Fundamentals of Thermal Conductivity in the Epoxy Polymer Network

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Abstract In metals, the heat is carried predominantly by electrons. However, it is observed in polymers that the thermal conductivity is driven by lattice vibrations known as phonons. The thermal conductivity through an epoxy polymer is controlled by the state, structure, and orientation of the polymer chain network. Basic understanding of the thermal conductivity of epoxy resins is explained through Debye's theory and Fourier's law. The theories of correlation between thermal conductivity and thermal diffusivity, explanation of phonon transport in a 2D epoxy network, and electronic contribution of thermal conductivity in undoped polymers lay foundation to the topic of thermal conductivity in epoxy resins. The heat transfer through the epoxy resin is controlled by incorporating high thermal conductivity fillers to form composites, or, by the intrinsic modification of the epoxy nanostructure for improved crystallinity. The thermal degradation of epoxy polymer is proportionally dependant on the thermal conductivity. This chapter covers the basic theories of thermal conductivity, methods to improve thermal conductivity, factors influencing thermal conductivity, and effect of thermal conductivity in the thermal degradation of epoxy resins.

Keywords Epoxy resins · Thermal conductivity · Thermal diffusivity · Phonon transport · Lattice vibration

1 Introduction

Often, materials are designed so that they spread heat very effectively for applications such as heat exchangers and microelectronics. Conversely, thermal insulators are designed for applications such as building insulation materials and space shuttle tiles. In such applications, low or no thermal conductivity is preferred. High temperature generated at the integrated circuits and electron flow regions of electronic devices require high thermal conductivity materials to carry the heat away. Heat generated

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from the integrated circuits, especially those demanding ultra-fast processing requirements, has become a performance decelerator for micro-electronics. Miniaturisation of electronic devices further enhances the heat production due to the increased resistance causing fire hazard. Materials with high thermal conductivity and low electrical conductivity are suitable to carry the heat away from the electronics [1]. It has been proven that proper thermal management of the electronic devices will effectively improve its reliability and service life [2].

Epoxy resins are the commonly used electronic packaging material due to their excellent chemical resistance, mechanical, and fatigue properties [3], where excellent thermal conductivity is indispensable [4, 5]. However, the thermal conductivity coefficient (λ) of epoxy resin is very low at ~ 0.2 W m^{-1} K^{-1} [6] due to the amorphous state of the molecular chain. The heat management applications of thermally conductive epoxy resins are not constrained within the electronic industry. In a recent research, ultra-high thermal conductivity of epoxy composites using multi-dimensional fillers composed of micro- and nano-silver particles further treated with trace amount of MXene increased the thermal conductivity of epoxy resin to 72.7 W m^{-1} K^{-1} [7]. The improved fire retardancy of thermally conductive epoxy resins extends its potential application in building, construction, automotive, and aerospace.

A proper understanding of the theories of thermal conductivity in epoxy matrices, factors affecting thermal conductivity, and technique to improve thermal conductivity, and thermal degradation of epoxy resins is explained in this chapter.

1.1 Thermal Conductivity in Epoxy Resins

Thermal conductivity of polymers depends primarily on its morphology [8, 9]. Polymers exist in crystalline, semi-crystalline, amorphous, solid, melt, and glassy states [10]. Hence, thermal conduction through polymers cannot be expressed in one mechanism. Thermal conductivity is higher in crystalline polymers and lower in amorphous polymers. The thermal conductivity of epoxy resins—for that being an amorphous polymer—is relatively lower than crystalline polymers due to the lack of crystallinity in epoxy matrix. Scattering of the propagation of thermal energy caused by voids, entanglements, chain ends, and impurities reduces thermal conductivity in epoxy polymers [11, 12].

In a perfect crystal, the surface atoms exposed to thermal energy gain vibrational energy and propagate thermal energy through the sample by transferring the vibrational energy to the adjacent atom. The vibration is in the wave form and is called phonon. The enthalpy or energy of that system can be linked to the total amount of thermal motion and interaction on a microscopic level [13]. It is important to understand the significance of thermodynamics of polymers where heat capacity is brought into account. Heat capacity for any polymer is a heat dependant quantity. Heat capacity is defined as the heat required to change its temperature by one degree. For an accurate useful quantity, specific heat capacity at constant pressure (C_P) is defined as the amount of heat required to increase the temperature of a material of

unit mass by 1 K or 1 °C at constant pressure. This is presented by Eq. (1)

$$C_P = \Delta Q / m \Delta T \tag{1}$$

where ΔQ is the heat required in Jules, m is the mass of the sample, and ΔT is the increase in temperature in K or °C. Heat capacity of a polymer is usually measured using differential scanning calorimetry or adiabatic calorimetry [10].

