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### CHARACTERIZATION OF POLYMERIC COMPOSITES WITH LOW CTE

### CERAMIC PARTICULATE FILLERS

By

PRADEEP U. SONJE

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#### A THESIS

Submitted to Michigan State University In partial fulfillment of the requirements For the degree of

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#### ABSTRACT

## CHARACTERIZATION OF POLYMERIC COMPOSITES WITH LOW CTE CERAMIC PARTICULATE FILLERS

#### By

#### **PRADEEP U. SONJE**

Use of particulate fillers is a potential approach to develop isotropic low coefficient of thermal expansion polymeric composite materials for electronic circuit board applications. Low coefficient of thermal expansion ceramic particulate fillers such as Cordierite, Beta quartz and BS-50 were incorporated into three different epoxy resins. The effect of different particulate fillers on the coefficient of thermal expansion of resultant composites was studied. In order to promote the adhesion with epoxy resin matrix, particulate fillers were treated with surface-active agents. Fracture study and microhardness testing of the composites in addition to coefficient of thermal expansion measurements revealed the dispersion of particulate fillers, nature of interfacial bonding and its effect on reducing coefficient of thermal expansion of the composites on the properties of the epoxy resins as well as on the properties of the particulate fillers along with other factors is discussed.

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### 1. INTRODUCTION

# 1.1 Necessity of polymer matrix composites with low coefficient of thermal expansion

Use of particulate fillers is a potential approach to develop isotropic low coefficient of thermal expansion (CTE) polymeric matrix composite materials for electronic circuit boards. One of the most common materials used for making the laminates for electronic circuit boards is the epoxy resin reinforced with E-glass fibers. The CTE of circuit boards ranges from 12 to 16 ppm/°C in the in-plane direction of fibers (x, y direction) while it takes value ranging from 40 to 120 ppm/°C in the out-of-plane direction (z direction). The CTE of leadless ceramic chip carriers that are mounted on the circuit board have the CTE values ranging from 5.9 to 7.4 ppm/°C. Table 1 lists CTE of various materials commonly used in printed circuit boards indicating the wide differences in the CTE of those materials. The in-plane CTE mismatch due to differences in CTE of various components of circuit board, affects the solder joint reliability. The out-of-plane CTE of circuit boards has much higher value than the CTE of copper plated through holes. This can lead to failure of copper in plated through holes [1]. Thus it is necessary to minimize the out-of-plane CTE of the circuit board materials along with the reduction of the in-plane CTE. Low CTE composites have wide range of applications, especially in electronic industry. One approach is to develop low CTE particulate reinforced epoxy resin matrix composites, which will have isotropic low-CTE value. Silica particles are often incorporated in epoxies for encapsulating integrated circuit devices [2]. In addition, it has been pointed out in the literature that negative CTE particulate fillers are more effective as additives to lower CTE of epoxy resin matrix composites at higher volume

Materials used in printed circuit board	CTE (ppm/°C)
Copper	17
Lead-tin solder (60Sn-40Pb)	24
Silicon	2.5
E glass fibers	5.0
Epoxy resin	81-117

 Table 1. CTE of materials commonly used in printed circuit boards [3].

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fractions of particulate fillers [4,5]. Table 2 compares the values of CTE achieved in composites by adding maximum quantities of different types of particulate fillers into the epoxy resin matrices. The data listed are for epoxy resin DGEBA cured with MPDA (Meta phenylene diamine). DGEBA stands for Diglycidyl ether of bispenol A. DGEBA is epoxy resin monomer equivalent to the epoxy resin monomers used in this study.

#### **1.2 Particulate reinforced polymer matrix composites**

Particulate reinforced polymer matrix composites is the class of materials, which consists of the particulate filler phase embedded in the polymer matrix phase. This encompasses a wide range of thermosets and thermoplastic polymers along with organic and inorganic particulate fillers.

Epoxy resins are the most common thermosets used as matrices for fiber reinforced composites for electronic applications. The epoxy resins are preferred in the electrical and electronics applications due to various advantages like low cost, optimum combination of various properties, superior adhesion, permeability, purity, superior corrosion resistance and stress resistance. In addition, the properties of epoxy resins can be altered by using various combinations of epoxy resin types, curing agents, modifiers and particulate fillers [6]. Introducing particulate fillers in the epoxy resin matrix modifies its microstructure and the state of residual stresses, and thus alters various resultant properties. The properties of epoxy resins that are affected by adding the particulate fillers include stiffness, strength, toughness, hardness, density, CTE, conductivity, machinability, electrical properties, flame retardation, rheology, adhesive properties and the cost [6,7,8]. The particulate fillers act as heat sink for the exothermic

Particulate filler	Maximum particulate filler by weight %	Value of CTE achieved in composites (ppm/°C)
Silica	68.6	26.1
Mica	37	37.8
Aluminum powder	63.6	33.5
Zirconium silicate	68	28
Lithium silicate	72.3	19
Iron powder	72.3	33
Copper powder	72.3	36
Hydrated alumina	30.7	41
Alumina	56.5	30

**Table 2.** Maximum quantity of particulate fillers added to DGEBA epoxy resin curedwith MPDA and CTE values achieved in the resultant composites [9].

Note- CTE of DGEBA can vary between 81-117 ppm/°C

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curing reactions of epoxy resins, decrease shrinkage during curing and add opacity or color to the resulting composites [10]. Particulate fillers can be the cheapest reinforcements that can produce isotropic properties. They may be reactive or inert. Various types of particulate fillers and their roles in enhancing the properties of epoxy resin are tabulated in Table 3 [11,12,13]. The particulate fillers do not improve mechanical properties as much as do the continuous fibers, but they allow the processing of epoxies in paste form, which is a very important criterion in electrical and electronics applications. [14,15].

Properties of the particulate reinforced composites are governed by following factors [6,8,15,16,17] -:

- 1. Type of epoxy resin -: The most significant properties of epoxy resin that affect processing and the resultant properties of composite include viscosity, chemical composition, density, elastic modulus, and tensile strength,
- 2. Type of curing agent,
- 3. Type of particulate filler -: The most significant properties of the particulate fillers that affect processing and resultant properties of composite are chemical composition, the internal geometry i.e. shape and size (average size as well as distribution), nature of surface, adsorption characteristics, density and elastic modulus,
- 4. Volume fraction of the particulate fillers,
- 5. Processing parameters -: Important parameters are amount of shear force applied during processing, interaction between matrix and particulate fillers, and type of dispersion achieved,
- 6. Presence of porosities in composite,

### Table 3. Effect of particulate fillers on the properties

of the epoxy resin matrix composites [11,12,13].

Particulate filler	Property improved
Silica, calcium carbonate	Cost
Glass micro balloons	Density
Fibrous glass, chopped nylon and glass	Impact strength
Asbestos, fluorocarbon micro fibers and other fibers	Tensile strength
Aluminum and copper powder, calcium carbonate and silicate	Flexural strength and machinability
Carbon black, asbestos	Heat resistance
Silica, metal powders	Dimensional stability
Metallic powders and fibers, silica, alumina and beryllium oxide	Thermal conductivity
Lithium aluminum silicate	CTE
Inorganic particulate fillers	Fire retardance and burning rate
Asbestos, powdered coal	Chemical resistance
Mica, silica, powdered coal	Moisture resistance
Silver or aluminum powder, carbon, graphite	Electrical conductivity
Mica, asbestos, silica, powdered glass	Electrical resistivity
Graphite, mica, molybdenum disulphide	Lubricity
Alumina, flint powder, carborundum, silica	Abrasion resistance
Barium titanate	Dielectric constant

7. Presence of additives, modifiers and diluents if any, and

8. Type of coupling agents used if any.

### 1.3 CTE

Most of the solid materials expand upon heating and contract on cooling. The change in length of solid material with temperature is expressed by-

$$\Delta l/l = \alpha \Delta T$$
,

where,

 $\Delta l$  = the change in length of the solid material,

 $\alpha$  = linear CTE of the solid material, expressed in parts per million i.e. ppm/°C or

µm/m/°C, and

 $\Delta T$  = the change in temperature.

We can also write,

$$\Delta V/V = \gamma \Delta T$$
,

where,

 $\Delta V$  = the change in volume of solid material, and

 $\gamma$  = cubical or volumetric CTE of the isotropic solid material.

For isotropic materials,

There is an universal relationship between linear and cubical CTE for all solid materials

and it is expressed as,

$$\gamma_{\text{Cubical}} = \alpha_x + \alpha_y + \alpha_z$$

where,

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$\gamma_{\text{Cubical}}$  = Cubical CTE of the anisotropic solid material, and

 $\alpha_x$ ,  $\alpha_y$ ,  $\alpha_z$  are linear CTE of the solid material in X,Y and Z directions respectively [18].

CTE of the composites is governed by properties of epoxy resin, curing agent, properties of particulate fillers, additives and processing parameters [19].

#### **1.4** Stresses in particulate reinforced epoxy resin matrix composites

There are two types of shrinkages in the epoxy resins. One is due to the reaction and compact rearrangements of the molecules that occurs during curing process. During curing of epoxy resin, the secondary bonds or van der Waals bonds between monomer molecules or monomer chains, with separation distance of about 3-5 A°, get converted into primary covalent bonds with separation distances of about 1.5 A°. This causes volume reduction or shrinkage [20, 21]. The other shrinkage is thermal shrinkage caused by cooling of the epoxy resin from high processing temperature to room temperature. Epoxy resins show 3-6.5% shrinkage during polymerization. Due to the shrinkage that occurs in polymerization of epoxy resins, stresses are developed, and they can be large enough to crack the component or the bond (when epoxy resin is used as adhesive). The maximum value of the stresses that develop depends upon the curing temperature, curing agent, type of catalyst and most importantly degree of cure. Values as high as 1500 Psi (0.01035 GPa) for this stress, at room temperature are reported in the literature [22].

There are two sources of the stresses in the particulate reinforced epoxy resin matrix composites. First source is stresses due to epoxy resin shrinkage. Overall shrinkage of epoxy resin reduces as the quantity of particulate fillers that are added into epoxy resin increases [23, 24]. Though the overall CTE and shrinkage of epoxy resin reduce on addition of particulate fillers, the composite is not stress free. The epoxy resin shrinkage during curing process in presence of particulate fillers sets up stresses at the interface of epoxy resin and particulate filler. So with addition of particulate fillers, the stresses are merely transferred to microscopic level arising at the interface of the particulate fillers and the epoxy resin matrix [25,26].

Second source of stresses in particulate reinforced composites is thermal stresses caused by high difference in the CTE of the epoxy resin matrix and the particulate fillers. Contraction of composites occurs during manufacture. Heating and the associated expansion of composites, takes place in service. In composites, particulate fillers and the epoxy resin are in intimate contact. Therefore there are constraints at the interface for expansion or contraction of epoxy resin as well as that of the particulate fillers. This creates geometric mismatch or shear stresses at the interface of the particulate fillers and the epoxy resin matrix. This mismatch created at the interface will be positive or negative depending upon the CTE of the particulate fillers and that of the matrix [27]. Warming the composite reverses the direction of the stresses. The stresses developed in composites affect the mechanical behavior and thermal characteristics of the composites to a great extent [28]. The magnitude of thermal stresses developed in composites depends upon CTE of the matrix, CTE of the particulate fillers, volumetric concentration of the particulate fillers, bulk modulii and elastic modulii of epoxy resins as well as particulate fillers, service temperatures, and glass transition temperature of the epoxy resin [29].

#### **1.5 Effect of volume of particulate fillers on CTE of composites**

Particulate fillers affect the properties of composites by partially occupying the volume of epoxy resin by rigid, immobile masses. This leads to disturbance of the matrix. The extent to which the state of stress of matrix is affected varies based upon the volume fraction of particulate fillers [30]. At low volume fractions of particulate fillers, the epoxy resin dominates the continuum and hence governs the CTE of the composite, and effect of CTE of particulate fillers on the CTE of the composites is negligible [31]. At low volume fractions of particulate fillers, the inter particle distances are very large. So the interaction between the particles is negligible [32]. Only at low volume fractions of particulate fillers, the interface of the particulates particulate fillers and epoxy resin matrix is in the state of compression due to polymerization shrinkage [33]. When the composite is loaded with high volume fraction of particulate fillers, the resin is confined to small areas between the particles. The interparticle distances are small. When curing process begins, the particles come even closer due to contraction of the matrix. The particles get packed closely, and several particles push against each other. Close packing of particles forces epoxy resin in interparticle spaces to complete the curing process at constant volume, setting up tensile stresses at the interface of epoxy resin and particles as the curing progresses to completion [21]. Decrease in interparticle spacing caused by increase in volume fraction of particulate fillers results in collisions, turbulence and rotation of the particulate fillers that produces a complex stress pattern in the matrix [32]. Cumulative effect is that, at higher volume fractions of particulate fillers, CTE of the particulate fillers has pronounced effect on the CTE of the composite [34]. At high volume fractions of particulate fillers, the interparticle spacing is such that, if there is

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perfect adhesion at the particle-epoxy resin interface, the interface and epoxy resin are in a state of hydrostatic tension. If the interfacial adhesion is poor or insufficient, void formation and separation can occur due to epoxy resin shrinkage away from the particulate filler surface. The extent to which the porosities form is a function of adhesive strength, type of particulate filler and their volume fraction [13,32].

## **1.6 Effect of adhesion of particulate fillers with the matrix on CTE of composites**

Effectiveness of particulate fillers as reinforcing agents in epoxy resin matrix depends upon the extent of adhesion between the particulate fillers and the epoxy resin matrix. If thermal stresses can be transferred across the interface of particulate fillers and the epoxy resin matrix, then overall CTE of composite reduces compared to the CTE of the matrix. Hence CTE value of composites can reveal the nature of adhesion between the particulate fillers and the epoxy resin matrix. Adhesion is created by the pressure increase arising from the shrinkage during polymerization of epoxy resins [35,36]

It is difficult to have perfect adhesion between the particulate fillers and epoxy resin matrix by any binding media due to the large differences between the CTE of the two materials. If one of the materials is thin enough to permit relief of stresses by bending or warping, then the perfect adhesion may be achieved. Otherwise stable and perfect adhesion is possible only if CTE of the two phases are matched. The adhesion between two phases of a composite depends upon following factors -

1. The dimensions of the phases,

2. The modulii of elasticity of the phases,

3. Changes in dimensions with changes in moisture content for all phases,

- 4. Temperature changes encountered in the service,
- 5. Value of CTE of the phases, and
- 6. The pressure of application during the manufacture.

There can be two extremes of adhesion, either absent of any adhesion between the particulate fillers and the epoxy resin matrix or there would be perfect adhesion between the epoxy resin and the particulate fillers. Both these are very uncommon situations and the most common situation is intermediate between the two. But discussing these two extremes can be useful to understand the effect of intermediate adhesion level on the CTE of composites.

