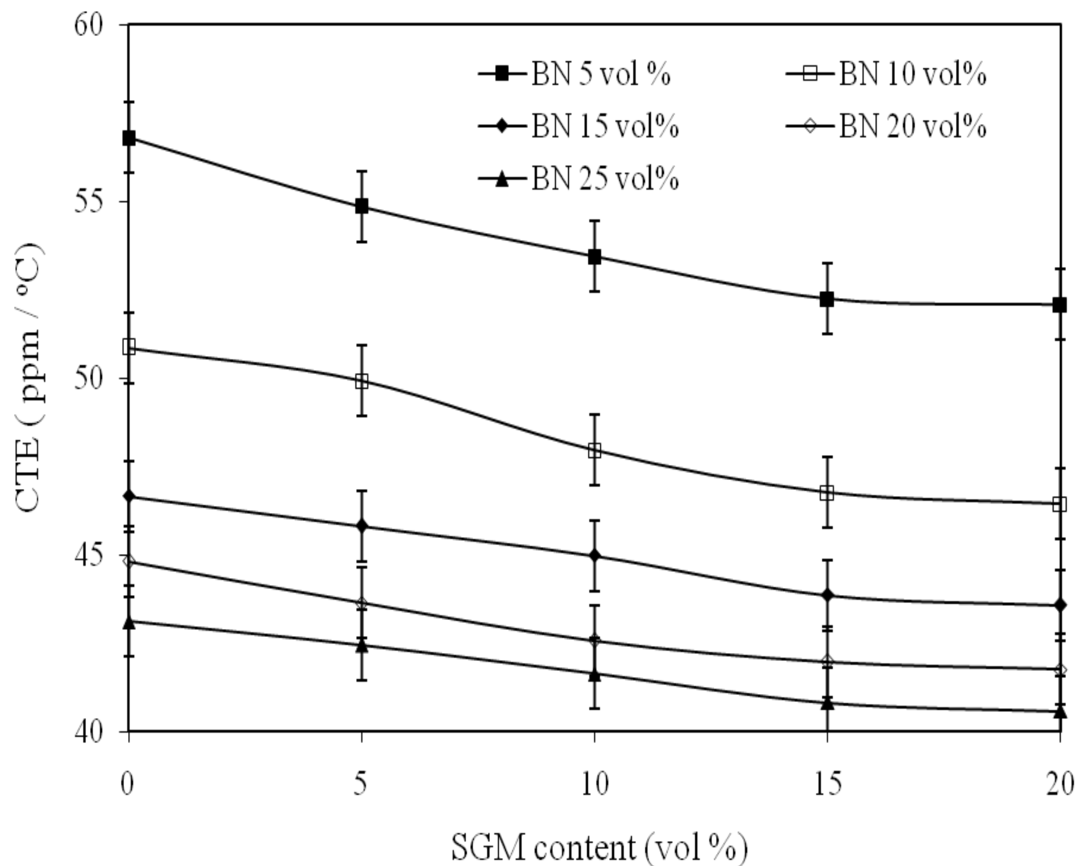


Fig. 6.30 Variation of CTE with filler content (BN+SGM) for hybrid composites

Figure 6.30 presents the variation of CTE for hybrid composites as the SGM and BN content in the composites change. It is seen that with increase in the volume fractions of SGM and BN, there is gradual decrease in the value of CTE. For the composite with 20 vol% SGM and 25 vol% BN, the value of CTE is recorded as 40.59 ppm/°C, which is 22.24 ppm/°C less than that of neat epoxy. This value of CTE is lower than that of some common commercial product e.g. 50 ppm/°C for PCL-FR-226 laminate/PCL-FRP-226 and PCL-FR-240 laminate / PCL-FRP-240 prepreg [177]. In applications such as printed circuit boards, the key to decreasing thermal stress is to decrease the CTE of the substrate material. Thus the hybrid composites under this research with reduced CTE would be helpful in these kinds of applications.

Chapter Summary

This chapter has provided:

- The results of the numerical analysis and experiments conducted to evaluate the thermal conductivity of the polymer composites under study
- The validation of theoretical models developed and proposed in Chapter 3 of this thesis through experimental results
- The effect of solid glass microspheres in improving the insulation capability of epoxy and the effect of boron nitride in enhancing the thermal conductivity
- The synergistic effects of both SGM and BN on effective conductivity of the hybrid composites
- A complete picture on the percolation behaviour exhibited by the fillers in regard to the conductivity of hybrid composites
- Effects of solid glass micro-spheres and boron nitride on the modified glass transition temperature and coefficient of thermal expansion of composites

The next chapter presents the dielectric characteristics of composites under this research which would enable us to explore possible use of the composites in potential application areas.

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Chapter - 7

Results and Discussion - III

DIELECTRIC CHARACTERISTICS OF THE COMPOSITES

This chapter presents the test results for some electrical properties such as electrical resistivity or volume resistivity (ρ), electrical conductivity (σ) and dielectric constant (D_k) of all the single and multi-filler composites under this investigation. The effects of addition of solid glass micro-spheres and/or boron nitride particles on ρ, σ and D_k are discussed.

7.1 Resistivity (Bulk or Volume Resistivity)/ Electrical Conductivity

7.1.1 Estimation of Volume Resistivity from theoretical correlation

Electrical resistivity (also known as specific electrical resistance or volume resistivity) quantifies how strongly a given material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electric charge. Many models exist to predict the properties of composites or mixtures and often the same models can be used to determine the mechanical, thermal, optical as well as electrical properties of these materials [178-182].

The simplest models for predicting the electrical resistivity of composites are simple mixing rules. These include series and parallel resistivity models [178] which are given in Eqns. 7.1 and 7.2 respectively.

$$\rho_M = v_i \rho_i + v_c \rho_c \qquad \textbf{(7.1)}$$

$$\frac{1}{\rho_M} = \frac{v_i}{\rho_i} + \frac{v_c}{\rho_c} \qquad \textbf{(7.2)}$$

It is assumed in Eqns. 7.1 and 7.2 that $v_i + v_c = 1$.

These models are based on the series and parallel electrical circuits, where ρ_M is the resistivity of the composite or mixture; ρ_i is the resistivity of the first filler phase; ρ_c is the resistivity of the matrix; and v_i and v_c the volume fractions of the first filler and matrix phases respectively. These correlations can be used for particulate filled composites and also for highly anisotropic materials such as continuous fibers or layered composites.

For the present investigation on hybrid filler epoxy composite systems, the mixing rule correlations have been modified as:

$$\rho_M = v_i\rho_i + v_j\rho_j + v_c\rho_c \quad \textbf{(7.3)}$$

$$\frac{1}{\rho_M} = \frac{v_i}{\rho_i} + \frac{v_j}{\rho_j} + \frac{v_c}{\rho_c} \quad \textbf{(7.4)}$$

where v_j and ρ_j are the volume fractions and resistivity of the second filler.

Another empirical model often used for predicting the electrical properties is Lichtenecker's rule [178], which proposes a correlation as:

$$\log\rho_M = v_i \log\rho_i + v_c \log\rho_c \quad \textbf{(7.5)}$$

where all the variables are defined as before. This model does not take into account any specific geometry but gives a very good approximation for random mixtures of two phases.