Heat capacity of a solid is largely contributed from atomic and molecular vibrations. This is presented by equation (2) below [14].

$$C_V = k \frac{\int_0^\infty \left(\frac{hv}{kT}\right)^2 e^{-\frac{hv}{kT}} g(v) dv}{\left(1 - e^{-\frac{hv}{kT}}\right)^2} \tag{2}$$

where k is Boltzmann's constant, h is Planck's constant, v is the frequency of oscillation, T is temperature, and $g(v)$ represents the vibrational density of states.

Majority of the basic theories of the thermal conductivity of epoxy resins is based on the heat capacity of the system.

2 Basic Theories of Thermal Conductivity in Epoxy Networks

The difference between temperature and heat is often misconceived. Temperature is the measure of the vibration of microscopic particles in a system that generates thermal energy. Heat is the transfer of thermal energy (vibration energy) from one part of the body to the other or to the adjacent body because of difference in temperature. In solids, heat transfer can occur through thermal conduction, convection, or radiation [1]. Thermal conductivity is the relationship between heat flux and thermal gradient. The mechanism of thermal conductivity is different for crystalline and amorphous solids. In a steady state system, the amount of heat conducted per unit time—heat flux—is proportional to the product of temperature gradient, area of the material, and thermal conductivity.

In the microscopic level of a solid, the atoms arranged in a regular structure, called lattice, will be on constant vibration about the equilibrium position when it is above the absolute zero temperature. The vibration increases proportionally with temperature. A quantum of vibrational energy associated with a particular normal mode is known as a phonon. In conjunction with this, there are free electrons which are travelling in random direction through solid. Heat transfer can occur through any of these interactions, such as lattice vibrations (phonons), electron–electron interaction, or electron lattice interaction.

The main contributing component of thermal conductivity in polymers is phonons. Phonon contribution for the thermal conductivity is high in polymers with strongly

bonded linearly arranged polymer chains. Electronic contribution for the thermal conductivity of a polymer is negligibly low.

2.1 Phonon Contribution of Thermal Conductivity in Epoxy Resins

Thermal conductivity is predominantly caused by phonon transport in polymers. Study of phonons is an important part of thermal conductivity research especially in condensed matter physics. Rate of heat transfer in polymers depends on three factors, area, length, and temperature difference at either end of the conductor. Fourier's law of heat conduction connects the relationship between these three variables.

2.1.1 Debye's Theory

The history of the concept of thermal conductivity and heat capacity in classical and quantum mechanics interestingly advances with filling the gaps. In 1907, Einstein proposed a model of a crystalline solid that contains large number of independent three-dimensional quantum harmonic oscillators. Einstein solid model can accurately predict heat capacity at high temperatures but failed to explain specific heat at lower temperature because all oscillations have one common frequency and specific heat value at lower temperature fast approaches to zero. In 1912, Peter Debye developed a model that treats atomic lattice vibration as particle in a box which treats the solid as individual, non-interacting quantum harmonic oscillators. Debye modelled the vibrations as the normal mode vibrations of a continuous elastic body [12]. Debye model accurately predicts low temperature dependence of heat capacity and is given by the equation

$$k(T) = \frac{1}{3} \sum_j \int C_j(\omega) v_j l_{j(\omega)} d\omega \qquad (3)$$

where $C_j(\omega)$ is the specific heat of phonons with branch index j and frequency ω, v_j is the group velocity of the phonons, and $l_{j(\omega)}$ is the mean free path.

The simplified Debye's equation will be $\lambda = \frac{1}{3} c_v u l$ where λ is the thermal conductivity, c_v is the volumetric heat capacity, u is the velocity, and l is the mean free path of phonon [15].

A phonon is the normal mode energy quantum of vibration lattice energy and is analogous to photon. The quantisation of energy becomes important when a polymer reaches characteristic Debye temperature. The normal vibrations with certain frequency, direction of the wave vector, and polarization are excited with possible oscillations [16].