#### **1.6.1** Non-adherent particulate fillers

If there is no adhesion between the particulate fillers and the epoxy resin matrix in the composite, then there will be no residual stresses across the interface. There will be no thermal stresses because on application of heat, the matrix will expand away from the particulate fillers without any resistance from particles to the expansion of the matrix. If there is no adhesion, no stress will be transferred across the interface of particulate fillers and epoxy resin. The particulate fillers will share no stresses. Hence the CTE of the composite will be independent of the volume of particulate fillers. Then the CTE of the composite will be same as that of the epoxy resin matrix [27,37].

#### **1.6.2** Perfectly adherent particulate fillers

If perfect adhesion exists between the particulate fillers and the matrix, thermal stresses will be completely transferred across the interface of particulate fillers and epoxy

р p p. p fc Ŋ :0 e, and the second e a resin. Hence perfect adhesion of the particulate fillers and the epoxy resin matrix will resist thermal stresses and the CTE of the composite will be substantially lowered with addition of even small quantity of particulate fillers with low CTE. The most important factor to achieve perfect adhesion is that the particulate fillers should be well dispersed in the epoxy resin matrix without formation of weak aggregates [37].

#### **1.6.3** Adhesion mechanisms

The degree of adhesion between the particulate fillers and epoxy resin matrix depends upon the interaction between them. There can be three types of interactions between the particulate filler and the epoxy resin, namely mechanical, physical and chemical. The surface chemistry of the particulate fillers and the chemistry of the epoxy resin decide the type of interaction between them. Mechanical interlocking of the particulate surfaces with the matrix can result in a strong adhesion between the particulate fillers and the matrix. In the absence of chemical interaction between the particulate fillers and the matrix, the mechanical adhesion plays a key role. The particulate fillers can remain physically attached to the matrix just due to compressive forces without interlocking. When the particulate fillers are chemically reactive with the matrix, a chemical bond may be created. Chemical bonds can also be created by use of coupling agent between the matrix and the particulate fillers. The particulate fillers that react chemically and become integral part of the cured system are the most effective reinforcements. Few examples of composites that have chemical bond between the particulate fillers and the polymer matrix are carbon black filler in rubber matrix, Mica in

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polymeric matrix. Talc can also pickup water during storage and react with the polymer matrix [35,38,39,40].

## 1.7 Effect of modulii of elasticity of particulate fillers and epoxy resin matrix on composite properties

Modulus of elasticity is defined as the ratio of stress to strain for a material under uniaxial tension or compression. The modulus of elasticity is a measure of the stiffness of the material. The greater the elastic modulus, the smaller the elastic strain resulting from the application of given stress.

The modulii of elasticity of the matrix and particulate fillers indicate the effectiveness of stress-strain transfer across the interface of the epoxy resin matrix and particulate fillers. The materials with lower elastic modulii deform more easily under the stresses [41]. If the modulus of elasticity of any one of the two adjacent phases is zero, the stresses set up between then will be zero [42]. If the modulus of the particulate fillers is as high as 100 times more than that of the matrix, then it will cause high stress concentration at the interface, which can result in breaking of any interfacial bond. A relationship applicable to many solids and composites is [43]-

$$E\alpha^2 = 150 \text{ dynes/cm}^{2^\circ} \text{ K}^2$$
,

where,

E= Elastic modulus of the material.

Above equation supports the close relation between elastic modulus and CTE.

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#### **1.8** Effect of arrangement of particulate fillers in the composites

The arrangement of particulate fillers in the epoxy resin matrix plays important role in affecting the properties of the composite. For spherical particles, the higher the packing factor, lower will be the hindrance for the shrinkage of the epoxy resin and so the magnitude of stresses developed in composites is lower. It is possible to compare various arrangements of the particles in the epoxy resin matrix with that of the arrangements of atoms in crystal systems like HCP, BCC, and FCC. Similarly the shape of the particles will affect the magnitude of the stresses that can develop [21].

### **1.9 Reduction of stresses developed in particulate reinforced** composites

From the ongoing discussion, it can be summarized that, the stresses set up in the particulate filled composite are function of the following variables:

- 1. Strength of epoxy resin,
- 2. Volume fraction of the particulate fillers,
- 3. Geometrical arrangement of particles,
- 4. Ratio of elastic modulii of epoxy resin and that of particulate filler,
- 5. Poisson's ratio of the epoxy resin as well as particulate fillers,
- 6. Shape of particulates,
- 7. Adhesion of particulate fillers to the epoxy resin matrix,
- 8. Percentage of inherent shrinkage of the epoxy resin,
- 9. Degree of polymerization in cured epoxy resin, and
- 10.Volume fraction of porosities.

Following are alternatives for reducing the residual stresses in composites -:

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- The lower the cure temperature, lesser will be the stresses that develop in composites. Hence epoxy resins with low glass transition temperatures are better as matrix for composites [44]. The more flexible epoxy resins will develop lesser stresses. Matrix resin can be selected accordingly.
- 2. Stresses developed in composites can be reduced by matching the CTE of the two phases of composites. (This is contradictory to the aim of this project.)
- 3. Addition of 1-3 % photosensitive fillers like cinnamic acid resins and cinnamal ketones in epoxy matrices, followed by exposure to strong ultraviolet rays relieves the internal stresses in cured epoxy resin system [45].
- 4. Annealing the composite slightly above its glass transition temperature can minimize thermal stresses. The cooling after the annealing process generates minimal thermal stresses [46].
- 5. It is possible to add carefully measured quantities of chemical agents that expand during curing of epoxy resin to nullify the effect of polymerization shrinkage [21].

#### **1.10** Effect of shape and size of the particulate fillers

The shape and size of the particulate fillers affect the powder flow, viscosity, mechanical properties (elastic modulus, tensile strength, impact strength etc.), thermal properties and optical properties of the composites [47]. The effective surface area of the particulate fillers is decided by their shape and size. Sizes and shapes of particulate fillers are decided by the following factors -

- 1. Origin of the particulate fillers,
- 2. Processing method, and

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#### 3. Chemical composition

Common shapes of particulate fillers are spherical, platy, acicular, blocky and irregular as indicated in Figure 1 [47]. Particulate fillers can occur in various forms in the composite, such as single or primary particles, agglomerates (weakly bonded particle collections) or aggregates (strongly bonded particle collections) or fragments [48]. Aggregates need maximum amount of energy for the breakdown and dispersion in the epoxy resin matrix. Fragments require the least amount of dispersion energy for dispersion in the matrix.

The shape of the particulate fillers is important because it decides the amount of epoxy resin that can be shielded and thus the amount of epoxy resin that need not deform. Shape of particulate fillers also increases the effective filler volume. Figure 2 shows the effect of particle shape in shielding the polymer. The aspect ratio is the ratio of the largest and the smallest dimensions of the particle. Aspect ratio is important quantity for describing the shape of particulate filler.

The fineness of the particles, the tendency to form flocks after addition of particles in liquid epoxy resin, and strength of the bond between the particulates in aggregates, affects the dispersion process of particulate fillers in the matrix during synthesis of composites. Intensive mechanical breakdown, ultrasonic mixing or use of dispersants, are the various alternatives to obtain better dispersion of the particulate fillers in the epoxy resin matrix [48]. Any powder sample consists of a range of particle sizes. Hence the average particle size as well as the distribution play important role in affecting

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Figure 1. Typical shapes of particulate fillers [49].



Figure 2. Schematic representation of effect of particle shape and occluded polymer

[49].

the composite properties [50]. Particle size decides the interparticle spacing. The interparticle spacing affects the composite properties by two ways. When the interparticle distances become small, the epoxy resin chains have less freedom of movement compared to the freedom they have in the bulk polymer. The surface of the particles may also participate in the growth of the polymers [17]. But it is difficult to measure these effects directly. Secondly, if there are shells of the epoxy resin adsorbed on the particles, then at some limiting distances, these shells will overlap as indicated in Figure 3 and affect the properties of the composite.

#### **1.11** Effect of wettability of particulate fillers

The nature of interaction between the epoxy resin and particulate filler depends significantly upon the wettability of the particulate fillers. Wettability can also affect the nature of adhesion between the particulate fillers and the matrix [51]. Surface energy is the free energy increase in a system on creating a unit area of new surface at constant temperature, pressure and composition. The surface energies of particulate fillers and polymers control the wettability and hence the compatibility between the two. Table 4 lists the surface energies of different particulate fillers. Wettability directly affects the dispersion process resulting into evenly distributed particulate fillers. Particulate fillers increase the viscosity of the epoxy resin systems. In most of the cases, equal weights of finer particulates increase the viscosity more than the coarse particulates due to the presence of higher wettable surface area [52]. High wettability of the particulate fillers can give rise to low viscosity of epoxy resin and particulate filler mixture, which facilitates the processing of the composite. Thus good wettability in turn allows



Figure 3. Effect of reducing inter-particle distance [17].

I. Inter-particle are more at low volume fractions of particulate fillers.

II. Inter-particle distances are less at high volume fraction of particulate fillers,

where the overlapping of shells of adsorbed epoxy resin matrix takes place.

Material	Surface energy (mJ/m <sup>2</sup> )	
Diamond	10000	
Glass	1200	
Titanium dioxide	650	
Kaolin	500-600	
Calcium carbonate	65-70	
Stearate coated calcium carbonate	28	
Talc	65-70	
Polymers	15-60	
Polypropylene	31	

**Table 4**. Surface energies for various particulate fillers and plastics [39].

maximum loading of particulate fillers. Higher the wettability, the chances of void formation in composite are less. Good processability, higher loading of particulate fillers and fewer porosities render better mechanical properties to the composites [53,54].

#### **1.12** Effect of chemistry of the particulate fillers

If there is hydroxyl group present on the surface of the particulate fillers, it may affect the curing reaction. If the particulate filler is sensitive to pH change, then there may be deflocculation and viscosity increase under alkaline conditions such as in presence of amine curing agents [52]. If the particulate fillers are reactive, then the stoichiometric ratio of curing agent needs to be adjusted depending upon the effect of particulate fillers on the rate of curing reaction [55].

#### **1.13** Viscosity of the mixture of particulate fillers and epoxy resins

Viscosity is an important parameter in composite manufacturing process. The particulate fillers increase viscosity of the epoxy resins the least while the fibrous particulate fillers increase it the most. Some particulate fillers are also sensitive to the shear rate in modifying the viscosity [56].

Low viscosity of the epoxy resin can facilitate the dispersion of the filler in the system [57]. The viscosity can be reduced by heating the resin or adding diluents (like styrene, butyl glycidyl ether, phenyl glycidyl ether and cycloaliphatic resins). Since, the use of diluents affects electrical properties of resulting composites, moderate heating of the epoxy resin is a better way of reducing viscosity up to a limited extent [9]. The extent to which resin viscosity is affected by filler addition is a function of particle size and

shape, chemical reactions, wettability etc.Viscosity is such an important processing criteria that certain particulate fillers are added only up to certain level of viscosity, instead of adding to certain volume percent. [58,59]. Table 5 shows effect of various particulate fillers on the viscosity of DGEBA cured with primary amine. The type and volume of the particulate fillers significantly affect the viscosity of the mixture of particulate fillers and the epoxy resin.

#### **1.14** Settling of particulate fillers in epoxy resin matrix

Centrifuging of the particulate filler- epoxy resin mixture is often necessary prior to curing in order to get rid of air bubbles. The particulate fillers can show settling tendency during centrifuging of the mixture. Settling of the particulate fillers depends on the specific gravity of the particulate fillers, the size of particulate fillers, specific gravity of the epoxy resin and the viscosity of mixture of epoxy resin and particulate fillers. The finer the particulate filler, lesser the tendency to settle. To achieve balance, sometimes some fine particulate fillers are added to the coarse particulate fillers to reduce the settling [60]. Bulk density of the particulate fillers is another important property that affects settling, mixing and distribution of the particulate fillers in the epoxy resin matrix.

#### **1.15** Curing of the composites

Epoxy resins are thermosetting polymers, which are converted into permanent shape by irreversible, exothermic chemical reaction called curing. They can be softened, but cannot be reformed [16]. Curing of epoxy resins is a highly exothermic reaction. The

Table 5. Effect of particulate fillers on viscosity of DGEBA,

cured with primary amine [24].

Particulate filler Volume % of particulate fillers	Viscosity at 25° C (Poise)			
	20%	35 %	50 %	65%
No filler	11	11	11	11
Quartz	21	37.5	131.5	1000
Mica	21	48	545	not available

epoxy resins have a low thermal conductivity and moderate heat capacity. Hence, in the polymerization reaction, the heat, if liberated during a short course of time, results in a substantial increase in temperature of the reactive mixture. This temperature increase is called as curing exotherm and measured using thermocouple. The order of curing reaction is independent of the type of particulate filler and filler content. But the rate constant of reaction or the monomer consumption decreases depending upon the type of particulate filler and content of particulate filler. Particulate fillers reduce the effective quantity of the epoxy resin in a given volume, thus reducing heat generated per unit volume of the mixture or in other words they lower peak exothermic temperatures encountered during curing. In addition, particulate fillers, due to higher thermal conductivity, act as heat sink and aid to reduce the maximum temperature reached during the curing reaction. Here the particulate fillers act as diluents. Table 6 lists the reduction in peak exotherm temperature of the epoxy resins due to addition of particulate fillers. The particulate fillers also alter the curing pattern of the epoxy resins. The important filler properties that affect curing process are the density and the specific heat, and presence of any specific chemical reaction between the particulate fillers and the epoxy resin [61,57]. If the curing agents are adsorbed on the particulate fillers, then it is possible to get higher cross-link density in the vicinity of the particulates surfaces, but this effect is difficult to measure [62].

#### **1.16 Density of composites**

Density of composites is an important property, that can be measured easily. Density indicates the packing of constituent phases [19]. If the value of density of

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**Table 6.** Effect of particulate fillers on peak exothermic temperature risein DGEBA cured with primary amine [24].

Particulate filler	Peak exothermic temperature rise (°C)			
Volume % of particulate fillers	20%	35%	50%	65%
No filler	223	223	223	223
Quartz	178	113	51	34
Mica	159	111	51	Not available

.

composite is less than expected, it indicates presence of air bubbles and formation of aggregates in the composites. Density value can also indicate the level of stresses in the composites. Higher than theoretically expected value of density of composite indicates error in the assumed values of densities. If the expected density and the observed density of the composite are exactly the same then one can assume that the packing of particulate fillers is perfect and the distribution of the particulate fillers is uniform [27].

#### **1.16.1 Porosity in composites**

Pores of various shapes and sizes can form in the particulate reinforced composites depending upon the nature of the epoxy resin, nature of the particulate fillers, the size of the particulate fillers, volume fraction of the filler, strength of adhesive bond between the particulate fillers and the epoxy matrix, and most importantly the processing method followed. The pores act as the inclusions with zero stiffness at room temperatures. At high temperatures, pores may exert pressure on the composite. Pores should not affect the CTE of the composite, but they can reduce the strength and elastic modulus of composites sharply. If the porosity is present on the composite surface, they can act as stress raisers. If porosities are present just below the surface of test specimen, they might affect CTE measurement. Volume of porosities can be estimated by observing polished surfaces or by Archimedes principle of specific gravity measurement or by using ultrasonic scanning. For calculating volume of porosities from specific gravity method, the exact values of densities and volume fractions of particulate fillers as well as those of epoxy resin matrix must be known. Agglomerates and aggregates contain porosities so their apparent volume is much greater than the real volume [63].