7.1.2 Experimental Determination of Volume Resistivity for composites

Volume resistivity of the epoxy composites filled with different proportions of SGM and micro-sized BN particles was measured using *High Resistance Meter (Type ZC36)* at a voltage of DC 1 kV. The tests were carried out at ambient temperature and pressure as per ASTM D 257. Theoretically estimated electrical resistivity values obtained from series model correlation (Eqn.7.1) for epoxy-SGM composites with filler content ranging from 0 to 35 vol% are plotted in

Figure 7.1. It also presents a comparison of the theoretical values with the corresponding experimentally measured resistivity values. It is seen that the values obtained from series model correlation are in good agreement with the measured values for a wide range of filler concentrations. It also indicates that the composite volume resistivity decreases with increase in SGM content in the composite.

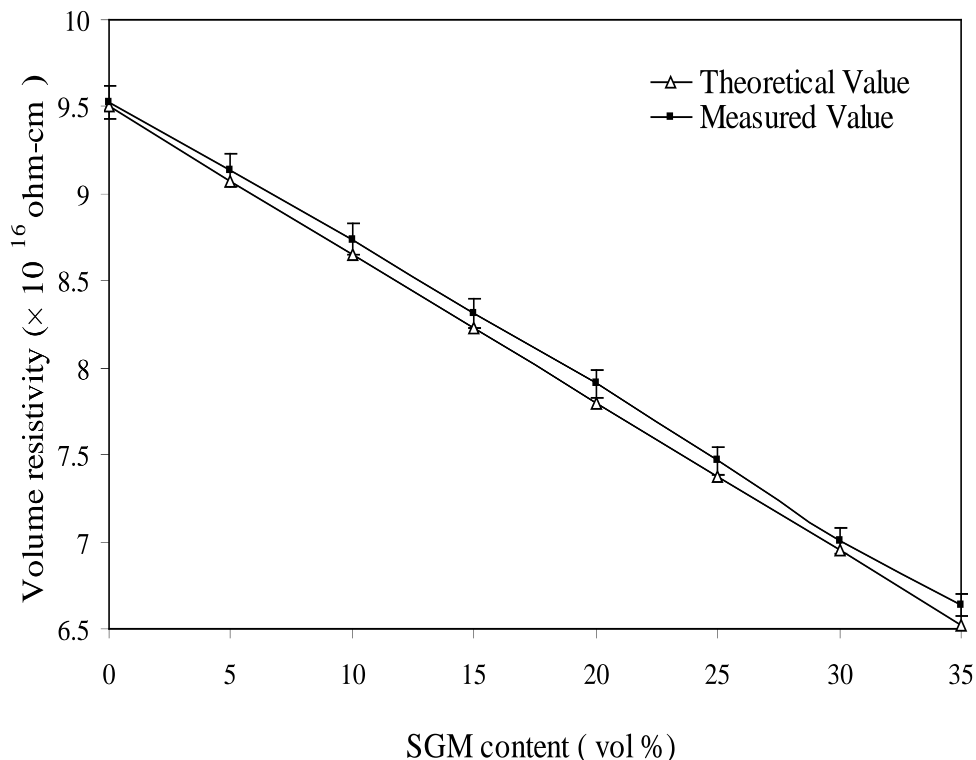

Fig. 7.1 Variation of resistivity of epoxy-SGM composites with filler content

Figures 7.2 to 7.5 present the variation of volume resistivity with BN concentrations for hybrid composites with fixed SGM content of 5, 10, 15 and 20 vol% respectively. These figures also present the comparison of theoretical values obtained from the modified series model correlation (Eqn. 7.3). The theoretical values are shown by solid lines, whereas the measured data are presented using solid lines with error bars in these figures. It is seen that the theoretical results are in fairly good agreement with the measured values of

electrical resistivity. It is also evident from these figures that the resistivity drops with increase in BN content in the composites.

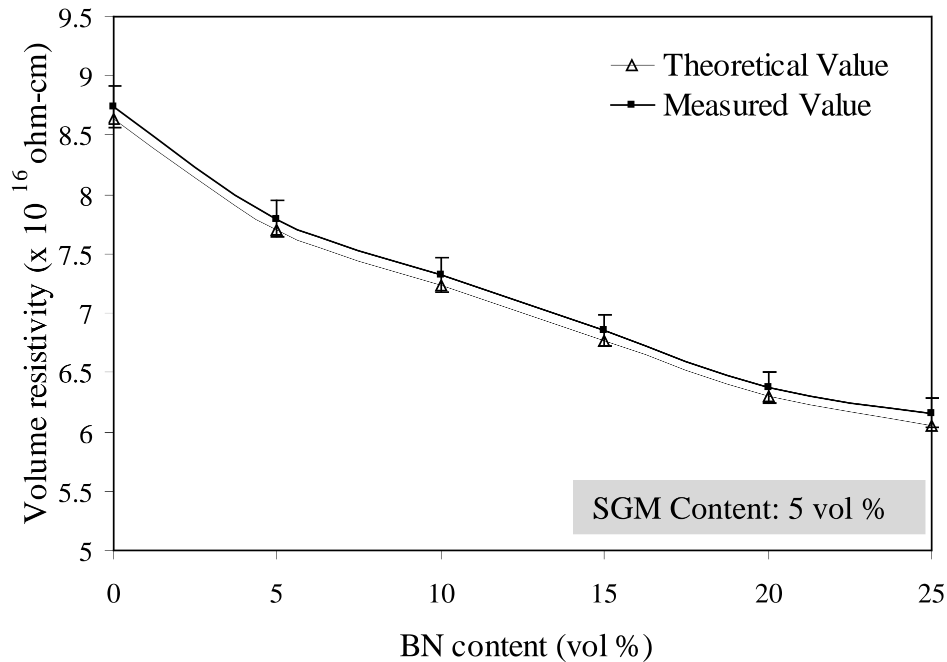

Fig. 7.2 Variation of resistivity of hybrid composite with BN content (Fixed SGM content: 5 vol %)

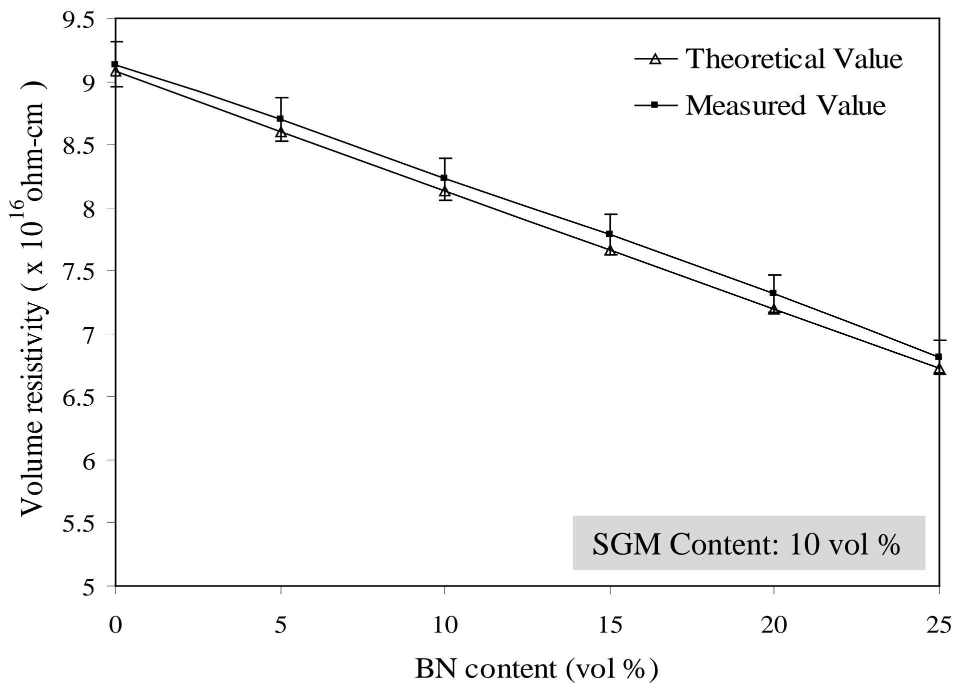

Fig. 7.3 Variation of resistivity of hybrid composite with BN content (Fixed SGM content: 10 vol %)