2.1.2 Fourier's Law of Heat Conduction

The area of conductor (A) is directly proportional to the rate of heat transfer (Q). This is because more electrons and atoms can participate in heat transfer. The length of conductor (L) is inversely proportional to the rate of heat transfer due to the higher chance of collision. The temperature difference (ΔT) between the objects is directly proportional the rate of heat transfer. A higher temperature difference results in vigorous heat transfer compared to a lower temperature difference. This relationship is plotted in (4).

$$Q \propto A(T_2 - T_1)/L \tag{4}$$

This proportionality relationship is converted into an equation by introducing a constant called the coefficient of thermal conductivity (K). The unit of K is watts per metre kelvin (W/mK).

$$Q = -KA(T_2 - T_1)/L$$

or it can also be represented as

$$Q = -KA\frac{\Delta T}{\Delta x}$$

This relationship is known as Fourier's law of heat conduction. The negative value is a correction factor for the direction of the heat flow; T_1 and T_2 are the temperatures at the colder and hotter regions of the conductor, respectively, and Δx is the thickness of the specimen.

2.2 Electronic Contribution of Thermal Conductivity in Epoxy Resins

Thermal conductivity of solids (K), especially metals, are well described by the movement of free electrons (K_e). Metals have the benefits of crystalline structure and delocalised free electrons to participate in thermal conductivity. In metals, atoms are bonded by metallic bonding where electrons are not bound to a particular atom. The electron sea model of metallic bonding describes this criterion clearly. These free delocalised charge carriers participate in the heat flow. Simultaneously, the lattice vibration—phonons—(K_p) contributes to the thermal conductivity as an independent entity. The overall thermal conductivity of metals, in general, solids consist of electronic contribution and phonon contribution [17, 18].

$$K = K_e + K_p$$

In metals, the phonon contribution to the thermal conductivity is negligibly low, i.e.,

$$K \approx K_e$$

However, in polymers, thermal conductivity caused by movement of electrons is insignificant due to the absence of free electrons except for doped polymers that contains polarons and free charge carriers [19]. The electronic contribution for thermal conductivity is significant compared to undoped polymers. Polaronic conduction through polymers is equated to electronic conduction through metals, and hence, the Wiedemann–Franz law for thermal conductivity in metals is applicable to polymers [20]. In 1853, Wiedemann and Franz reported that thermal conductivity of metals at room temperature is proportional to electrical conductivity [21, 22]. The law is represented by equation $Ke = \left(\frac{kb}{e}\right)^2 L\sigma T$, where kb is the Boltzmann constant, e is the elemental charge, and L is the Lorenz factor. The validity of Wiedemann and Franz has been in question due to the lack of theoretical understanding and challenges in thermal conductivity measurements of conducting polymers [23]. In general, a good electronic conductor is a good heat conductor.

2.3   Thermal Conductivity and Thermal Diffusivity

Thermal diffusivity is the measure of the rate of heat transfer to achieve equilibrium. It is the heat conducted away from the material to the heat stored in the material [24]. In a homogenous body, thermal conductivity λ and thermal diffusivity a are interrelated by specific density ρ and specific heat capacity C_P as per the equation below. Thermal diffusivity is the measure of rate of heat transfer to achieve equilibrium [25].

$$\lambda = aC_P\rho \tag{5}$$

Thermal diffusivity in epoxy polymers is measured by transient methods related to laser flash analysis [26]. The specimen is heated by the laser flash, and the diffused heat from the specimen is measured by infrared radiation sensor. The instrument set-up is illustrated in [27] (Fig. 1).