#### **1.17** Role of silane coupling agents

Surface chemistry of particulate fillers is important for adhesion of the particulate fillers with the matrix. Better the adhesion, stronger the interface and better the mechanical properties of the composite [64]. One way to achieve best adhesion of particulate reinforcements with the polymer matrix is by use of coupling agents. The coupling agents are bifunctional additives that form strong covalent bonds to the fillers and then bond to a polymer by variety of mechanisms. The most common coupling agents are organosilanes and organotitanates. Silane coupling agents are the organosilanes that are commonly used for silica type fillers. Silane coupling agents have two different types of reactive functional groups as indicated below: -

where,

'X' represents the functional group that reacts with organic materials like synthetic resins and may be selected from the following types of functional groups: vinyl, epoxy, amino, methacryl, acryl, isocyanato, mercapto. OR represents the alkoxy functional group that may be one of the following: methoxy, ethoxy, acetoxy. These alkoxy groups react with hydroxyl group or water commonly by hydrolysis mechanism. Water for this hydrolysis is deliberately added water or water absorbed from environment. The organometallic hydroxide that forms then, condenses with the hydroxyl group present on the surface of inorganic fillers like glass, metals, silica etc. The particulate fillers treated with coupling agents are then mixed with polymer matrix.

Silane coupling agents are commonly used in fiber-reinforced composites to achieve better adhesion between fibers and the matrix. Silane coupling agents are commonly used in particulate filled composites for better adhesion between inorganic particulate fillers and epoxy resin matrix that can result in better mechanical strength and improved chemical resistance in the composite. Treating surfaces of particulate fillers with silane coupling agents can make interfaces of composites so strong that the failure mechanisms of composites may change from interfacial failures to transparticle failures or to matrix failures. Curing process of the epoxies can be affected strongly by the glass and mineral particulate fillers, but can be corrected by longer curing times. It is observed by other researchers that the silane treatments of particulate fillers can overcome cure inhibition in the epoxies. Particulate fillers treated with silane coupling agents show improved wettability and are much easier to disperse in epoxy resin matrix because the water layer on the surface of particulate fillers is replaced by organofunctional silanes after treating with silane coupling agent. Improved wettablity of particulate fillers can avoid aggregate formation and will result in uniform distribution of particulate fillers in epoxy resin matrix. Due to uniform distribution of more wettable particulate fillers, density of composite will be closer to the expected ideal density. Treating particulate fillers with silane coupling agents also affects the viscosity and flow of the mixture of epoxy resin and particulate fillers [65]. Thus, treating the particulate fillers with silane coupling agents can improve dispersion of particulate fillers, adhesion between phases,

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curing characteristics, tensile strength, flexural strength and electrical properties of composites [66].

#### **1.18** Fracture study of particulate reinforced composites

Fracture study of particulate reinforced composites reveals the nature of adhesion at the interfaces of reinforcements and the epoxy resin matrix. Epoxies are brittle due to their highly cross-linked structure. But at the same time they have highest fracture energy amongst cross-linked glassy polymers [67]. Pure epoxy resins have less fracture toughness due to shrinkage stresses. Toughness can be increased by addition of particulate fillers without marginal decrease in tensile or flexural strength [68]. When the failure of particulate reinforced composites begins, with the applied load the crack travels between the particulate fillers, deflects into matrix and gets arrested near the particulate fillers. Thus particulate fillers increase fracture toughness of epoxy resin matrix by arresting the cracks more often, which results in higher fracture toughness in the composites. The important considerations are the size of particulate fillers, the volume fraction of particulate fillers and the adhesion between the particulate fillers and epoxy resin matrix [69]. Crack propagation in the composite can take place by trans-particle fracture, by interfacial failure or by failure of the matrix. The trans-particle fracture can take place if the particles are weaker compared to the interface. If the particulate fillers are strong enough, then the crack propagates around the particle [70]. One of the mechanisms for explaining the increase in toughness is crack pinning mechanism. This mechanism assumes that the rigid particulate fillers act as obstacles for crack propagation in epoxy matrix and force the cracks to bow. The increase in fracture energy is given bywhere,

 $\gamma_{\text{composite}}$  = fracture energy of the composite,

 $\gamma_{\text{resin}} = \text{fracture energy of resin},$ 

2c= interparticle distance, and

 $T = 2r/3(\gamma_{resin})$ , where 2r is the particle diameter.

Another mechanism to explain increase in the toughness of particulate filled composites is by decohesion of the particles from the matrix in front of the crack causing blunting of crack tip [70]. Fracture toughness values of composites varies with the particle size. Detailed discussion of the effect of particle size on the fracture toughness of particulate reinforced epoxy resin matrix composites are available literature [71].

## **1.19** Weight fraction to volume fraction conversion of particulate filler addition

It is convenient to use weight fraction of particulate filler addition for manufacturing the composites, but most of the composite properties are correlated with the volume fractions of the particulate fillers. Also most of the mathematical models about composite properties are based on the volume fractions of the particulate fillers. The relation for converting the weight fraction to volume fractions of the phases is as follows [72]: -

 $V_{\alpha} = [W_{\alpha} / \rho_{\alpha}]/[W_{\alpha} / \rho_{\alpha} + W_{\beta} / \rho_{\beta}]$ , and

 $W_{\alpha} = [V_{\alpha}\rho_{\alpha}] / [V_{\alpha}\rho_{\alpha} + V_{\beta}\rho_{\beta}],$ 

where,

 $V_{\alpha}$  = volume fraction of  $\alpha$ ,  $W_{\alpha}$  = weight fraction of  $\alpha$ ,  $\rho_{\alpha}$  = density of  $\alpha$ ,  $V_{\beta}$  = volume fraction of  $\beta$ ,  $W_{\beta}$  = weight fraction of  $\beta$ , and  $\rho_{\beta}$  = density of  $\beta$  [72].

# **1.20** Mathematical models to predict CTE of particulate reinforced composites

Characterization of particulate reinforced composites is complex. For fiber reinforced composites, slab model is used most often to predict the properties of the composites. Slab model is used to analyze the behavior of aligned, long fiber reinforced composites based on the reasoning that the composite can be treated as if it were composed of parallel slabs of two constituent bonded together with relative thickness in proportion to the volume fractions of matrix and fiber. In the particulate reinforced composites, since changes occur from point to point, it is not possible to apply the slab model for predicting the composite behavior. Several other mathematic models are developed to predict the CTE of the composites. These models allow the design of composite with particular CTE by selecting the CTE of the particulate fillers and the volume fraction of particulate fillers. These models make various assumptions about shape and size of the particles to simplify the treatment. They predict the CTE of the composites based on the elastic behavior of the constituents involved. Hence these predictions may not be valid at very high temperatures when the amount of internal

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stresses becomes very high, and the matrix may undergo creep or plastic flow, in turn altering the dimensions of the composite [73].

The most basic model to predict CTE of the composites is called rule of mixture. Rule of mixtures is the first order approximation for calculating CTE of the composites [74]. In a well-annealed composite, the rule of mixture is applicable unless the particulate fillers are strongly adhered to the matrix [4]. For a two-phase system, rule of mixture for predicting CTE of composites is described as-

$$\alpha_{\text{composite}} = \alpha_{\text{matrix}} V_{\text{matrix}} + \alpha_{\text{filler}} V_{\text{filler}},$$

where,

 $\alpha_{\text{composite}} = \text{CTE of the composite,}$ 

 $\alpha_{\text{matrix}} = \text{CTE of the matrix,}$ 

 $V_{\text{matrix}}$  = volume fraction of the matrix,

 $\alpha_{\text{filler}} = \text{CTE}$  of the particulate fillers, and

 $V_{\text{filler}}$  = volume fraction of the particulate fillers.

Most of the experiments show, that the CTE of composites do not simply follow the rule of mixtures. Stresses developed in the composites, variations in processing parameters and variations in the degree of adhesion produced between the particulate fillers and epoxy matrix are some of the reasons due to which most of the composites do not follow rule of mixtures. Hence various other models for predicting the CTE of the particulate reinforced composites are developed and are discussed in literature [27,36,75]. The two commonly used mathematical models, namely Turner's model and Kerner's model, were selected for comparing experimental CTE values of composites in this study and are discussed here.

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## **1.20.1 Turner's model**

The oldest mathematical model to predict the CTE of the composites is Turner's equation [42]. This is more like a lower bound for the CTE values of the particulate filled composites. Turner's model is based on the fact that the CTE of the composites will depend on the relative compressibilities of the matrix and particulate fillers, CTE of the particulate fillers and proportions of the two phases in the composite.

Assumptions made in deriving Turner's equation -

- 1. The sum of the internal forces in composite can be equated to zero because the internal stresses of the system are such that stresses are not sufficient enough to disrupt the composite.
- 2. Each component in the composite is constrained to change dimensions with temperature changes at the same rate as the aggregate and the shear deformation is negligible.
- 3. The composite is homogeneous. No cracks develop in the composites. All the microstresses are hydrostatic in nature.

Turner's equation is as follows-

$$\alpha_{composite} = \frac{\frac{\alpha_1 P_1 K_1}{d_1} + \frac{\alpha_2 P_2 K_2}{d_2}}{\frac{P_1 K_1}{d_1} + \frac{P_2 K_2}{d_2}}$$

,

where,

- $\alpha_1$  = linear CTE of phase 1 in composite,
- $\alpha_2$  = linear CTE. Of phase 2 in composite,
- $P_1$  = fraction or percent by weight of phase 1,

 $P_2$  = fraction or percent by weight of phase 2,

 $d_1$  = density of phase 1,

 $d_2$  = density of phase 2,

 $K_1 =$  bulk modulus of phase 1, and

 $K_2 =$  bulk modulus of phase 2.

According to above equation of Turner's model, CTE of the composite is related to the volume fractions of the phases, if the constituent phases of the composite have same bulk modulii. This equation had been applied to various metallic systems.

If the constituent phases have nearly equal values of Poisson's ratios, the bulk modulii are proportional to the corresponding Young's modulii. Also in many cases the bulk modulii of the constituents of composite are not available. Hence substituting Young's modulii in place of bulk modulii, above equation is transformed into a simplified form written as follows -

$$\alpha_{composite} = \frac{\frac{\alpha_1 P_1 E_1}{d_1} + \frac{\alpha_2 P_2 E_2}{d_2}}{\frac{P_1 E_1}{d_2} + \frac{P_2 E_2}{d_2}}$$

,

where,

 $E_1$  = Young's modulus of phase 1, and

 $E_2$  = Young's modulus of phase 2.

Rest of the terms, are same as explained in previous equation of Turner's model. Simplified equation of Turner's model is successfully applied to composites containing aluminum oxide in polystyrene matrix. It is also applied to composite containing glass fibers in phenol formaldehyde matrix.

In the case of polymer matrix composites, the size and shape of the particulate fillers have an effect on the resultant CTE of the composites. Above equations do not account for the effect of particle size and shape. Hence above equations can be further modified by substituting an empirically determined constant C in place of K/d for each material. The constant C is not the ratio of K/d, but is proportional to K/d. The proportionality factor is also dependent on the shape and size of the particles and the distribution of the material in the matrix. It is also assumed that the constant C for each specific filler and each plastic material is independent of the other components of a composite if the ingredients are evenly distributed. The details of this modified equation are patented and are not available in literature [42].

#### **1.20.2 Kerner's model**

Another mathematical model for predicting CTE of particulate reinforced composites, which is commonly used and shows good agreement with the experimental results, is Kerner's model [76]. Kerner's model takes into account the effect of shear stresses at interfaces. The assumptions made in applying the Kerner's equation to thermosets are as follows [18] –:

- 1. Composite is macroscopically isotropic and homogeneous
- 2. Particles are suspended in and bonded to matrix.
- 3. Particles are distributed spatially at random and they are spherical.
- 4. The thermosets are stable during the measurement.

5. The thermosets are fully cured and no posturing occurs, no transitions occur, no enthalpy or volume relaxations occur and no weight changes occur during CTE measurement.

6. The thermosets are below glass transition temperature during measurements.

Kerner's equation that is applied to particulate reinforced, thermoset matrix composites, is as follows -:

$$\gamma_{\text{composite}} = \gamma_{\text{matrix}} V_{\text{matrix}} + \gamma_{\text{filler}} V_{\text{filler}} - (\gamma_{\text{matrix}} - \gamma_{\text{filler}}) V_{\text{matrix}} V_{\text{filler}} \theta$$

where,

$$\theta = \frac{(1/K_{matrix}) - (1/K_{filler})}{(V_{matrix} / K_{matrix}) + (V_{filler} / K_{filler}) + (3/4G_{matrix})} ,$$

where,

 $K_{matrix}$  = bulk modulus of the matrix,

 $K_{\text{filler}}$  = bulk modulus of the particulate filler,

 $V_{matrix}$  = volume fraction of the matrix,

 $V_{\text{filler}}$  = volume fraction of the particulate filler,

 $G_{matrix}$  = shear modulus of the matrix,

 $\gamma_{\text{matrix}}$  = volumetric CTE of the matrix , and

 $\gamma_{\text{filler}}$  = volumetric CTE of the matrix.

## **1.21** Aim of this study

Following were the objectives of this study -:

- 1. To study the effect of low and negative CTE particulate fillers such as Beta quartz, Cordierite and BS-50 on reducing the CTE of epoxy resin matrices.
- 2. To develop isotropic low CTE composites, that have wide range of applications, especially in electronic industry. Application of the above-mentioned particulate fillers in epoxy resin matrix to reduce its CTE is not documented in the published literature.
- 3. To evaluate the role of surface treatments of particulate fillers with silane coupling agents on the dispersion of the above ceramic particulate fillers in the epoxy resin matrices and to study their influence on the CTE of the resultant composites.
- 4. To conduct density measurements, microhardness testing and microstructure studies to evaluate the quality of processing, and to analyze distribution and adhesion of the particulate fillers with the epoxy resin matrix.
- 5. To compare the experimentally observed values of CTE of the composites with those predicted by theoretical models.

# 2. EXPERIMENTAL PROCEDURE

## 2.1 **Properties of materials used in this study**

## 2.1.1 Epoxy resins

The composites used in this study were prepared by using three types of epoxy resins. The epoxy resins with brand names EPON Resin 8280, EPON Resin 8281 and EPON Resin 9405 were obtained from Resolution Performance Products, formerly known as the Resins and Versatics Business of Shell Group of Companies. The properties of these epoxy resins are listed in Table 7. The epoxy monomer for all these epoxy resins is DGEBA (Diglycidyl ether of bispenol A). The structure of DGEBA is in given Figure 4.