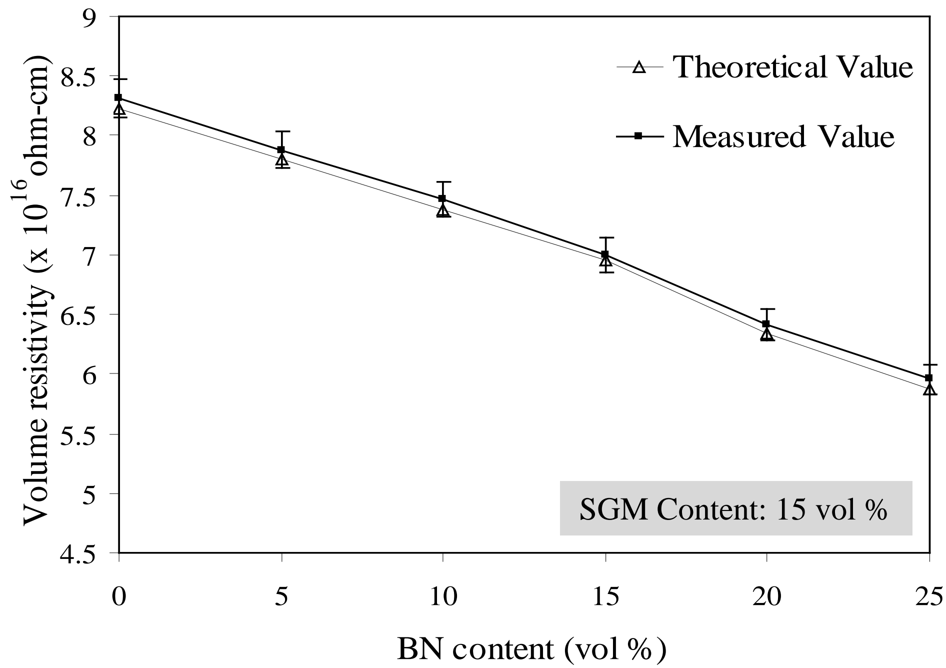

Fig. 7.4 Variation of resistivity of hybrid composite with BN content (Fixed SGM content: 15 vol %)

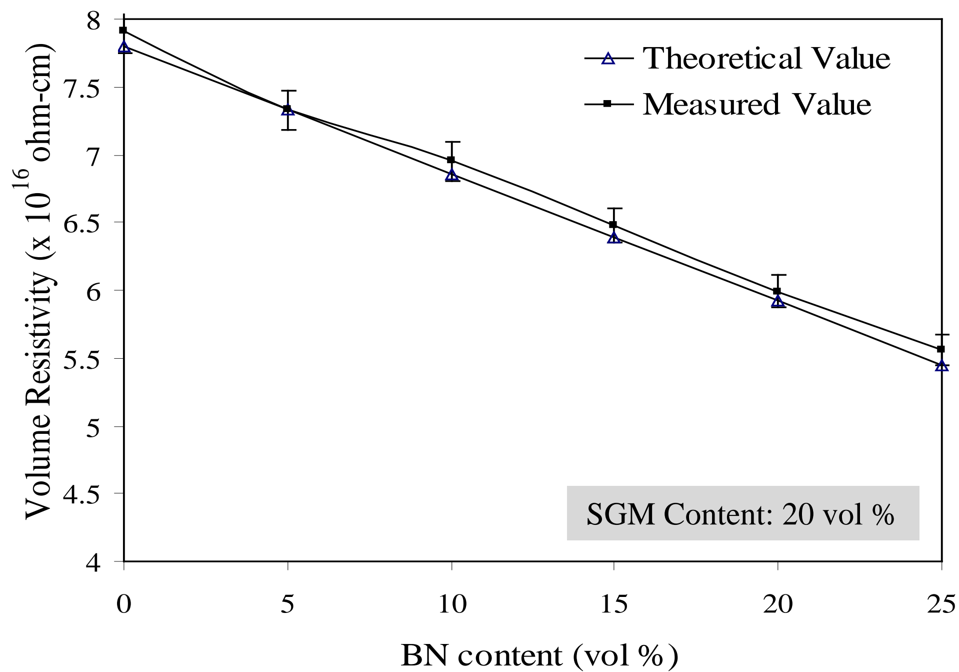

Fig. 7.5 Variation of resistivity of hybrid composite with BN content (Fixed SGM content: 20 vol %)

The reciprocal of resistivity of any sample is recorded as the electrical conductivity of that composite. The electrical conductivity values thus obtained for epoxy-SGM-BN hybrid composites are shown in Figure 7.6. It is observed that for composites with fixed SGM content, the electrical conductivity values increase as the BN content in the composites is increased.

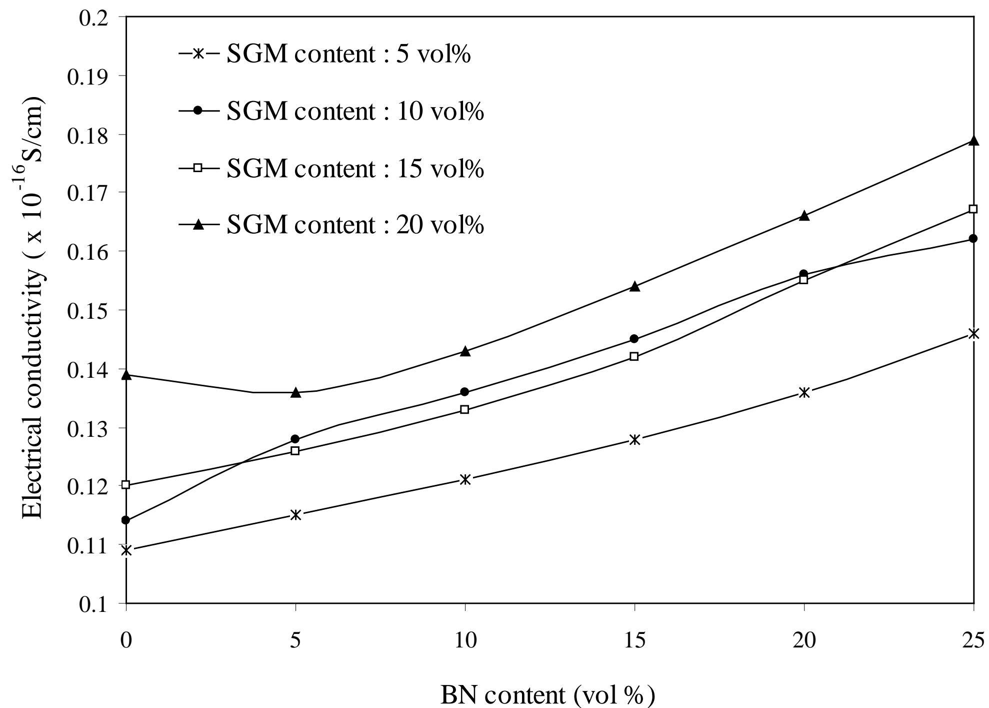

Fig. 7.6 Variation of electrical conductivity of hybrid composites with BN content

The increase in electrical conductivity of the composites with BN content is relatively less as compared to the improvement in its thermal conductivity. For the epoxy-SGM composite with fixed SGM content of 20 vol%, the electrical conductivity is improved by about 30% when the BN content is increased from 0 to 35 vol%. At the same time, with the same increase in BN content, the improvement in the effective thermal conductivity is recorded to be as high as 85%. So, the small rise in electrical conductivity of epoxy by the incorporation of SGM and BN would not have any detrimental effect as far as its use in electronic components is concerned.