## 2.1.2 Curing agents

For curing of EPON Resin 8280 and EPON Resin 8281, curing agent EPI-CURE 3223 was selected. For curing of EPON Resin 9405, curing agent Ancamine 9470 was selected as a curing agent based on manufacturer's recommendations. Both curing agents were also obtained from Resolution Performance Products. The properties of these curing agents are listed in Table 8. Ancamine 9470 contains 80% Diethyltoluenediamine and 20% proprietary diluent. Ancamine 9470 is commonly used as curing agent for manufacturing composite laminates. EPI-CURE 3223 is commonly known as DETA or diethyl triamine and has chemical formula  $H_2N- (CH_2)_2 - NH - (CH_2)_2 - NH_2$ . DETA is a general purpose-curing agent useful for making small castings, rigid laminates, medium strength adhesives and baking-type solution castings [77]. Most commonly used

EPON Resin 9405	<ul> <li>Modified EPON Resin 828 with</li> <li>reactive comonomer</li> <li>and low viscosity at room</li> </ul>	Bisphenol A- Epichlorohydrin based epoxy resin (92.2%), Styrene (7.4%), Proprietary catalyst (0.4%)	Common epoxy resin used for composite materials.	Not available	11-15	1.15	195-215	For advanced composite structures using filament winding, resin transfer molding, pultrusion, or prepreg.
EPON Resin 8281	Modified EPON Resin 8280 for silic particulate fillers.	Bisphenol A/Epichlorohydrin based epoxy resin (99.85%).	Better for silica fillers	1.17	110-140	Not available	182-195	Adhesives, electrical encapsulants, molding compounds, tooling compounds.
EPON Resin 8280	Low viscosity di functional epoxy resin.	Bisphenol A/Epichlorohydrin based epoxy resin (99.85%)	Epoxy resin used for electronic applications. Good antisettling resistance, less foaming tendency	1.168	110-150	Not available	185-195	Electrical encapsulating adhesives, high solids coatings, tooling, floorings, construction
Property	Epoxy resin type	Chemical composition	Reason for selection	Specific gravity	Viscosity (Poise)	Density (g/cc)	Epoxide equivalent weight	Typical applications

Table 7. Properties of epoxy resins used as matrix in this study [source - product literature].



Figure 4. Structure of DGEBA

Note: In these prepolymers, 'n' can be as high as 25.

Property	EPI-CURE 3223 (used for curing EPON Resin 8280 and EPON Resin 8281)	Ancamine 9470 (used for curing EPON Resin 9405)
Formula	Diethylenetriamine [DETA](100 %)	Diethyltoluenediamine (80%), proprietary diluent (20%)
Specific gravity	0.95	Not available
Density (g/cc)	Not available	1.03
Viscosity (Poise)	10 x 10 <sup>-2</sup>	1.2 x 10 <sup>-2</sup> -1.7x 10 <sup>-2</sup>
Formula molecular Weight	103	Not available
Stoichiometric ratio (phr)	11	28

**Table 8.** Properties of curing agents used in this study [source – product literature].

stoichiometric ratio of DETA is 11phr i.e. parts by weight of amine curing agent per 100 parts resin. Sometimes, stoichiometric ratio of curing agent is reduced so as to reduce curing exotherm and permit castings of larger masses. Lowering the quantity of curing agent also reduces the deflection temperature of the epoxy resin. Deflection temperature or heat distortion temperature is the temperature range over which the polymer begins to soften and get deformed under the influence of load. During curing of DGEBA epoxy resins, with amine curing agents, reactivity is very high, resulting in quick liberation of heat and high exotherms [78]. The stoichiometric ratio of curing agents to epoxy resins is calculated as explained below [55].

phr of curing agent = AHEW x 100/ EEW,

where,

phr = parts by weight of curing agent per hundred parts resin,

 $AHEW = \frac{Molecular \ weight \ of \ the \ amine \ in \ the \ curing \ agent}{number \ of \ active \ amine \ hydrogen \ sin \ the \ curing \ agent}$ 

AHEW = amine hydrogen equivalent weight, and

EEW = epoxide equivalent weight of the resin.

EEW is defined as the weight of resin in grams, which contains one-gram equivalent of epoxy. EPI-CURE 3223 is used for curing EPON Resin 8280. In this case, the quantity of EPI-CURE 3223 is calculated as follows.

EPI-CURE 3223 (i.e. DETA) has AHEW = 103/5 = 20.6, and

EEW of EPON Resin 8280 = 185,

Hence, stoichiometric ratio of EPI-CURE 3223 required for curing of EPON Resin 8280 is equal to 11 phr, (20.6 x 100/185).

## 2.1.3 Cured epoxy resins

Various properties of DGEBA cured with DETA adapted from literature are listed in Table 9. Table 10 lists important properties of cured epoxy resins that were used in this study. These properties were measured for cured epoxy resins without any particulate filler reinforcements.

## **2.1.4 Particulate fillers**

Three particulate fillers that were used in this study are Beta quartz, Cordierite and BS-50. Beta Quartz has a negative CTE of -1 ppm/° C, which makes it very useful in applications requiring thermal stability. Cordierite ceramics are important due to their low CTE and good thermal shock resistance. CTE of Cordierite can vary with the processing method and usually in the range of 0.6 to 2.3 ppm /°C. BS-50 belongs to the class of NZP ceramics i.e. alkali and alkaline earth zirconium phosphates. NZP ceramics have very low and tailorable CTE and high thermal shock resistance. NZP materials have lesser tendency towards microcracking, high melting temperature (in excess of 1800°C), excellent high temperature stability and strength retention, and low thermal conductivity. Typical composition of BS-50 is indicated in Table 11.Typical properties of the particulate fillers used in this study are listed in Table 12. Figures 5 through Figure 7 show size and shape of these particulate fillers under SEM (scanning electron microscope). Cordierite particles do not agglomerate. Beta quartz particles seem to form card-pack type agglomerates. BS-50 particles form card-house type agglomerates.

Property	Typical value of property
Shrinkage	4.5%
Elastic modulus (GPa)	3.5
Hardness (Rockwell L)	118
Fracture toughness (MPa√m)	0.6
Density (g/cc)	1.11-1.40
Dielectric constant (100 Hz- 10 MHz)	3.8
Thermal conductivity (W/mK)	0.19
Poisson's ratio	0.34

 Table 9. Typical properties of epoxy resin DGEBA cured with DETA [79].

 Table 10. Measured values of properties of cured epoxy resins, used in this study.

Property	EPON Resin 8280 cured with EPI-CURE 3223	EPON Resin 8281 cured with EPI-CURE 3223	EPON Resin 9407 cured with Ancamine 9470
CTE (ppm/°C)	82.3	81	72.5
Density (g/cc)	1.188	1.19	1.165
Modulus (GPa)	3.8	3.8	3.6
Hardness (GPa)	0.244	0.244	0.232
Estimated bulk modulus (GPa)	3.96	3.96	3.75
Estimated shear modulus GPa	1.418	1.418	1.343
Glass transition temperature [Tg] (°C)	~125	~125	~175

No particulate reinforcements.

Theoretical weight %					
Ba	Zr	Р	Si	0	
18.1	32.1	13.6	2.5	33.7	

 Table 11. Typical composition of BS-50 [80].

Property	Beta quartz	Cordierite	BS-50
Chemical Formula	SiO <sub>2</sub> and small quantities of ZnO- Al <sub>2</sub> O <sub>3</sub>	2MgO.2Al <sub>2</sub> O <sub>3</sub> .5SiO <sub>2</sub> Magnesium alumino silicate	Ba <sub>1.5</sub> Zr <sub>4</sub> P <sub>5</sub> SiO <sub>24</sub> Barium zirconium phosphate
Crystal structure	Hexagonal	Hexagonal	Hexagonal
Density (g/cc)	2.533	2.508	3.50 (provided by manufacturer)
CTE (ppm/°C)	-1 Negative along c axis, constant along a axis.	2.3 Positive along a axis and negative along c-axis.	-2.5 Positive along c axis and negative along a-axis.
Modulus of elasticity (GPa)	100.6	117.3	74.5
Bulk modulus (GPa)	56.5	129	44.34
Shear modulus (GPa)	41.8	54	30.53
Hardness (GPa)	~8.2	~8.2	~ 4.5
Poisson's ratio	0.203	0.31	0.22
Dielectric Constant	~4.0 [100 Hz- 1 MHz]	~5 [1KHz -10KHz]	~7 [1000KHz - 3GHz]
Thermal conductivity (W/mK)	~1.4	~3.222	~1

 Table 12. Properties of the particulate fillers used in this study [81,82,83,84,85,97].



Figure 5. Micrograph of Beta quartz particles



Figure 6. Micrograph of Cordierite particles.



Figure 7. Micrograph of BS-50 particles. These particles tend to agglomerate.

#### 2.1.5 Silane coupling agents

In this study, silane coupling agents with trade names Z6020 and Z6040 procured from Dow Corning Corporation were used. The properties of silane coupling agents used in this study are tabulated in Table 13.

## 2.2 Specimen preparation

Following specimen preparation method was followed to prepare the composite specimens.

Glass tubes of 10mm diameter and 70mm length were coated with release agent Miller-Stephenson MS.122N/CO2 few hours in advance. The epoxy resin was preheated at 50/60° C for 2 hours to lower its viscosity and to melt the crystals formed during storage of epoxy resin. The epoxy resin was subjected to vacuum for 15 minutes to get rid of air bubbles. Globules present in the particulate filler sample were broken and the powder samples were sieved, whenever required. Drying the particulate fillers helps to remove water or moisture in particulate fillers. Heating under vacuum is the most satisfactory procedure. Adding hot particulate fillers in epoxy resin also aids the dispersion of the particles [55]. Hence the particulate fillers were dried at 150 ° C for 4 hours. The powders were added into the resin in required proportion as soon as they were taken out of the oven. The particulate fillers were mixed in hot epoxy resins by applying shear force using wooden spatula to achieve complete wetting of the particulate fillers and to distribute particulate fillers intimately without agglomeration [54]. The overall process of dispersion of particulate fillers can be divided into various steps -

1. Wetting of the particle surfaces by the epoxy resin,

Property Z 6020 Z 6040	N- (β-amino ethyl-γ-aminopropyltrimethoxysilane)         3-glycidoxypropyltrin           Formula         (CH <sub>3</sub> O) <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> NH2         (CH <sub>3</sub> O) <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH <sub>2</sub> OH           and silane dimmers         and silane dimmers         (CH <sub>3</sub> O) <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	Inorganic reactivity Methoxy Methoxy	Organic reactivity Amino Epoxy	Typical applications     Fiberglass reinforced thermosets     Glass fibers, minera       Typical applications     reinforced plastics and acting	Specific gravity 1.03 1.07
Z6040	ycidoxypropyltrimethoxysilane 3SiCH2CH2CH2OCH2CHCH2 0	Methoxy	Epoxy	ass fibers, mineral surfaces in ed plastics and adhesion promoter in coatings	1.07

**Table 13.** Properties of silane coupling agents used in the study [source – product literature].

#### 2. Rupture of the aggregates, and

3. Separation and distribution of the aggregates so that they do not agglomerate again.

After the particulate fillers were distributed uniformly, curing agent was added in the required stoichiometric ratio or as per the recommendation of the manufacturer. After uniform mixing of curing agent, the mixture was poured in glass tubes, treated with release agent. Centrifuging was conducted for 2 minutes at 2000 rpm to remove air bubbles. The composites were cured as per the recommendations of the manufacturer. Curing cycle for EPON Resin 8280 and 8281 cured with EPI-CURE 3223 was overnight at room temperature followed by cure at 100° C for 2 hours. The cured composites were taken out of glass tubes and they were available in the form of rods. The surfaces of the rods were polished to remove any surface discontinuities and residues of release agent. Then the composite rods were machined and polished to required sizes and shapes. Composite samples were annealed for 2 hours at a temperature 20°C above their glass transition temperature, and cooled to room temperature in air to reduce the residual stresses. Figure 8 shows the flow-chart of preparation of composite specimens.

For some batches of composites, air release agent A500 from BYK Chemie was added to the mixture of particulate fillers and epoxy resins. Air release agents are additives with low surface tension and demonstrate insolubility in the medium to be defoamed. They have positive entering coefficient and positive spreading coefficient. Air release agent draws the neighboring foam bubbles within the resin together, enlarges size of bubble and increases the rising speed of the foam bubbles from mixture of particulate fillers and resin to the surface.

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Dry Beta quartz particles at 150° C for 4 hours.

Heat EPON Resin 8280 up to 50° C and maintain for 2 hours. Vacuum treat the epoxy resin. Coat glass tubes with release agent.

Add dried Beta quartz particles in the epoxy resin and mix well.

Add 11phr of EPI-CURE 3223.

Cure composite at room temperature overnight, followed by 2 hours at 100° C.

Cut composite rod to required sizes. Machine and polish them. Anneal 20° C above the glass transition temperature for 2 hours. Conduct testing.

Figure 8. Flow-chart for preparing composite reinforced with Beta quartz. Matrix - EPON Resin 8280 cured with EPI-CURE 3223.

#### **2.2.1 Effect of process variables**

It was noted during preparation of composite specimens that the process variations influence the properties of the composites significantly. The most important of them are,

- 1. The temperature to which epoxy resin is preheated prior to addition of particulate fillers,
- 2. Temperature and mechanism used for drying the particulate fillers, and
- 3. The mixing efficiency of particulate fillers in epoxy resin matrix.

These factors were maintained constant during the preparation of composite specimens.

## **2.2.2** Treating particulate fillers with silane coupling agents

Particulate fillers were treated with silane coupling agents Z6020 and Z6040 prior to addition into the epoxy resin matrix. Z6020 has diamino group for organic reactivity and trimethoxysilyl group for inorganic reactivity. Z6040 has epoxy group for organic reactivity and trimethoxysilyl group for inorganic reactivity. Epoxy reactivity allows Z6040 to undergo ring-opening reactions with acids, amines, alcohols and epoxides. Trimethoxysilyl group is subjected to hydrolysis in water or water/alcohol solutions. The initial product of hydrolysis is silanetriol. Silanetriols undergo condensation with the hydroxyl groups at the surface of particulate fillers. After condensation, the remaining silanol groups are capable of hydrogen bonding or condensing with adjacent silanol groups. Thus the coupling agent is bonded to the particulate surface by the combination of hydrogen bonding and covalent bonding. Figure 9 shows important steps in treatments

Step I. Hydrolysis reaction

R Si (OCH<sub>3</sub>)<sub>3</sub> +  $3H_2O \rightarrow R$  Si (OH)<sub>3</sub> +  $3CH_3OH$ 

Silane coupling Silanetriol agent Z6040

Step II. Reaction of silanetriol with hydroxyl group present on the mineral surface.



Step III. The particulate filler reacts with epoxy resin matrix.

Figure 9. Important steps in treating particulate fillers with silane coupling agent Z6040.

of particulate fillers with silane coupling agents. Silane coupling agents may form monolayer or multilayers on the surface of particulate fillers.

The process of treating particulate fillers with silane coupling agents was recommended by the manufacturer of the coupling agents and it was carried out in the following manner -:

For prehydrolysis, 40 parts of silane coupling agent, 55 parts of solvent, (methanol, in this case), and 5 parts of water were used. Solubility of silane coupling agents was enhanced by alcohol. The pH of water was adjusted to 4.5-5.5pH to produce rapid prehydrolysis and relatively stable silanols. Methanol was mixed with pH adjusted water. After stirring the solution, to form a vortex, silane coupling agent was slowly added into the solution. It was allowed to complete hydrolysis overnight. 2.5 ml of this solution was added to 50ml methanol, to achieve 2% concentration of silane coupling agent. 30 gm particulate fillers were added to this solution and mixed well for 2 minutes. Time of two hours was allowed for the condensation reaction to complete with surface of particulate fillers. The excess methanol was filtered using filter paper, and the particulate fillers were used immediately to prepare composite specimens.

## 2.3 Testing of composites

## **2.3.1** Measurements of density of composites

Density measurement of composites was conducted to ensure proper dispersion of the particulate fillers and to detect the level of porosity. For density measurements, guidelines in ASTM Standard D792-98 were followed. This standard describes

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displacement method for measuring density and specific gravity of plastics. Samples of various sizes were cut from the composites specimens. These composite pieces were weighed in air, then immersed in water using a thin wire and weighed in water. The specific gravity of composite pieces was determined using following formula:

Specific gravity of composite at  $23/23^{\circ}$  C= a/ (a+w-b),

where,

a = apparent mass of specimen in air without wire,

b = apparent mass of specimen completely immersed in water and the wire partially immersed in water,

w= apparent mass of wire partially immersed in water, and

23/23°C is the ASTM standard designation to indicate that mass of specimen in air is measured at 23°C and weight in water is also measured when water is at 23° C.

Density of composite in kg/m<sup>3</sup> at 23° C = specific gravity at 23/23°C x 997.6.

## **2.3.2** Measurements of CTE of composites using TMA

CTE measurement was the most important step in characterizing composites in this project. TMA (thermo mechanical analyzer) was used for measuring CTE of materials i.e. linear changes in specimen dimensions with rise in temperature under nonoscillatory load were measured. TMA can also be used to determine the glass transition temperature of epoxy resins. For CTE measurement, ASTM standard E831-93 which describes standard test method of measuring linear thermal expansion of solid materials by thermomechanical analysis, was followed. CTE measurement was conducted using TMA 2940 of Thermal Analysis Instruments. TMA was calibrated at the beginning of CTE measurement experiments as well as after testing10 specimens. TMA has a provision for calibrating -

1. temperatures,

2. variations in the length the probe due to heating, and

3. loads, if load is to be applied during CTE measurement of certain materials.

Aluminum specimen of known CTE provided by the TMA manufacturer was used for the calibration purposes. TMA has inbuilt softwares to monitor calibration process.

The specimens used for CTE measurements in this study were cylindrical rods up to 12 mm length and 4-7 mm diameter. The specimens were machined and polished to tolerance +/-  $25\mu$ m. The specimens were annealed at a temperature approximately 20 °C above the glass transition temperatures of the epoxy resins just prior to CTE measurements. The CTE measurement process was carried out as explained below.

The specimen was placed inside the furnace of TMA on a flat support. Furnace of TMA is a small unit with electric heating coils, which heats up the specimen at a uniform, predefined heating rate. A thermocouple is fitted close to the specimen support. For low temperature CTE measurement experiments, liquid nitrogen circulation accessories are available in TMA. A probe rests on the top of the specimen, which measures the changes in the specimen dimension by means of a transducer. The probe as well as the base support for the specimen are generally made from materials like quartz or silica, which have low and precisely known CTE. Various configurations of the probe can be used with or without application of compressive loads. Flat tipped standard probe without load is used to measure the CTE of the composites. In this study, specimen were heated at the

rate of 4° C/min, which is neither too fast nor too slow. The range used for measuring the CTE of composites was from 40°C to 100° C, which was well below their glass transition temperatures of the resins. The specimen deforms on heating. The changes in specimen dimension are converted into the upward movement of the probe resting on the top of the specimen. A plot of the changes in length of specimen versus the temperature change, in similar unit systems, is generated. The slope of this plot gives the value of linear CTE for the composites [86]. The CTE was measured for three different specimens of each type of composite and an average value was obtained.

## **2.3.3** Effect of testing parameters on CTE of composites

It was noted during testing and analysis of particulate reinforced composites that certain testing parameters affect the measurement of CTE of composites within a few ppm/°C. These parameters are-

1. Heating rate during CTE measurement experiment,

2. The temperature range over, which CTE measurements are carried out,

3. Surface finish of the specimen, and

4. Length of the specimen.

Hence all these parameters were maintained constant for all the CTE measurement experiments to avoid any discrepancies.

## 2.3.4 Microhardness measurements of composites

Microhardness testing of materials is a very common tool for micromechanical characterization of materials. It is described in details in literature along with its use for the characterization of epoxies. Microhardness testing applied to fiber reinforced epoxy resin matrix and polyamide matrix composites, is also discussed in literature [87,88,89].

Microhardness testing was conducted to study the reinforcing effect of various particulate fillers on the epoxy matrices. Microhardness testing was conducted using microhardness tester of Leco Corporation M-400-G1. These measurements were carried out at room temperature using a diamond square pyramid indenter with included angle of 136° at the tip. A load of 50gm was applied for 15 seconds from the time of contact till the load was removed. The length of the diagonals formed by the pyramid indenter was measured immediately after removing the load. Microhardness of the composites was calculated using the equation,

 $H = (2\sin 68^\circ) (P/D^2) = 1.854^* (P/D^2),$ 

where,

P = the applied load, and

D = the average diagonal of the indentation.

The average microhardness values were calculated from 15 indents on representative samples. Numerous readings at different locations of the sample surface ensured that the hardness value obtained is true representation of the average value of the composite hardness. Figure 10 shows the micrograph of composite, which has indentation marks from microhardness testing. This Figure shows that the microhardness values are true representation of composite hardness because the indentation diagonals cover the area composed of particles as well as matrix.



Figure 10. Micrograph showing the diagonals of the indenter of a microhardness tester. Diagonals are spread along the epoxy resin matrix as well as particulate fillers, hence the microhardness value represents hardness of composite.

## **2.3.5** Microscopy for observing composite microstructures

Microstructure analysis is a qualitative technique for observing the dispersion of particulate fillers in the polymer matrices as well as for studying the nature of interfaces in composites. Low magnification examination is useful to obtain the features such as porosities, overall distribution of particles etc. SEM was used for studying fracture surface because the specimens can be prepared easily and thick samples can be used without any modification. In addition, SEM gives high resolution and high depth of field. SEM model Hitachi S-2500C was used for studying microstructures. The composites in the current study were electrically non-conductive. In composites reinforced with high volumes of particulate fillers, the particle pullout is a problem during observation of the composite surface. For these two reasons, surfaces of composites were gold coated. The evaporation or sputtering technique of gold coating involves the erosion of gold atoms by energized gas plasma of argon via the production of glow discharge. This produces a continuous gold coating layer on the specimen surface [90]. All samples were coated with ~14nm thick gold coating layer. Sides of the specimens were covered with multiple layers of carbon tape to achieve better electrical conductivity. An accelerating voltage of 13 KeV and the working distance of 13mm were used to have optimum resolution.

## **2.3.6** Fracture study of composites

Fracture of the composites was studied to evaluate the adhesion between phases and the effect of silane coupling agents on the adhesion of particulate fillers with matrices. Fracture toughness testing was carried as per the guidelines in ASTM standard E1304-97. This standard describes guidelines for measuring plane strain fracture toughness of metallic materials. Fracture testing was conducted at room temperature. Short rod type of specimens with chevron notch, were prepared. The specimen geometry is discussed along with drawings in the abovementioned standard. All specimen dimensions were measured carefully prior to testing. During fracture testing of composites, a pair of grips was fitted inside the specimen in a groove machined on the specimen and an outwardly directed force was applied causing a crack to initiate at the tip of chevron notch. A plot of load versus mouth opening displacement of the specimen was plotted. Epoxy resins showed crack jump behavior. Crack jump behavior means that the crack advanced through rapid jumps rather than smooth crack growth. Each crack jump was accompanied by a decrease in applied loading force. Between the jumps, as the loading continued, the crack was nearly stationary until the load was increased to a level, which caused the next jump. For each type of composite, three specimens were tested. Fracture toughness of composites was calculated using following formula -:

$$K_{ICSR} = A_r C_c (F - 1/2 \Delta F_H) / B^{3/2}$$

where,

K<sub>ICSR</sub>= plane-strain critical stress intensity factor,

 $A_r$ = compliance constant,

 $C_c$ = correction factor,

F= load,

 $\Delta F_{H}$ = hysterisis in load which was ignored for all specimens, and

B = diameter of the specimen.

The fractured specimens were preserved in a desiccator, subsequently gold coated and studied using SEM.

# 3. RESULTS AND DISCUSSION

## **3.1 CTE of composites**

The CTE of various epoxy resin matrix composites with three types of particulate filler reinforcements prepared in this study, are tabulated in Tables 14, through 20. As can be observed from these tables, the CTE of the composites decrease as the volume fraction of the particulate fillers in the epoxy resin matrices increases. The ordering of intrinsic CTE values of the particulate fillers used in this study is BS-50 (-2.5 ppm/°C) < Beta quartz (-1 ppm/°C) < Cordierite (2.3 ppm/°C). As the results indicate, equal volume fractions of these particulate fillers do not decrease the CTE of composites in the same order in which the CTE of particulate fillers varies. Comparison of Tables 15 and 18 shows that Cordierite is more effective as reinforcement than Beta quartz in EPON Resin 8281, which means that processing parameters play significant roles in influencing CTE of the composites, apart from the properties of matrix. The variables that affect the CTE of the composites are discussed along with the various experimental results.

## **3.1.1 Effect of volume fraction of particulate fillers**

Figures 11 and 12 show that as the volume fraction of particulate fillers in the epoxy resin matrices increases, the inter-particle distances decrease. Hence increased volume fraction of particulate fillers, influences the CTE of composites significantly.

Table 14. CTE of composites reinforced with Beta quartz particles.

Volume % of Beta quartz in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	82.3	0
12.29	69.1	16.04
13.52	67.7	17.74
19.32	62.8	23.69

Matrix-EPON Resin 8280 cured with EPI-CURE 3223.

 Table 15. CTE of composites reinforced with Beta quartz particles.

Volume % of Beta quartz in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	81	0
13.17	67	17.28
15.77	59	27.16

Matrix-EPON Resin 8281 cured with EPI-CURE 3223.

**Table 16.** CTE of composites reinforced with Beta quartz particles.

Matrix-EPON Resin 9405 cured with Ancamine 9470.

Volume % of Beta quartz in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	72.5	0
2.36	71.75	1.03
4.86	71.6	1.20
12.08	65.33	9.90
25.76	46.96	35.23
Table 17. CTE of composites reinforced with Cordierite particles.

Volume % of Cordierite in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	82.3	0
13.64	67.4	18.10
23.25	58.6	28.80

Matrix-EPON Resin 8280 cured with EPI-CURE 3223.

 Table 18. CTE of composites reinforced with Cordierite particles.

Volume % of Cordierite in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	81	0
13.16	61.4	24.20
13.54	59.64	26.37

Matrix-EPON Resin 8281 cured with EPI-CURE 3223.

**Table 19.** CTE of composites reinforced with BS-50 particles. Matrix- EPON Resin8280 cured with EPI-CURE 3223.

Volume % of BS-50 in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	82.3	0
10.16	72.6	11.79
17.22	67.6	17.86

**Table 20.** CTE of composites reinforced with BS-50 particles. Matrix- EPON Resin8281 cured with EPI-CURE 3223.

Volume % of BS-50 in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	81	0
6.9	70.8	11.35
10.47	67.4	16.80



Figure 11. Micrograph of composite reinforced with 2.35 volume % of Beta quartz. Matrix- EPON Resin 9405 cured with Ancamine 9470. Interparticle distances are high due to low volume fraction of the particulate fillers.



Figure 12. Micrograph of composite reinforced with 25.76 volume % of Beta quartz particles. Matrix- EPON Resin 9405 cured with Ancamine 9470. Interparticle distances are very less due to high volume fraction of the particulate filler.

### **3.1.2 Effect of properties of matrix**

It can be seen from Table 16 that, at low volume fractions of Beta quartz, in a matrix of EPON Resin 9405 cured with Ancamine 9470, the composites have CTE values same as the CTE of the matrix. Particulate fillers do not exhibit any effect on the properties of the composites. Hence the matrix simply expands according to its original value of CTE without any resistance from particulate fillers. At higher volumes of Beta quartz, the trend changes. It can also be observed from table 16 that, even 12.1 volume % reinforcement with Beta quartz in matrix EPON Resin 9405 reduces CTE of the composite only by 9.9%. This CTE reduction is less compared to the reduction achieved by Beta quartz in two other epoxy resin matrices. Poor performance of EPON Resin 9405 with Beta quartz reinforcements in terms of CTE reduction, must be attributed to its low viscosity. EPON Resin 9405 has one tenth of the viscosity of EPON Resin 8280 and EPON Resin 8281, as listed in Table7. EPON Resin 9405 is modified EPON Resin 8280. It contains more than 7% styrene added to reduce its viscosity. Hence particulate fillers can be mixed easily with least shear force in EPON Resin 9405 than in the other two epoxy resins. The polished surfaces of composites made using EPON Resin 9405 do not show any air bubbles. But due to low viscosity of resin, Beta quartz particulates show significant settling in EPON Resin 9405. This results in higher CTE of composites than expected.

Due to dilution, EPON Resin 9405 has density 1.165 g/cc after curing, as against 1.19 g/cc in EPON Resin 8280 and 8281 cured with EPI-CURE 3223. The lower density of EPON Resin 9503 may be causing poorer packing of the Beta quartz particles in the matrix compared to that in other two epoxy resins (EPON Resin 8280 and EPON Resin

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8281). Hence particulate fillers share no load on application of stress at low concentration of the particulate fillers. Since the particulate fillers do not form direct bonds with the epoxy resins, the density of the epoxy resin is may play an important role. As the particulate filler volume increases, as can be seen in Figure 12, decreased inter-particle distances lead to increased packing of particles, increased interaction between the particles, increased interaction with the epoxy resin matrix and reduced settling. Higher packing density results into improved stress transfer across the interface of particulate fillers and the epoxy resin matrices. Hence at higher volume fractions, the CTE of composites is strongly affected by CTE of Beta quartz particles. EPON Resin 9405 cured with Ancamine 9470 has much higher glass transition temperature (~175°C) compared to cured EPON Resin 8280 and EPON Resin 8281 (~125°C), this may be causing more thermal stresses in composites with EPON Resin 9405 as matrix, than in the other two epoxy resins.