7.2 Dielectric constant (D_k)

7.2.1 Determination of dielectric constant: Theoretical Models

Various theoretical models for the estimation of dielectric constant of mixtures and composites have been proposed in the past [99]. The simplest models for predicting the dielectric constant of composites are based on rules of mixture. The correlation based on simple mixing rule that is widely used for predictive purpose is as follows:

$$\varepsilon = (1 - V_i)\varepsilon_1 + V_i\varepsilon_2 \tag{7.6}$$

where V_i is the volume fraction of the filler, ε_1 is the dielectric constant of the matrix material and ε_2 is the dielectric constant of the filler material at any particular frequency. In this research, the values of dielectric constants of epoxy resin, glass micro-spheres and boron nitride at 1MHz are taken as 3.98, 3.67 and 4.88 respectively.

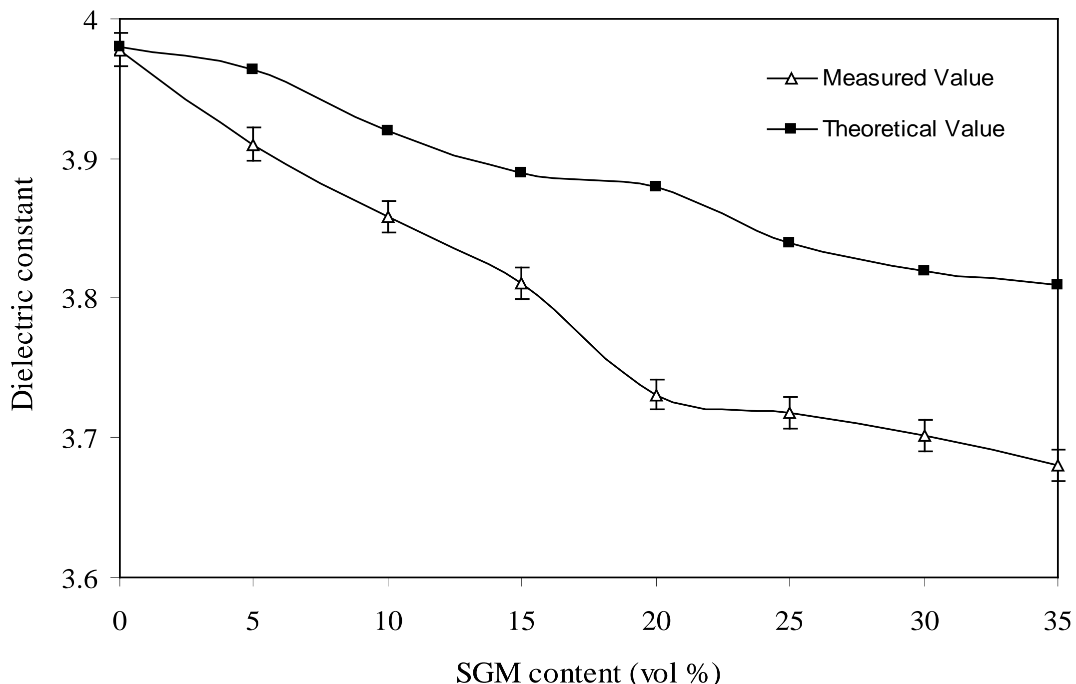

Fig. 7.7 Comparison of theoretical and measured values of dielectric constant of epoxy-SGM compsites

7.2.2 Experimental Determination of Dielectric constant for composites

The dielectric constant measurements for the epoxy-SGM, epoxy-BN and the epoxy-SGM-BN hybrid composites are done using *Hioki 3532-50 Hi - Tester LCR Analyzer* (Chapter-4, Fig. 4.18) with an applied voltage of 500 mV and in frequency range 1 kHz – 1 MHz. The dielectric constant (D_k) is found out from the measured capacitance by using the relationship: $D_k = Ct/\varepsilon_0 A$, where C is the capacitance, t is the thickness of disc, ε_0 is the electrical permittivity of free space and A is the disc area.

Figure 7.7 presents a comparison between the experimentally measured dielectric constant values at 1 MHz with those obtained from the theoretical correlation (Eqn.7.6) for epoxy-SGM composites with different filler concentrations.

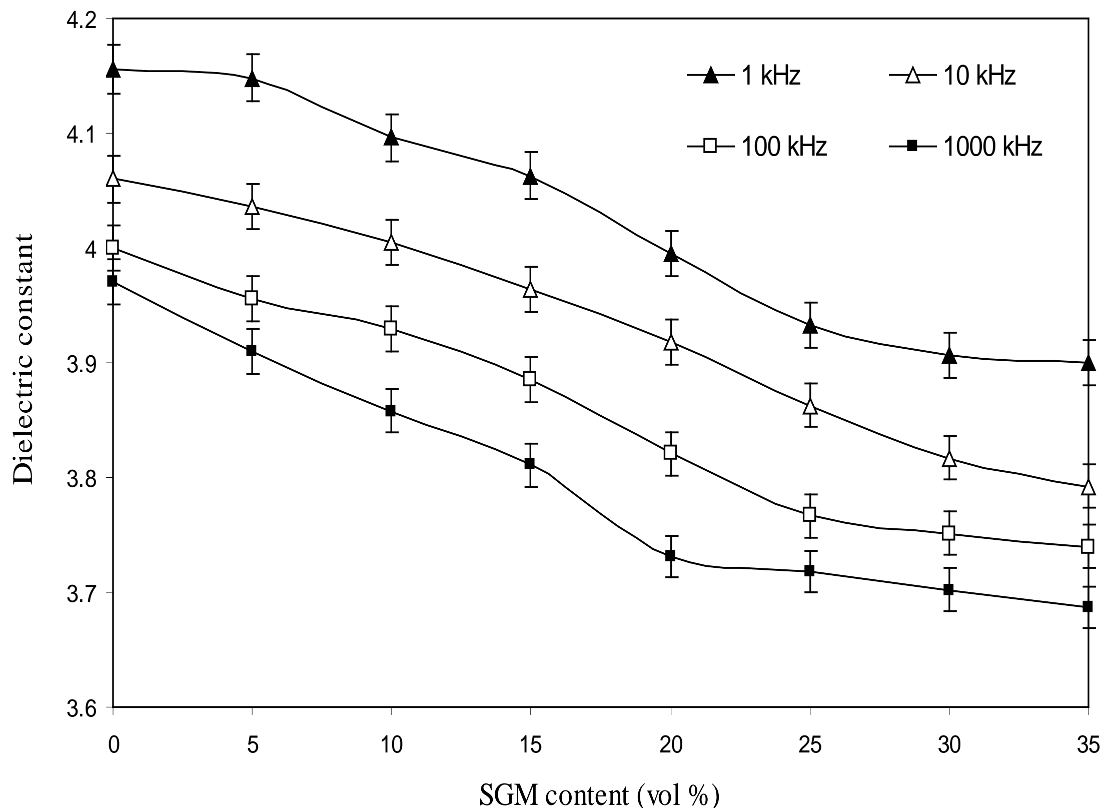

Fig. 7.8 Variation of dielectric constant of epoxy-SGM compsites with filler content at different operating frequencies

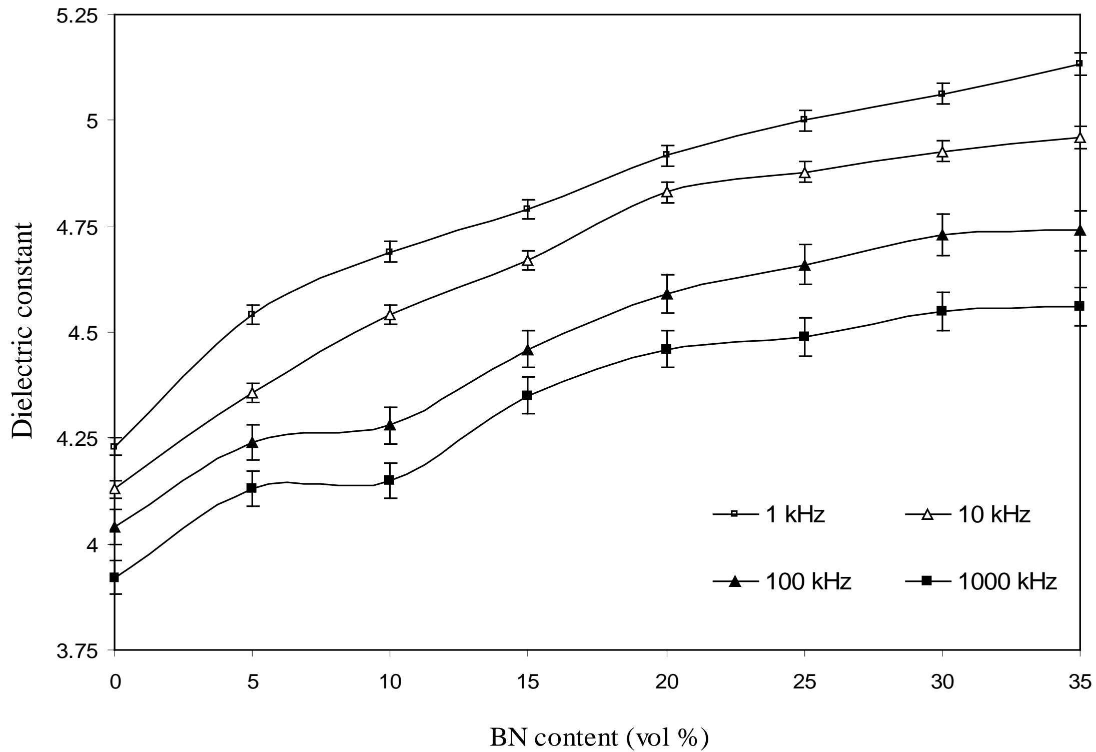

Fig. 7.9 Variation of dielectric constant of epoxy-BN compsites with filler content at different operating frequencies

Figure 7.8 shows the typical dielectric constant curves for epoxy-SGM compsites with SGM content at different frequencies. With increase in SGM content, D_k of the composite keeps on decreasing. This drop in D_k can be attributed to the addition of glass micro-spheres into the epoxy resin causing the charge migration [135]. Similar observation with hollow glass bead filled polymers has been reported previously by Park et al. [135] and Yung et al. [91]. Similarly, in Figure 7.9, the variations of dielectric constants for epoxy-BN compsites with BN content at different frequencies are shown. Contrary to the trend exhibited by Epoxy-SGM composites, it is found in this case that D_k of the composite increases with increase in the BN content.

7.2.3 Dielectric constant of epoxy-SGM-BN hybrid composites

Figures 7.10, 7.11, 7.12 and 7.13 present the values of measured dielectric constants of epoxy-SGM-BN hybrid composites with fixed SGM content of 5, 10, 15 and 20 vol% respectively. These figures illustrate the variation in the values of effective dielectric constant with BN content in the composites at different working frequencies.

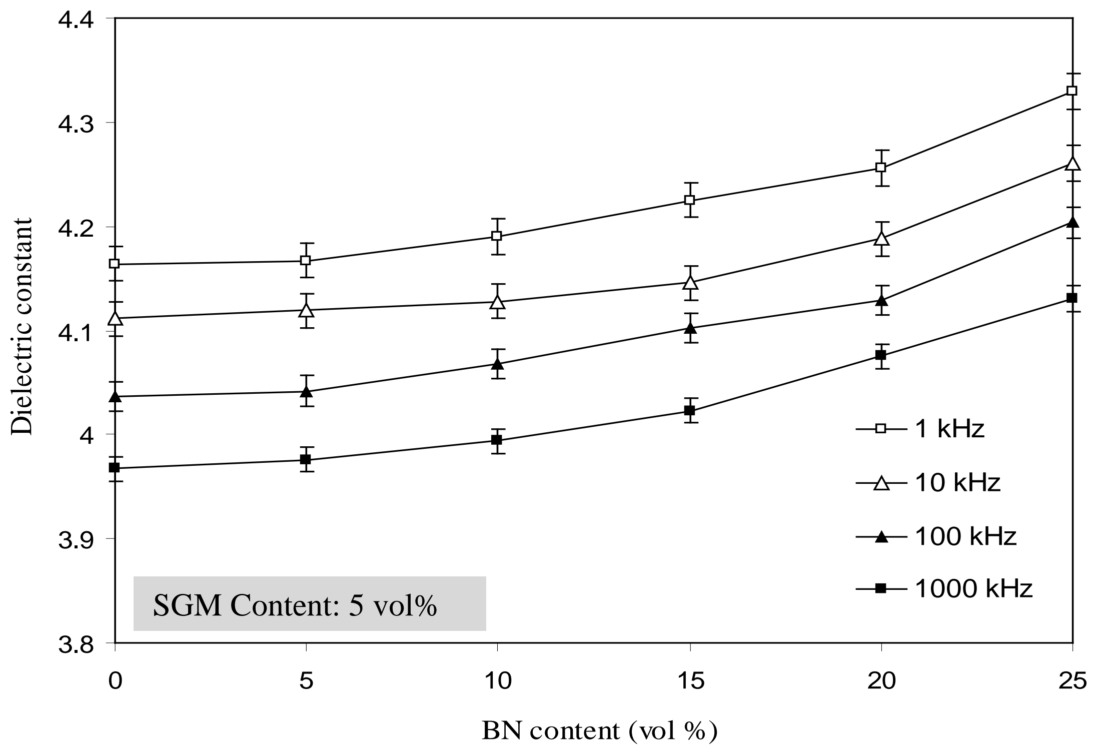

Fig. 7.10 Variation of dielectric constant of hybrid composites with BN content at different frequencies (SGM content 5 vol %)