## **3.1.3 Effect of size and shape of particulate fillers**

Table 21 lists observations about shape, size and behavior of particulate fillers in epoxy resins and the effects of particulates on the composite processing. Figures 13, through 18 show the micrographs of various composites with 3 types of particulate fillers. It can be observed that shape and surface area of Beta quartz particles allow the best mechanical interlocking with the epoxy resin matrices. BS-50 particles have the poorest mechanical adhesion with the epoxy resin matrices due to small particle size and least surface area. Figures 17 and 18 also show that the BS-50 particles form aggregates.

Property	Beta quartz	Cordierite	BS-50
Particle shape	Elongated, polygonal, high aspect ratio	Polygonal, low aspect ratio,	Round
Particle size (µm)	~0.3 to 10	~0.5 to 5	~ 0.3-0.6
Nature of particles	card-pack type agglomerates	no agglomerates	card-house type agglomerates
Surface of particles	Rough	Partly smooth, partly rough	Smooth
Observed effect on viscosity of epoxy resins	Least increase in viscosity.	Intermediate increase in viscosity amongst 3 fillers.	Increases viscosity significantly.
Observed wettability	High wettablity, mixes easily in all epoxy resins.	High wettability, mixes well after applying shear force.	Poor wettabilty, takes high shear force to break the agglomerates.

 Table 21. Properties and behavior of particulate fillers used in this study.



Figure 13. Micrograph of composite reinforced with 13.54 volume % of Beta quartz. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.



Figure 14. Micrograph of composite reinforced with 13.16 volume % of Beta quartz. Matrix- EPON Resin 8281 cured with EPI-CURE 3223. It shows the mechanical interlocking of the particles with the matrix.



Figure 15. Micrograph of composite reinforced with 13.64 volume % of Cordierite. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.



Figure 16. Micrograph of composite reinforced with 13.54 volume % of Cordierite. Matrix- EPON Resin 8281 cured with EPI-CURE 3223.



Figure 17. Micrograph of composite reinforced with 10.16 volume % of BS-50. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.





Figure 18. Micrograph of composite reinforced with 10.47 volume % of BS-50. Matrix- EPON Resin 8281 cured with EPI-CURE 3223.

Since the three particulate fillers belonged to quite different ranges of the particle sizes and had different shapes, this project does not compare the relative influences of particle sizes on CTE of composites. It appears that particle size to achieve optimum CTE values for composites should exist for each type of particulate filler and each resin system. This argument is supported by the fact that, for many materials including composites, product of CTE and elastic modulus is a constant. Alter et al. have shown that elastic modulus of particulate reinforced composites is inversely proportional to the particle size [91]. These two results suggest that selecting particular range of particle size will have the optimal influence on the CTE of the composites. It is not clear on the basis of this study whether the crystal structure and composition of particulate fillers may have any influence on the CTE of the composites.

## **3.1.4 Effect of wettability of particulate fillers**

It was observed during preparation of composites that Beta quartz particles show the best wettability with all three epoxy resins. Cordierite has intermediate wettability and BS-50 has poorest wettability amongst three particulate fillers. BS-50 particles form small agglomerates, which do not mix well with the epoxy resins and also require higher shear force and longer times for thorough mixing with the epoxy resins. Good wettability results in good mechanical interlocking of particulates with the matrices, which in turn makes it possible to achieve higher elastic modulus for the composites compared to the elastic modulus achieved in composites containing particles with lower wettability. Hence it can be predicted that, higher elastic modulus will be achieved with Beta quartz reinforcements than with two other particulate fillers.

# 3.1.5 Effect of aggregates of particulate fillers

Table 22 enlists the nature of distribution of various particulate fillers in different epoxy resins. Figures 19, through 21 show the distribution of particulate fillers in EPON Resin 8280 and pores in composites. Figure 22 shows that BS-50 particles tend to form significant number of aggregates, even though the particulates were dried before adding them to the epoxy resin. Aggregates may be formed due to van der Waals forces and charges present on the surface of particulates. Cordierite particulates don't aggregate, but do exhibit limited aggregation when added to the epoxy resins. Since, Beta quartz particles flow freely both prior to and after adding to the epoxy resins and do not form aggregates. Hence it can be seen from Figures 19 through 21, that the most uniform distribution in the epoxy resins is achieved with Beta quartz particles. The aggregates increase the hardness of composite locally, since aggregates are harder compared to individual particles.

# **3.1.6 Effect of settling of particulate fillers**

Settling of particulate fillers in epoxy resin matrix was not observed during the course of this study. This was confirmed by measurement of CTE of specimens obtained from different regions of a composite rod. No difference in CTE values with respect to the locations in the specimen was observed. All the composites studied had good antisettling resistance.



Figure 19. Micrograph of fracture surface of composite reinforced with 13.52 volume % of Beta quartz. Matrix- EPON Resin 8280 cured with EPI-CURE 3223. Few pores are present as indicated.



Figure 20. Micrograph of fracture surface of composite reinforced with 13.54 volume % of Cordierite in EPON Resin 8280 cured with EPI-CURE 3223. Few pores and an agglomerate are present indicated.



Figure 21. Micrograph of fracture surface of composite reinforced with 10.16 volume % of BS-50. Matrix- EPON Resin 8280 cured with EPI-CURE 3223. Composite contains aggregates of particles as well as pores.



Figure 22. Micrograph of composite reinforced with 10.16 volume % of BS-50. Matrix- EPON Resin 8280 cured with EPI-CURE 3223. Fracture surface shows the aggregates as indicated.

#### **3.1.7** Density measurement of the composites

Plots provided in Figures 23 through 29, show density variations due to particulate additions in various composites. It is clear from these figures that the density of composites increases as the volume fraction of the particulate fillers increases, due to higher density of particulate fillers as compared to the density of epoxy resins. Density of all the composites was found to be close to the expected value or slightly lower, which indicated the lack of significant pores and absence of generation of water as bye-product. Comparison of Figures 28 and 29 indicates that, BS-50 reinforced in EPON Resin 8280 matrix composites show wider range of density values. Such an observation points out that distribution of BS-50 particles in EPON Resin 8280 is less uniform as compared to that in EPON Resin 8281.

## **3.1.8 Pores in composites**

Figures 19 through 21, show the pores in composites reinforced with the three particulate fillers in epoxy resin matrices. BS-50 and Cordierite reinforced composites show larger pores formed near the aggregates. Composites reinforced with Beta quartz show no specific locations of pores within the specimen. Hardness measured in regions adjacent to the pores is low. It was about one-half the value of hardness measured on specimen surface in a region devoid of pores. Though pores do not affect the CTE of composites directly, they could be used as a measure to indicate the quality of the composite processing and the uniformity of distribution of the particulate fillers [73].



Figure 23. Density variation in composites reinforced with Beta quartz. Matrix- EPON Resin 9405 cured with Ancamine 9470



Note: Error bars not visible for certain volume % of Beta quartz in the scale presented. Figure 24. Density variation in composites reinforced with Beta quartz. Matrix- EPON Resin 8280 cured with EPI-CURE 3223







Figure 26. Density variation in composites reinforced with Codierite. Matrix- EPON Resin 8280 cured with EPI-CURE 3223











Figure 29. Density variation in composites reinforced with BS-50. Matrix- EPON Resin 8281 cured with EPI-CURE 3223

# **3.1.9 Microhardness measurements of composites**

Plots provided in Figures 30 through 39, indicate the variations in microhardness values of composites as well as the average microhardness values for various composites. Addition of particulate fillers increased the microhardness of the composites. Most of the composites showed uniform scatter in microhardness values. It is important to note that the composites reinforced with 10.16 volume % BS-50 in EPON Resin 8280 (Figure 38), showed wide scatter in hardness values indicating non-uniform distribution of particles and presence of porosity.

Increase in hardness of composites with BS-50 reinforcements is less than that with Beta quartz and Cordierite. This is so because, BS-50 has inherently low hardness (~4.5 GPa) compared to hardness of Cordierite and Beta quartz. (~ 8.2 GPa). BS-50 particles are small in size and are rounded in shape with poor wettability with epoxy resins. Hence BS-50 particles have poor adhesion with the epoxy resin matrices and are less effective in reinforcing them. BS-50 particles also form aggregates in the epoxy resins. Since these particles tend to aggregate, they do not distribute uniformly in the epoxy resins. The non-uniform distribution of BS-50 is clear from Figure 21, as well as from the wide scatter in microhardness values and density values in composites reinforced with BS-50. It is interesting to note that the trend in improvement in hardness is similar to the trend in decrease of the CTE values.

Generally higher the volume fraction of particulate fillers, lesser the inter-particle distances and higher the hardness of the composites. Hardness value improvement indirectly reflects the improvement in mechanical properties of epoxy resins resulting from the presence of particulate fillers. Measured hardness values can indicate presence

96











Figure 32. Hardness variation in composites due to particulate filler reinforcements.



Figure 33. Hardness variation in composites reinforced with Beta quartz.

100



Figure 34. Hardness variation in composites reinforced with Beta quartz. Matrix - EPON Resin 8281 cured with EPI-CURE 3223.







Figure 36. Hardness variation in composites reinforced with Cordierite. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.


Figure 37. Hardness variation in composites reinforced with Cordierite. Matrix- EPON Resin 8281cured with EPI-CURE 3223.

104



Figure 38. Hardness variation in composites reinforced with BS-50. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.

105



Figure 39. Hardness variation in composites reinforced with BS-50.

of aggregates and pores because aggregates have excess hardness values while regions containing pores will have lower hardness values.

The composites can exhibit much higher hardness values when the adhesion between the particulate fillers and the epoxy resin matrices is perfect. In this study, the particulates do not have perfect adhesion with the matrix. Hence on application of indentation load to the composite, the load is not fully transferred across the interface and it is not shared between the particulate fillers and the matrix. In addition, the distribution of the particles is uneven in some composites.

#### **3.1.10** Effect of additives in epoxy resins

It can be seen from Tables 14 and 15 that, 19.3 volume % reinforcement of Beta quartz in EPON Resin 8280 reduced the CTE of the composite just by 23.7% while 15.8 volume % reinforcement of Beta quartz in EPON Resin 8281 reduced CTE of the composites by 27.16%. Tables 17 and 18 show that, 13.6 volume % reinforcement of Cordierite in EPON Resin 8280 reduced its CTE by 18.1%, while 13.2 volume % reinforcement of Cordierite in EPON Resin 8281 achieved 24.2% reduction in CTE of composite. Tables 19 and 20 show that, 10 volume % of BS-50 reinforcement in EPON Resin 8280 achieved 11.8% reduction in composite CTE, while 10.5 volume % reinforcement of BS-50 in EPON Resin 8281 achieved 16.8% reduction in CTE. Thus it is observed that the performance of all three particulate fillers in EPON Resin 8280. Similar trend can be noted from microhardness values of composites as well.

EPON Resin 8281, has a very small quantity of additive ( $\sim 0.15\%$ , the details of additive are proprietary) different from EPON Resin 8280. This additive is specially used to avoid settling of silica particles. The specified viscosity values of resins EPON Resin 8280 and EPON Resin 8281 are almost same. The densities of both epoxy resins after curing are almost same. Therefore, improved reduction in CTE of composites with EPON Resin 8281 as matrix, has to be attributed to some other factors. The additive in EPON Resin 8281 probably causes uniform distribution of particulate fillers in it. It also provides better interlocking of particulates fillers with the epoxy resin matrix. BS-50 particulates show more uniform distribution in EPON Resin 8281 than in EPON Resin 8280, which is clear from comparison of Figures 17 and 18, and also from the density variation and hardness variations as discussed previously. The particles of Beta quartz show better interlocking with EPON Resin 8281 than with EPON Resin 8280 as can be seen from Figure 13 and 14. It is also likely that the additive in EPON Resin 8281, has some stress relieving effects, which make particulate fillers more effective in reducing the CTE. Thus, it can be concluded, that the small quantity of additive in EPON Resin 8281 resin seems to aid in reducing the CTE of the composite.

## **3.1.11** Effect of varying curing agent quantity

Quantity of curing agents may affect the CTE of composites, hence the results of the experiment in which curing agent quantity was varied in composites, are shown in Figure 40. In particulate reinforced composites, curing agent may be adsorbed on the surface of particulates and the effective quantity of curing agent participating in curing process may be reduced. It is also possible that if curing agent is added more than the





stoichiometric ratio, the cross-link density of epoxy reins may increase, resulting into decreased CTE of the composites. Above two effects were evaluated by increasing the quantity of curing agent by 20% than its stoichiometric ratio. The particulate fillers may have hydroxyl group adhered on their surfaces, which may accelerate the curing reaction. Hence rate of curing reaction can be controlled, by reducing the quantity of curing agent. This effect was evaluated by reducing curing agent to 20% less than its stoichiometric ratio. These experiments were carried out for EPON Resin 8280 cured with EPI-CURE 3223 with no particulate fillers and with 12.29 volume % of Beta quartz. As seen from Figure 40, reducing the quantity of curing agents in epoxy resins did not change the CTE of the CTE of composites. This result confirmed that Beta quartz particulate fillers do not accelerate the curing reaction in a way that will affect the CTE of the composites. This leads one to conclude that Beta quartz particles are inert in curing reaction of epoxy resins. Increase in the quantity of curing agent exhibited no effect on the CTE of the composites as well. This result confirmed that curing agent was not consumed by the Beta quartz particulates through adsorption on the surface. The CTE of epoxy resins did not change significantly by reduction or addition of curing agent quantity, which meant that curing of epoxy resins was almost complete by using stoichiometric ratio of the curing agent.

### **3.1.12** Nature of interfaces of composites

Figures 41, through 43 show fracture surfaces of various composites. As observed in these figures, failures occurred at the interfaces of particulate fillers and the epoxy resin matrix for composites with all three particulate fillers. It proved that the interface of



Figure 41. Micrograph of fracture surface of composite reinforced with 13.52 volume % of Beta quartz. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.



Figure 42. Micrograph of fracture surface of composite reinforced with 13.64 volume % of Cordierite. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.



Figure 43. Micrograph of composite reinforced with 10.16 volume % of BS-50. Matrix-EPON Resin 8280 cured with EPI-CURE 3223. Fracture surface of the composite indicates effect of aggregates diverting the cracks.

epoxy resins and particulate fillers is weak due to high stress concentration present at the interfaces. From the measured CTE values of the composites, it can be concluded that the adhesion between the particulate fillers and the epoxy resins is not perfect because CTE reduction achieved is minimal even after adding large volumes of particulate fillers. Perfect adhesion at interfaces would have resulted in trans-particle and matrix failures, and much less CTE of composites. Composites reinforced with Beta quartz and Cordierite particles show crack propagation around the particle-matrix interfaces. In composites reinforced with BS-50, with presence of aggregates, stress and strain concentration occurs at the interface of the aggregates and matrix. Thus aggregate interfaces are weak spots for mechanical failures. Figure 43 shows that crack got diverted around the interface of aggregates and matrix, indicating presence of high stress concentration at the interface of aggregates and the matrix. Aggregate-matrix interfaces can also be weak spots for initiating mechanical or chemical failures.

It can be seen from Figures 13 through 18, and Figures 41 through 43, that the main mechanism for adhesion between the particulate fillers and the epoxy resins seems to be mechanical interlocking of the particulate fillers with the matrices. Hence particles of Beta quartz and Cordierite with rougher surfaces and high wettability seem to have better adhesion with epoxy resins as compared to those with BS-50 particulate fillers.

The main reasons for weak interface are, lack of chemical bonding between the matrix and the particulate fillers and high difference in CTE values of the phases in composites. The particulate fillers were treated with silane coupling agents to create chemical bonds with the epoxy resin matrices and the results are discussed in following sections.

#### **3.2** Effect of treating particulate fillers with silane coupling agents

CTE of various composites made with particulate fillers treated with silane coupling agents are given in Tables 23 through 28. CTE values provided are based on CTE of three specimens of each type of composite. Treatment of particulate fillers with silane coupling agents has multifold effects.

#### **3.2.1** Effects of silane coupling agent treatment on CTE of composites

Figures 44 through 46 show that, treating particulate fillers with silane coupling agents did not result in any decrease of the CTE of composites. CTE of some of the composites have actually increased slightly after treating particulate fillers with silane coupling agents, instead of resulting into any reduction.

## **3.2.2** Effects of silane coupling agent treatment of particulate fillers on dispersion in epoxy resins and density of composites

Table 29 lists effects of treating particulate fillers with silane coupling agents on the dispersion of particulate fillers in epoxy resin matrices. It can be observed in Figures 47 through 52, that treatment of particulate fillers with silane coupling agents increased the wettability of the surfaces and reduced aggregation. Treating particulate fillers with silane coupling agents has also reduced the pores in some composites such as Beta quartz treated with Z6020 and BS-50 treated with Z6040. Hence the density of composites containing particulate fillers treated with silane coupling agents is closer to the expected density of the composites. Table 30 lists effects of treating particulate fillers with silane coupling agents on the density of the composites. Figures 53 through 55 show the effect

**Table 23.** Effect of treating Beta quartz particles with silane coupling agent, on the CTEof composites. Matrix-EPON Resin 8280 cured with EPI-CURE 3223.

Volume % of Beta quartz in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	82.3	0
13.52	67.7	17.74
13.52, treated with Z6020	71.27	13.40
13.52, treated with Z6040	70.53	14.30

**Table 24.** Effect of treating Beta quartz particles with silane coupling agent, on the CTE

Volume % of Beta quartz in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	81	0
13.17	67	17.28
13.20, treated with Z6020	68.25	15.74

of composites. Matrix-EPON Resin 8281 cured with EPI-CURE 3223.

Table 25. Effect of treating Cordierite particles with silane coupling agent, on the CTE

of composites. Matrix-EPON Resin 8280 cured with EPI-CURE 3223.

Volume % of Cordierite in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	82.3	0
13.64	67.4	18.10
13.64 treated with Z6020	70.33	14.54
13.64 treated with Z6040	71.93	12.60

**Table 26.** Effect of treating Cordierite particles with silane coupling agent, on the CTEof composites. Matrix-EPON Resin 8281 cured with EPI-CURE 3223.

Volume % of Cordierite in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	81	0
13.16	61.4	24.20
12.35 treated with Z6020	68.9	14.93

**Table 27.** Effect of treating BS-50 particles with silane coupling agent, on the CTE of<br/>composites. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.

Volume % of BS-50 in composites	CTE of composites (ppm/°C)	% Reduction in CTE	
0	82.3	0	
10.16	72.6	11.79	
10.16 treated with Z6020	75.7	8.02	
10.16, treated with Z6040	75.1	8.75	

**Table 28.** Effect of treating BS-50 particles with silane coupling agent, on the CTE of<br/>composites. Matrix- EPON Resin 8281 cured with EPI-CURE 3223.

Volume % of BS-50 in composites	CTE of composites (ppm/°C)	% Reduction in CTE
0	81	0
6.9	70.8	11.35
10.47	67.4	16.80
9.22 treated with Z6020	70.8	12.60











Matrix	Silane coupling agent used for treating particulate filllers	Beta quartz	Cordierite	BS-50
EPON Resin		Some pores,	Pores and a	Pores, and
8280 cured		no	few	large
with EPI-		aggregates.	aggregates.	aggregates.
CURE 3223.		(Figure 19).	(Figure 20).	(Figure 21).
EPON Resin 8280 cured with EPI- CURE 3223.	Z6020	No pores, no aggregates. (Figure 47).	Pores and a few aggregates. (Figure 49)	Pores, aggregates. (Figure 51).
EPON Resin 8280 cured with EPI- CURE 3223.	Z6040	Some pores, no aggregates. (Figure 48).	No aggregates, few pores. (Figure 50).	Pores, but smaller aggregates. (Figure 52).

 Table 29. Observations about the effects of silane coupling agent treatment on dispersion of particulate fillers in epoxy resin matrices.



Figure 47. Micrograph of fracture surface of composite reinforced with 13.52 volume % of Beta quartz treated with Z6020. Matrix- EPON Resin 8280 cured with EPI-CURE 3223. No porosities and no aggregates are observed.



Figure 48. Micrograph of fracture surface of composite reinforced with 13.52 volume % of Beta quartz particles treated with Z6040. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.Few pores are present as indicated.



Figure 49. Micrograph of fracture surface of composite reinforced with 13.64 volume % of Cordierite treated with Z6020. Matrix: EPON Resin 8280 cured with EPI-CURE 3223. Few pores are present as indicated.



Figure 50. Micrograph of fracture surface of composite reinforced with 13.64 volume % of Cordierite with Z6040. Few pores are present as indicated. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.



Figure 51. Micrograph of fracture surface of composite reinforced with 10.16 volume % of BS-50 treated with Z6020. Matrix- EPON Resin 8280 cured with EPI-CURE 3223. Fracture surface shows pores and aggregates as indicated.



Figure 52. Micrograph of fracture surface of composite reinforced with 10.16 volume % of BS-50 treated with Z6040. Matrix- EPON Resin 8280 cured with EPI-CURE 3223. Composite shows fewer pores and smaller aggregates compared to the composite containing untreated BS-50 particles, shown in Figure 22.

**Table 30.** Observations about the effects of silane coupling agents on the density of thecomposites. Matrix-EPON Resin 8280 cured with EPI-CURE 3223.

Particulate filler	No coupling agent treatment to particulate fillers	Particulate fillers treated with 2% Z6020	Particulate fillers treated with 2% Z6040
1 3.5 volume % Beta quartz	Measured density less than expected.	Measured density close to expected.	Measured density more than expected, may be due to experimental error.
13.6 volume % Cordierite	Measured density less than expected.	Measured density very close to expected.	Measured density very close to expected.
10.2 volume % BS-50	Measured density less than expected.	Measured density close to expected.	Measured density very close to expected.



Figure 53. Effect of silane coupling agents on density of composites reinforced with Beta quartz. Matrix- EPON Resin 8280 cured with EPI-CURE 3223



Figure 54. Effect o silane coupling agents on density of composites reinforced with Cordierite. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.



Figure 55. Effect of silane coupling agents on density of composites reinforced with BS-50. Matrix- EPON 8280 cured with EPI-CURE 3223.

of particulate fillers on the density of composites. The reason for increased wettability of particulate fillers after treating with silane coupling agents may be that, the water layer on the surface of particulate fillers is replaced by organofunctional silanes after treating with silane coupling agent. Comparison of Figures 47 and 48, shows that treating Beta quartz with Z6020 results in better dispersion in epoxy resins. Comparison of Figures 49 through 52 shows that treating Cordierite and BS-50 particles with Z6040, results in better dispersion of these fillers in epoxy resin.

# **3.2.3** Effect of silane coupling agent treatment on fracture behavior of composites

Figures 56 through 58 show the effects of treating particulate fillers with silane coupling agents on fracture toughness of composites. Fracture toughness of composites did not increase substantially after treating the particulate fillers with silane coupling agents as would be expected. In some composites, the fracture toughness has rather decreased. Figures 59 through 61 show the representative microstructures of fracture surfaces of composites treated with silane coupling agent Z6020. Even after treating the particulate fillers with silane coupling agents, fracture in all the composites took place at interfaces of particulate fillers with silane coupling agents did not create strong enough bonds at interfaces to result in trans-particle failures.

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Figure 56. Variation in fracture toughness of matrix and composites reinforced with 13.5 volume % of Beta



Composite type



Composite type



Figure 59. Micrograph of fracture surface of composite reinforced with 13.52 volume % of Beta quartz treated with Z6020. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.



Figure 60. Micrograph of fracture surface of composite reinforced with 13.6 volume % of Cordierite particles treated with Z6020. Matrix - EPON Resin 8280 cured with EPI-CURE 3223.



Figure 61. Micrograph of fracture surface of composite reinforced with 10.16 volume % of BS-50 treated with Z6020. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.
## **3.2.4** Reasons for ineffectiveness of silane coupling agent treatment of particulate fillers on CTE and fracture toughness of the composites

There are various possible reasons for the ineffectiveness of silane coupling agent treatment of particulate fillers on CTE and fracture toughness of composites. They are as follows-

1. The concentration of silane coupling agents may have been too high while treating the particulate fillers. This can result in the excessive adsorption of silane coupling agents instead of monolayer, on the surface of particulate fillers [92]. The excess adsorbed layer of silane coupling agent supposedly diffuses into the epoxy resin. It can create blend of epoxy resin and silane coupling agent, near the surface of particulate fillers, and this blend presumably has inferior properties than the epoxy resin matrix. Graf et al. have shown that the decrease in strength of composites is directly proportional to the increase in concentration of silane coupling agent for fibrous fillers [92]. If the particulates fillers with known particle size distribution or known surface area are used, it is possible to calculate exact quantity of the silane coupling agent required to form monolayer on the surface of particulate fillers. An alternate approach is to carry out several trials with varying quantities of silane coupling agents.

2. The silane coupling agent treatment of particulate fillers is conducted in two steps, hydrolysis of the mixture of silane coupling agent, water and methanol, to generate silanetriols followed by condensation of silanetriols with the hydroxyl group present on the surface of the particulate fillers. One may hypothesize, since the hydrolysis time was 12 hours, it is likely that the condensation reaction has completed, even before adding the particulate fillers into the solution of silane coupling agent, water and methanol.

3. The differences in the CTE of the matrices and the particulate fillers are very high. The glass transition temperatures of the epoxy resins used in this study are high. Hence high thermal stresses are generated at the interface. One may hypothesize that, the strength of bond formed due to silane coupling agents is not enough to withstand the thermal stresses developed at the interfaces.

4. Exact nature of functional groups present on the surface of particulate fillers is not known. It is difficult to predict the chemical products formed and pH changes that occurred on treating the particulate fillers with silane coupling agents.

One more possibility is that the silane coupling agent treatment is successful, but there are no effects on the CTE of composites. The elastic modulus and CTE of composites are related. It has been observed that silane coupling agent treatment of particulate fillers does not alter the elastic modulus of composites, although it reduces the degradation of elastic modulus when exposed to water [93]. Such anomalies may explain why there is no noticeable change in CTE of composites even if the silane coupling agents might have formed bond between the epoxy resins and the particulate fillers.

#### **3.2.5** Effect of excess silane coupling agents on CTE of epoxy resins

There is a possibility that excess silane coupling agent present on the particulate fillers may have blended with epoxy resin to form complex phase, which decreased the CTE of the epoxy resins and so effectively decreased the CTE of composites. The effect of blending excess coupling agent with the epoxy resin on the CTE of epoxy resin was tested. 1% of Z6020 and 1% of Z6040 silane coupling agents by weight were deliberately added in the epoxy resins, containing no particulate fillers and the CTE of the cured

epoxy resins were measured. Figure 62 shows the effect of deliberate addition of excess silane coupling agents to epoxy resin matrices. It is clear that the excess silane coupling agents added to the epoxy resin matrices did not significantly affect the CTE of epoxy resin matrices used in this study.

## **3.2.6 Recommendations for improving the silane coupling agent treatment of particulate fillers**

Recommendations to improve performance of silane coupling agents:

- 1. Z6020 and Z6040 silane coupling agents were selected based on the manufacturer's recommendation, because these coupling agents were found to be successful with silica fillers by other users, in past. It is likely that other coupling agents with different functionalities may prove to be more compatible with the particulate fillers used in this study.
- 2. Various ways to improve the treatments of particulate fillers with silane coupling agents can be explored. One way is not to prehydrolyze the silane coupling agents and reduce the silane coupling agent addition to 0.5 % from 2%. Another way is to prehydrolyze silane coupling agents, but reduce the amount of silane coupling agent added.
- 3. Condensation reaction might complete in the aqueous solution itself if hydrolysis time is prolonged. Hence it is important to treat particulate fillers with hydrolyzed solution of silane coupling agents when the solution is most reactive.



Figure 62. CTE variations cured epoxy resins by addition of excess

# **3.3** Comparison of experimental CTE values of composites with those predicted by mathematical models

Figures 63 through 69 compare experimental values of CTE of composites containing three types of particulate fillers in three epoxy resin matrices, with those predicted by various mathematical models. These observations are compiled in Table 31. For EPON Resin 9405, at low volume fractions of Beta quartz reinforcement, CTE of composites is same as the CTE of matrix. CTE of these composites vary as per Kerner's model at high volume fractions of Beta quartz. CTE of the composites reinforced with Beta quartz and Cordierite particulate fillers in EPON Resin 8280, vary according to the CTE values predicted by Kerner's model. CTE of composites reinforced with BS-50 particulate fillers in EPON Resin 8280, vary according to the rule of mixtures. CTE of the composites with EPON Resin 8281 as matrix are lower than those predicted by Kerner's model for all particulate fillers. Equation of Turner's model and simplified equation of Turner's model yield same value of CTE for the composites when the particulate fillers and the matrix have nearly same values for the Poisson's ratio. This happens in the case of Cordierite, which has Poisson's ratio of 0.34, a value same as that for epoxy resin used.

Tummala et al. have shown that CTE of particulate reinforced composites closely agree with the CTE values predicted by Kerner's model. [18,94]. The mathematical models made assumptions regarding the size, shape and surface area, distribution of the particulate fillers to facilitate the computations. But presence of aggregates i.e. non-homogeneous composites, and insufficient adhesion between the particulate fillers and matrices, result in higher CTE values of composites than those

Measured CTE values - Rule of mixtures – - - – Turner's model-simplified — — Kerner's model Turner's model • values predicted by various mathematical models. Reinforcement- Beta quartz. Matrix- EPON Resin 9405 cured with Ancamine 9470. Volume % of Beta quartz in composites . I ę. C<sup>o</sup>/mqq setisoqmoo to ETC

Figure 63. Comparison of experimentally observed CTE values of composites with CTE





Figure 65. Comparison of experimentally observed CTE values of composites with CTE







Figure 67. Comparison of experimentally observed CTE values of composites with CTE

Figure 68. Comparison of experimentally observed CTE values of composites with CTE values predicted by various mathematical models. Reinforcement- BS-50. Matrix- EPON Resin 8280 cured with EPI-CURE 3223.