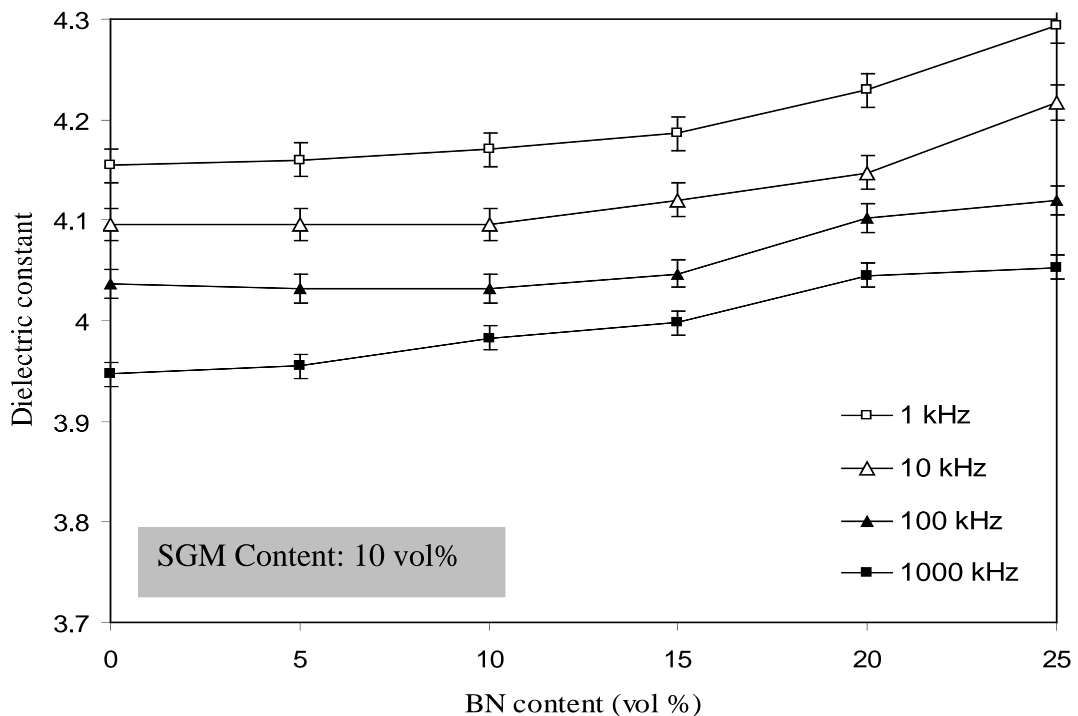

Fig. 7.11 Variation of dielectric constant of hybrid composites with BN content at different frequencies (SGM content 10 vol %)

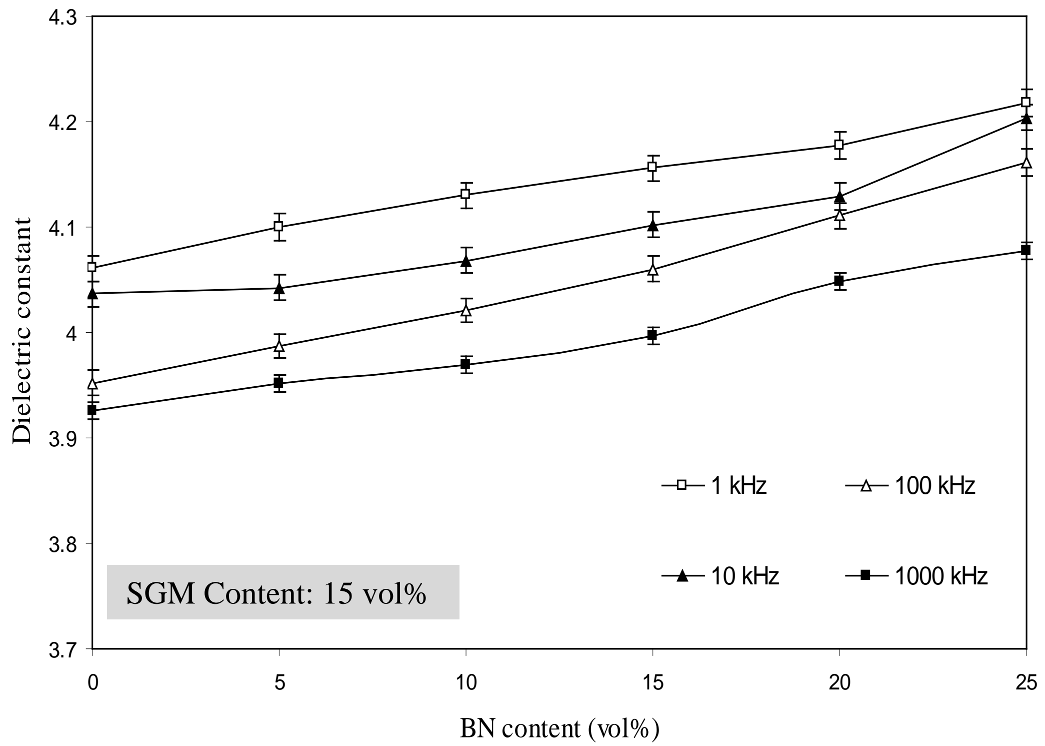

Fig. 7.12 Variation of dielectric constant of hybrid composites with BN content at different frequencies (SGM content 15 vol %)

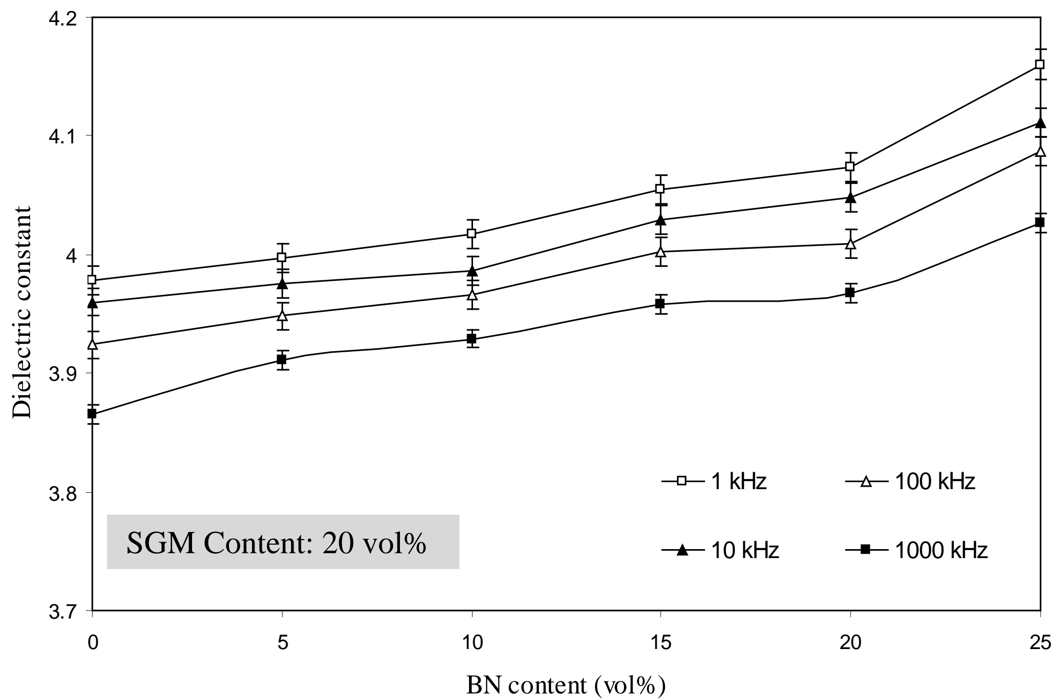

Fig. 7.13 Variation of dielectric constant of hybrid composites with BN content at different frequencies (SGM content 20 vol %)

Synergistic effects of SGM and BN fillers are reflected in the dielectric constant values of the hybrid composites. It is seen that for the composites with fixed SGM content, the effective dielectric constant is increasing with BN content. But for same BN content, the composite with higher SGM content exhibits lower value of dielectric constant. For the hybrid composite with 20 vol% SGM, the value of D_k increases from 3.85 to 4.05 (increment of about 5%) as the BN content increases from 0 to 25 vol%. It is further seen that in case of all the composites under this investigation, the composite dielectric constant is decreasing with increase in frequency.

Discussion

The introduction of inorganic fillers having a permittivity value higher than the base polymer increases the effective permittivity of the polymer composite due to the influence of filler particles, hence with the increase in filler content, the dielectric constant increases with increase in BN content. Similarly, the decrease in D_k of the composites with increasing SGM content is obvious as the D_k of SGM is lower than that of the epoxy. In the present study, the D_k values (3.85 - 4.05) obtained for epoxy-SGM-BN composites at 1 MHz are smaller than that of the common commercial product (e.g., D_k = 4.5 for PCL-FR-226 laminate/PCL-FRP-226 and PCL-FR-240 laminate/PCL-FRP-240). The decrease in D_k with increase in the frequency can be explained as follows:

Dielectric constant of a polymeric material depends on interfacial, dipole, electronic and atomic polarization. The dielectric behaviour involves different polarizations and the polarization rate is dependent on temperature and frequency. At low frequencies, the polarization will have more time to complete compared with that at high frequencies. Thus, the degree of polarization of material is high and the dissipation of polarization is low at low frequencies. The decrease in dielectric constant with an increase in frequency is ascribed to the reason that the interfacial dipoles have less time to orient themselves in the

direction of the applied field [183]. This reveals that the dielectric constant decreases with increasing frequency.

Chapter Summary

This chapter has provided the experimental findings related to the volume resistivity and dielectric behaviour of different particulate filled epoxy composites. The effects of solid glass micro-spheres and/or boron nitride on electrical conductivity and dielectric constant of the composites are discussed.

The next chapter provides the summary of the research findings, outlines specific conclusions drawn and suggests ideas and directions for future research.

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Chapter 8

SUMMARY AND CONCLUSIONS

The research reported in this thesis broadly consists of three parts:

- The first part is about the development of two theoretical heat conduction models based on which two mathematical correlations have been proposed for estimation of effective thermal conductivity of polymer composites with single as well as multiple fillers.
- The second part has provided the description of the materials used and the details of the experiments that are done during this research. It also presents the test results in regard to the physical, mechanical and micro-structural characteristics of the epoxy composites filled with solid glass microspheres (SGM) and/or micro-sized boron nitride (BN).
- The last part has reported on the thermal and dielectric characteristics of the composites under this investigation. It includes an assessment of the effective thermal conductivity of these composites using finite element method and the proposed theoretical models. The results are validated by simultaneous measurement of thermal conductivity of the composites in the laboratory using a Unitherm™ Model 2022 test set up. Effects of inclusion of SGM and/or BN on the effective thermal conductivity (k_{eff}), glass transition temperature (T_g), coefficient of thermal expansion (CTE), electrical resistivity (ρ) and dielectric constant (D_k) are presented.

8.1 Summary of Research Findings

The performance of any new composite product is often judged by its response under different mechanical, thermal and electrical conditions as it becomes essential for selecting the material of proper composition for any given application. Therefore, in the present work, a wealth of property data has been generated for a series of epoxy-SGM-BN composites by fabricating them in the laboratory and by conducting various physical, mechanical, thermal and dielectric tests under controlled laboratory conditions. It is found that by incorporating the chosen particulate fillers (SGM and BN) into epoxy, their combined effects, as expected are achieved in the form of modified physical and mechanical properties. Due to the presence of these two fillers, synergistic effects are exhibited also in their heat conduction behaviour. When BN is added along with SGM fillers to epoxy matrix, the effective thermal conductivity is ameliorated as BN is conductive in nature. Boron nitride is a solid lubricant that improves the rheological properties of the polymer system. This increases the mobility of the hexagonal BN particulates which, in turn, promotes their natural tendency to attach themselves to each other by their basal planes. Thermal bridges are formed across these planes throughout the system resulting in an improvement of conductivity. It is seen that there is a sudden jump in the composite thermal conductivity at the percolation threshold even in the presence of non-conducting SGM in hybrid systems. Effects of SGM and BN on the glass transition temperature and coefficient of thermal expansion of the composites are also found to be substantial. The experimental findings during this work further reveal that while the dielectric constant of epoxy-SGM composites decreases with increase in SGM content, that of epoxy-BN composites increases with BN content. However, in case of hybrid composites, dielectric constant is found to be marginally increasing with filler concentration. Further, it is seen that dielectric constant drops with increasing frequency for all the composite samples under this study.

8.2 Conclusions

This analytical and experimental investigation on epoxy composites filled with solid glass micro-spheres has led to the following specific conclusions:

1. Successful fabrication of particulate filled epoxy-SGM, epoxy-BN composites and multi-filler epoxy-SGM-BN hybrid composites by hand lay-up technique is possible.

2. Incorporation of these fillers modifies the tensile and compressive strengths of the composites. It is noticed that with addition of SGMs, tensile strength of the composite is decreased and this decrement is a function of the SGM content. While the tensile strength of neat epoxy is 58 MPa, it decreases by about 5 % to 55.06 MPa with the incorporation of 35 vol% of SGMs in it. In case of epoxy-BN composites too, the tensile strength is found to be decreasing with BN content and the reduction is more as compared to the epoxy-SGM composites.

3. The micro-hardness, density and porosity of these composites are also greatly influenced by the type and content of fillers.

4. Two theoretical correlations to estimate the effective thermal conductivity of single filler and multi-filler hybrid composites are proposed based on development of one dimensional heat conduction models. It is seen that the analytical models serve as very good empirical models for spherical inclusions and that the proposed correlations can very well be used to estimate k_{eff} for composites within the percolation limit.

5. It is propitious that the incorporation of SGM results in significant improvement in the thermal insulation capability of epoxy resin. It is found that with increase in the SGM content, the value of effective

thermal conductivity (k_{eff}) decreases irrespective of the particle size and a reduction as high as 66% is recorded for epoxy filled with 35 vol % of SGM (100 μm).

6. With increasing BN content in the composite, the value of k_{eff} keeps on increasing. It is seen that the results obtained from the proposed correlation are in good agreement with the experimental results up to a filler concentration of about 20 vol%. The BN particles show a percolation behaviour at this volume fraction (20%) at which a sudden jump in the thermal conductivity is noticed. This is the critical concentration, called the percolation threshold, at which BN particles start contacting with each other and hence the actual size of the agglomerates becomes larger.

7. The experimental findings suggest that the effective thermal conductivity of the hybrid filler composites is always higher than that of neat epoxy. For the composite with fixed SGM content of 10 vol%, the k_{eff} is about 1.65 W/m-K when the BN content is 25 vol%. This enhancement in k_{eff} is about 354% with respect to the thermal conductivity of neat epoxy (0.363 W/m-K). Similarly, the k_{eff} of the hybrid composite with 20 vol% SGM and 27.55 vol% BN is found out to be 1.47 W/m-K, which is about four times the conductivity of epoxy. These data indicate that the effective thermal conductivities of hybrid composites are always higher than that of neat epoxy despite the presence of SGMs in them.