Volume % BS-50 in composites

Figure 69. Comparison of experimentally observed CTE values of composites with CTE

**Table 31.** Observations about best fit mathematical models for predicting CTE of the composites, developed by reinforcing three types of epoxy resins with three types of particulate fillers, in this study.

Matrix	Beta quartz	Cordierite	<b>BS-50</b>	
EPON Resin 8280 cured with EPI- CURE 3223	Kerner's model	Kerner's model.	Rule of mixtures.	
EPON Resin 8281 cured with EPI- CURE 3223	Lower experimental CTE Values,than predicted by Kerner's model	Lower experimental CTE values, than predicted by Kerner's model	Lower experimental CTE values, than predicted by Kerner's model.	
EPON Resin 9405 cured with Ancamine 9470	At low volume fractions of Beta quartz, CTE of composites is same as the CTE of matrix. CTE varies as per Kerner's model at high volume fractions of Beta quartz.			

predicted by mathematical models. Kerner's model serves as upper bound and Turner's model serves as the lower bound for predicting the CTE of the particulate reinforced composites. It is desirable to achieve CTE values as low as predicted by Turner's model in particulate reinforced epoxy resin matrix composites. There have been findings that Turner's equation may be used to predict CTE of various composite systems, and predicted values in the systems cited closely matched with the experimental values of CTE of the composites [42,75]. CTE of metal-metal composites, ceramic-metal composites and polymer composites reinforced with fibers, show good agreement with Turner's equation. All these cases are discussed on an individual basis. The differences between the properties of phases of composites used in this study, and those of composites for which Turner's model has been successfully applied, are pointed out. According to Turner's model -

$$\alpha_{composite} = \frac{\frac{\alpha_1 P_1 K_1}{d_1} + \frac{\alpha_2 P_2 K_2}{d_2}}{\frac{P_1 K_1}{d_1} + \frac{P_2 K_2}{d_2}}$$

where,

 $\alpha_1$  = linear CTE of phase 1 in composite,

 $\alpha_2$  = linear CTE. Of phase 2 in composite,

 $P_1$  = percent by weight of phase 1,

 $P_2$  = percent by weight of phase 2,

 $d_1$  = density of phase 1,

 $d_2$  = density of phase 2,

 $K_1$  = bulk modulus of phase 1, and

 $K_2 =$  bulk modulus of phase 2.

As indicated in introduction, bulk modulii can be replaced by elastic modulii provided the Poisson's ratio of both the phases present in the composite are comparable. The bulk modulus is the ratio of the hydrostatic pressure to the dilation, that it produces, and it is indicated by the letter K. Density is the mass per unit volume, and it is indicated by letter 'd'. K/d or E/d ratio for the particulate filler and that of the matrix are the significant terms in Turner's equation for predicting the CTE of composite. The elastic constants and K/d ratios and E/d ratios for various particulate fillers and composite matrices discussed here, are listed in Table 32.

Turner's equation was used to predict CTE of the composites prepared by mixing magnesia and tungsten in various volumetric proportions [95]. Turner's equation was also used to predict CTE of composites prepared by mixing silica glass and aluminum in various volumetric proportions. These composites were prepared by pressing the mixed powders followed by sintering. The important points to be noted in these composites are, the difference in the CTE values of the two phases i.e. magnesia and tungsten as well as that between aluminum and silica are much smaller compared to the differences in the CTE of epoxy resin and particulate fillers, used in this study. Smaller CTE difference between phases of composites results in lesser thermal stresses in composites. Additionally, in magnesia-tungsten composites as well as aluminum-silica composites, there is high probability that bonding will be generated between the phases. The K/d ratio of magnesia and aluminum are high. It can be verified from Turner's equation that the least CTE of the composites will be obtained when both phases have equal bulk modulii. When the difference between CTE of the two phases of composites is small, CTE of the composite is low even with when difference between K/d ratio of the phases is high.

Material	Density 'd' (g/cc)	Elastic modulus 'E' (GPa)	Poisson' s ratio	Bulk modulus 'K' (GPa)	E/d	K/d	CTE (ppm/° C)
Beta quartz	2.533	100.6	0.203	56.5	39.7	22.3	-1
Cordierite	2.508	117.3	0.31	129	46.8	51.4	2.3
BS-50	3.50	74.5	0.22	~29.76	21.3	8.5	-2.5
Epoxy resin	1.19	3.8	0.34	3.96	3.2	3.33	81
MgO	3.58	207	0.169	154.1	57.8	43.0	13
w	19.3	355.35	0.287	308.1	18.4	15.9	4
Silica glass	2.2	69.7	0.17	35.20	31.7	16.0	0
Aluminum	2.702	70.8	0.348	77.5	26.2	28.7	23.6
Antimony	6.7	80.3	0.207	45.6	12	6.81	11
Lead	11.34	28.1	0.39	42.7	2.5	3.8	29
Beryllium	1.8	307.7	0.117	133.9	171	74.4	12
Phenol formal- dehyde	1.3	6.9	-	-	5.3		59
Glass fibers	2.58	72.5	-	-	28.1		7.44
Poly- styrene	1.05	2.75	0.33	2.69	2.6	2.56	70
Aluminum Oxide	3.99	380	0.23	252	95.2	63.2	8.7
Calcium carbonate	2.65	179	~0.19	~96.24	67.6	36.3	10
Anhydrous kaolin	2.58	138	~0.28	~104.55	53.5	40.5	8

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Table 32. Elastic constants for various fillers and matrix materials [3,43,47,82,97].

Material	Density 'd' (g/cc)	Elastic modulus 'E' (GPa)	Poisson' s ratio	Bulk modulus 'K' (GPa)	E/d	K/d	CTE (ppm/° C)
Talc	2.8	138	-	-	49.3	-	8
Mica	2.79	100.8	0.227	61.5	61.5	22.6	8
Wolla- stonite	2.9	207	-	-	71.4	-	6.5
Lithium Aluminum Silicate	2.3	68	~0.28	51.52	29.6	22.4	0.5

Table 32. (cont'd)

Note- Units for K/d and E/d are GPa/g/cc

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Turner's equation uses weight percent of the phases. Lower the value of density of any of the phases in composite, higher will be the volume of that phase in composite and CTE of the composite will be lower as can be seen from the Turner's equation.

If one of the phases of composite has high K value, then the stresses will be transferred easily across the interface of two phases, resulting into minimal CTE for the composite. Suppose particulates with high bulk modulus are surrounded by matrix with low bulk modulus and bonded to the matrix. During thermal expansion of such a composite, particulates with higher bulk modulus will restrain the matrix from expansion, resulting in low CTE composite.

Turner's equation was successfully applied to many alloy systems. In the original paper it is applied to lead-antimony and beryllium-aluminum composites [42]. It can be noted that the difference in the CTE of antimony and lead is very small. Difference in CTE of beryllium and aluminum is also small. The CTE values of these composites, as predicted by rule of mixture, by Turner's model and by Kerner's model, are very close. In beryllium-aluminum system, K/d is high for beryllium. Most importantly, since both lead-antimony and beryllium-aluminum form solid solutions, the bonding between the phases present will be very strong.

The observed values of CTE of glass fibers reinforced phenol formaldehyde matrix composites were very close to those predicted by Turner's equation [42]. In this composite, the difference in CTE of the phenol formaldehyde and fibers is high, but still not as high as the difference in the CTE of ceramic particulate fillers and epoxy resins used in present study. The lower difference in CTE of phases of composite, generate smaller thermal stresses. The E/d ratio of the fibers is higher compared to the phenol

formaldehyde, this will allow transfer of stresses across the interface of fibers and phenol formaldehyde. Density of phenol formaldehyde is 1.3g/cc, which is higher, as compared to density of epoxy resins (1.19 g/cc) used in this study. High density of phenol formaldehyde results in better packing of fibers in the matrix. Unlike particulate fillers, the uniform arrangement of continuous fibers constrains the matrix most [96]. This results in significant improvement in the mechanical properties of the composites due to maximum transfer of stresses across the interfaces.

Turner's equation was also used to predict the CTE of composites reinforced with aluminum oxide particles in polystyrene matrix. [42]. The difference between the CTE of these two phases is ~60 ppm/°C, while the difference between the CTE of particulate fillers and epoxy resins used in this study is ~80 ppm/°C. Smaller difference in CTE of the phases in a composite generates smaller thermal stresses. Additionally, aluminum oxide has very high K/d ratio compared to that of Beta quartz, Cordierite and BS-50.

From the ongoing discussion, one can conclude that the most important differences between the phases of composites used in this study and those of the composites for which Turner's equation was successfully applied are-

- 1. Difference in the CTE of the particulate fillers and the epoxy resins used in this study is the highest, compared to the CTE differences in phases of all the composites discussed so far. High CTE differences cause maximum thermal stresses.
- 2. No bonds are formed between the particulate fillers and epoxy resins, used in this study. Particulate fillers are adhered to the epoxy resin matrix mainly through mechanical interlocking.

- 3. The density of the epoxy resins is lower as compared that of phenol formaldehyde.
- 4. The K/d ratio of ceramic particulate fillers is smaller compared to that of aluminum oxide. Mica, Wollastonite which are commercially popular particulate fillers for reducing CTE of polymer matrices, have higher K/d ratio, as compared to ceramic particulate fillers used in this study, as shown in Table 32. Lithium aluminum silicate, is also commonly used for reducing the CTE of the polymer matrix composites. K/d ratio for Lithium aluminum silicate and Beta quartz are very close. K/d ratio of Cordierite is higher than Beta quartz. BS-50 has very small value of K/d ratio compared to Beta quartz, Cordierite and other particulate fillers. During the course of this investigation, it was found that the CTE reduction is least with BS-50 reinforcements as compared to that with other two particulate fillers. One of the factors responsible for poor performance of BS-50 may be its low K/d ratio.

### **3.4 Conclusions**

- Amongst three epoxy resins used in this study, cured EPON Resin 9405 shows the best distribution of particulate fillers with no agglomeration along with minimal porosity. However, the low viscosity monomer, results in lower density of cured epoxy resin and it does not provide the lowest CTE composite.
- 2. EPON Resin 8281, which has uses high viscosity monomer and has high density after curing, gives minimal CTE for composites reinforced with any of the three particulate fillers.
- 3. Amongst three particulate fillers used in this study, Beta quartz particulates show maximum wettability, and least agglomeration with the epoxy resins. BS-50 particulate form maximum aggregates as well as maximum pores in the composite. The CTE reductions achieved with Cordierite and Beta quartz are comparable. BS-50 particles give minimal CTE reduction in composites.
- 4. Treating the particulate fillers Beta quartz, Cordierite and BS-50 with silane coupling agents Z6020 and Z6040, did not reduce CTE of the composites.
- 5. However, treating the Beta quartz particulates with silane coupling agent Z6020, and treating Cordierite and BS-50 particulates with silane coupling agent Z6040 improved the distribution of these particulate fillers in the epoxy resin matrix.

#### **3.5 Recommendations for future work**

- 1. It is observed in this study, that uniform distribution of particulate fillers is essential to achieve maximum possible reduction in CTE values. To achieve this uniform distribution of particulate fillers, mechanical mixing or ultrasonic mixing should be employed in the preparation of the composites.
- 2. Thermal strain at the interfaces of epoxies and particulate fillers is proportional to the difference in CTE of the two phases and to the temperature difference between temperature of stress free state and room temperature. Hence it is important to use epoxy monomer and curing agent combination, which will result in minimum thermal stresses at the interface region. These thermal stresses can cause interfacial debonding and make the reinforcements ineffective. Selecting epoxy resins with low glass transition temperature may also help in reducing thermal stresses.
- 3. The most effective mechanism of adhesion between particulate fillers and the polymer matrices is chemical bonding. If this cannot be achieved, use particulate fillers with rough surfaces can facilitate mechanical interlocking.
- 4. Wettability of particulate fillers plays key role in effective processing of composites. Wettability is difficult to measure. Polymers have lower surface energies compared to ceramic particulate fillers. It has been pointed out, that higher the difference in surface energies of particulate fillers and the polymer, higher will be the wettability. For solid materials, generally, higher the hardness, higher is their surface energy. BS-50 particles had least hardness and also least

wettability. Hence particulate fillers with high hardness values should be selected for making composites.

- 5. Higher the K/d ratio of the particulate filler, lower is the CTE of particulate reinforced polymer matrix composites. Hence is important to select particulate fillers with high K/d values.
- 6. If the concentration of silane coupling agents used for the treatment of particulate fillers is excess then there may be deteriorating effects on the composite properties. If the concentration of silane coupling agents is less, then sufficient bonding cannot be produced at the interfaces of particulates and the epoxy resins. Yamaguchi et al. have demonstrated the use of formula for calculating the exact concentration of silane coupling agents required for the monolayer coverage of particulate fillers [98]. This formula or similar method should be used to calculate exact concentration of silane coupling agents, when the size of particulate fillers is known.
- 7. Low viscosity of epoxy monomer helps in easy distribution of particulates, while high viscosity avoids settling of particulate fillers. Hence it is important to use epoxy monomer of optimum viscosity. The viscosity can be tailored by controlling temperature and by adding diluents.
- 8. Size of particulate fillers plays key role in affecting CTE of composites. Fine particles have significant tendency to agglomerate. But fine particles show least settling tendency. Hence it is important to establish optimum size of particulate fillers for the particular type of epoxy resin.

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- 9. Drying of particulate fillers at high temperatures and use of vacuum for drying can be more effective to reduce absorbed water and it may also reduce agglomeration of particulate fillers.
- 10. Both silane coupling agents used in this study had methoxy group for reacting with particulate fillers. Silane coupling angents with different reactive groups or other type of coupling agents should be checked for their effectiveness.
- 11. Presence of pores can affect the CTE of composites in various ways. If the pores contain air, that air may expand and may result in compressive stresses in matrix. Other possibility, as indicated by Hatta et al., is that presence of small volume percent of pores can cause additional reduction in CTE of composites [99]. The rationale for this is as follows: in particulate reinforced composites, the particles are in tension while the matrix is in compression. Pores have zero stiffness. Hence they help reduce the compressive stresses of the matrix, and the presence of such pores reduces the overall CTE of composites.

The exact effect of pores on CTE of composites needs to be understood. If the effect of pores is found to be detrimental, it is possible to control pressure and temperature of curing process in order to control the amount of porosity. It is also possible to add air release agents in order to reduce the pores in composites.

12. In order to reduce stresses in composites, photosensitive fillers such as cinnamic acid resins and cinnamal ketones can be added up to 1-3%, to epoxy resins and then these epoxies can be exposed to strong ultraviolet rays to relieve internal stresses [45]. This might reduce the CTE of composites further.

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