8. It is observed that the glass transition temperature (T_g) of neat epoxy is about 104^0C and it gradually increases to 124°C as the SGM content increases from 0 to 35 vol%. The increase in T_g of the composites can be attributed to strong interaction between the SGMs and the epoxy-matrix. The interaction between the microspheres and the polymer restricts the mobility of the polymer chain, which results in an increase in the glass

transition temperature. On the contrary, it is observed that the T_g of neat epoxy gradually drops to about 98.5^{0}C as the BN content increases from 0 to 35 vol%. However, it is encouraging to note that the hybrid composites under this investigation, exhibit improved T_g as compared to that of neat epoxy, confirming a more reticulated and less mobile structure.

9. The coefficient of thermal expansion (CTE) of the composite decreases with the increase in SGM content. While the CTE of the neat epoxy is about 62.83 ppm/^{0}C, it gradually decreases to 40.19 ppm/°C with an increase in the SGM content and a maximum decrease of about 34% in CTE is obtained for the composite with SGM content of 35 vol%. Incorporation of BN also substantially reduces the CTE of BN-epoxy composites. There is a drop of 12.71 ppm/°C in the CTE for BN-epoxy composites with BN content of 35 vol%. For the epoxy-SGM-BN hybrid composites, it is found that with increase in the volume fractions of SGM and BN, there is gradual decrease in the value of CTE. For the composite with 20 vol% SGM and 25 vol% BN, the value of CTE is recorded as 40.59 ppm/^{0}C, which is 22.24 ppm/^{0}C less than that of neat epoxy.

10. Synergistic effects of SGM and BN fillers are reflected in the dielectric constant values of the hybrid composites. It is seen that for the composites with fixed SGM content, the effective dielectric constant is increasing with BN content. But for same BN content, the composite with higher SGM content exhibits lower value of dielectric constant. For the hybrid composite with 20 vol % SGM, the value of D_k increases from 3.85 to 4.05 (increment of about 5%) as the BN content increases from 0 to 25 vol%. It is further seen that in case of all the composites under this investigation, the effective dielectric constant decreases with increase in the frequency.

8.3 Recommendations for Potential Applications

1. With light weight and improved insulation capability, the solid glass micro-spheres filled epoxy composites can be used for applications such as insulation boards, food containers, thermo flasks, building materials, space flight and aviation industry etc.

2. With enhanced thermal conductivity, improved glass transition temperature, reduced thermal expansion coefficient and modified dielectric characteristics, the epoxy composites with appropriate proportions of solid glass micro-spheres and boron nitride can be used in micro-electronics applications like electronic packaging, encapsulations, printed circuit board substrates etc.

8.4 Scope for Future Work

The present research work leaves a wide scope for future investigators to explore many other aspects of such hybrid composites. Some recommendations for future research include:

- Possible use of ceramic fillers other than boron nitride and polymeric resins other than epoxy in the development of new hybrid composites.
- Exploring the possibility of using natural fibers along with ceramic particulates to fabricate such composites with improved functional properties.
- Cost analysis of these composites to assess their economic viability in industrial applications.

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Appendices

Appendix- A1

List of publications from this research work

Journals

1. Debasmita Mishra, Alok Satpathy (2012), *Processing and Thermal Conductivity Characterization of Solid Micro-spheres Filled Polymer Composites*, **Advanced Materials Research**, 445: 526-529.
2. Debasmita Mishra, Alok Satapathy (2012), *A simulation study on thermal conductivity of glass bead embedded polymeric system*-- **International Journal of Plastics Technology,** 16(1): 24-38.
3. Debasmita Mishra, Alok Satapathy (2013), *Development of Theoretical Model for Effective Thermal Conductivity of Glass Microsphere filled Polymer Composites*, **Plastic and Polymer Technology,** 2(2): 39-47.
4. Debasmita Mishra, Alok Satapathy (2013), *Thermal and dielectric characteristics of Solid glass microsphere filled epoxy composites*, **Composites Science and Technology** (communicated and is under review)

Conferences

1. Debasmita Mishra, Lucy Mohapatra, Alok Satapathy and Amar Patnaik -- *Determination of Thermal Conductivity of Polymer Composites Filled with Solid Glass Beads* --- International Conf. on Advancement in Polymeric Materials (APM 2011): Chennai, March-2011.
2. Debasmita Mishra, Alok Satapathy, Amar Patnaik --- *Processing and Thermal Conductivity Characterization of Solid Glass Micro-Spheres Filled Polymer Composites* -- International Conf. on Advances in Materials and Processing Technologies AMPT-2011, Istanbul, Turkey, July 2011.
3. Debasmita Mishra and Alok Satapathy -- *Effect of Micro-Sphere Size and Content on Heat Conductivity of SGM Filled Epoxy Composites* -- 21st National and 10th ISHMT-ASME Heat & Mass Transfer Conference, Chennai, Dec-2011.
4. Debasmita Mishra and Alok Satapathy --A Study on Thermal Conductivity of Metal Particle Filled Polymer Composites-- International Conference on Advancement in Polymeric Materials (APM 2011): Chennai, March-2011
5. Debasmita Mishra, Abhijit Halder, Abhisek Panda and Alok Satapathy --A Study on the Dielectric properties of SGM-Filled Epoxy Composites --

International Conference on Advancement in Polymeric Materials (APM 2012): Ahmedabad, Feb, 2012.

6. Debasmita Mishra and Alok Satapathy --An Investigation on the Dielectric properties of epoxy-filled with Glass Micro-spheres and Boron-Nitride-- International Conference on Advancement in Polymeric Materials (APM 2012): Ahmedabad, Feb, 2012.

7. Debasmita Mishra and Alok Satapathy--Numerical Investigation of Thermal Conductivity of Boron Nitride Filled Epoxy Composites using Finite Element Method-- International Conf. on Advancement in Polymeric Materials (APM 2013): March, 2013, Lucknow.

8. Debasmita Mishra, Lucy Mohapatra and Alok Satapathy -- *A Study on Heat Conductivity of Glass Bead Embedded Polymeric System* -- National Conference cum Workshop on Recent Developments in Engineering Materials, Birla Institute of Technology, Mesra, May, 2011.

9. Debasmita Mishra and Alok Satapathy ---*Effect of filler size and content on thermal conductivity of SGM filled epoxy composites*--- Proceedings of the International Conference on Mechanical Engineering (ICME2011), December 2011, Dhaka, Bangladesh.

Appendix- A2

Brief Bio-data of the Author

The author, Ms Debasmita Mishra, born on 01-10-1982 graduated in Mechanical Engineering from Biju Patnaik University of Technology (BPUT) in the year 2005. Before joining for the Ph.D. programme at the National Institute of Technology, Rourkela, she had served as a faculty in the Department of Mechanical Engineering at Eastern Academy of Science and Technology, Bhubaneswar and then at Silicon Institute of Technology, Sambalpur. She had obtained her M.Tech. degree from University College of Engineering (now Veer Surendra Sai University of Technology), Burla in 2008.

She has authored 04 research papers in International Journals and has 12 papers in various International & National Conferences to her credit. During the postgraduate programme, she had worked in the area of analysis of capillary tube characteristics and scope of use of alternative refrigerants for domestic refrigerators & air-conditioners. Since 2010, she has been engaged in her Doctoral Research in the area of particulate filled composites at N.I.T, Rourkela under the Institute Research Fellowship scheme.

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