Assuming there is no heat loss, the normalised temperature increase on the bottom side is given by the equation below.

$$V = 1 + 2\sum_{n=1}^{\infty}(-1)^n\exp(-n^2)\omega$$

where $\omega = \pi^2\alpha t/L^2$, $V = T/T_m$ which is the dimensionless temperature increase of the rear face, T, instantaneous temperature increase of the rear face of the specimen; $T_m = Q/\rho c_p L$ which is the maximum temperature increase of the rear face, Q, input
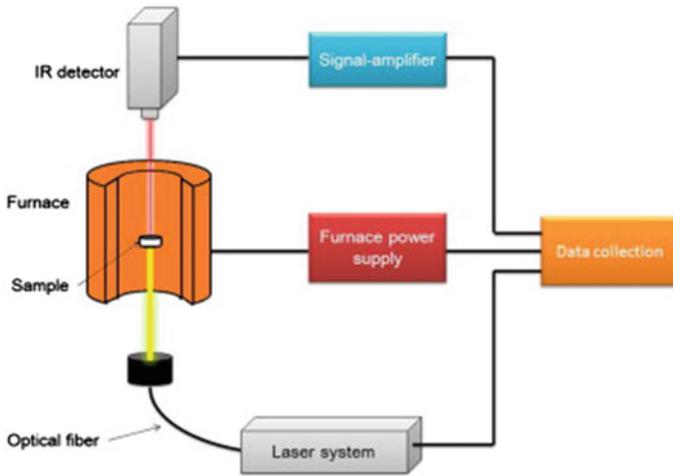
Fig. 1 Laser flash analysis instrument schematic diagram [27]. (Reproduced with permission from Elsevier Ltd.)

energy on the front face; ρ, density; c_p, specific heat; L, specimen length; t, time; and α, thermal diffusivity [28].

2.4 Phonon Mean Path

A fundamental understanding of thermal transport in 2D materials and its epoxy composites is obtained by analysing the phonon mean free path (MFP). Phonon mean free path is the average travelling distance between two consecutive phonon scattering events [29]. The phonon MFP is affected by scattering of phonon by an impurity, phonon–phonon scattering, and/or phonon boundary scattering. The effective mean free path $\left(l_{eff}\right)$ of phonon scattering can be expressed as

$$\frac{1}{l_{eff}} = \frac{1}{l_{p-p}} + \frac{1}{l_{p-b}}$$

where l is the phonon mean free path, and the subscripts $p - p$ and $p - b$ are the phonon–phonon and phonon-boundary scattering [30]. Dynamic scattering is caused by the inharmonic vibration of the molecules and static scattering is caused by defects [31].

In epoxy composites, phonon scattering at the boundaries is explained based on kinetic theory of phonon transport. According to the kinetic theory of phonon transport, thermal conductivity K is given by

$$K \sim \sum_i C_i v_i l_i$$

where C_i is the specific heat, v_i is the group velocity, and l_i is the mean free path of the phonon in mode i with angular frequency ω.

Therefore, the effective mean free path l_{eff} is determined as [32]

$$l_{eff} = \sum_i C_i v_i$$

3 Methods to Improve Thermal Conductivity in Epoxy Resins

Formulating epoxy composites with highly thermally conductive metallic or inorganic materials is a modest method to improve thermal conductivity of epoxy resins. The intrinsic thermal conductivity of the filler contributes to the enhanced thermal conductivity of the epoxy composite with that filler. Unfortunately, adding high content of the fillers in most cases destroys the flexibility, failure strength, and processability of the epoxy resin mainly due to high interfacial thermal resistance [33, 34]. Moreover, despite the highest loading levels, the thermal conductivity of the composites will never reach the individual thermal conductivity of the filler. Another commonly used method to improve thermal conductivity of epoxy resin is the molecular re-designing of epoxy matrix to synthesise intrinsically modified thermally conductive epoxy resins. Introducing liquid crystal units to the molecular structure is a widely used idea [35, 36]. This places molecular chain orientation in order, for a continuous heat transfer through the matrix [37].

3.1 By Forming Epoxy Composites

Generating effective three-dimensional thermal conduction pathways in epoxy matrix gives rises to increased thermal conductivity of epoxy resins. Various types of thermally conductive nano-fillers such as graphene, graphite, boron nitride, carbon nanotubes, metal powder, aluminium nitride, ceramic particles, cellulose nanofiber [38–46], and filler combinations [40, 47, 48] were studied in this region with significant thermal conductivity improvements. Figure 2 illustrates the synergistic effect of multi-particle composite system of epoxy matrix where micro-silver, nano-silver, MXene, and graphene work together to create a bridging effect that creates a continuous path for heat transfer between particles [7].

The high intrinsic thermal conductivity of the fillers enhances the overall thermal conductivity of the epoxy matrix by forming a continuous three-dimensional thermal
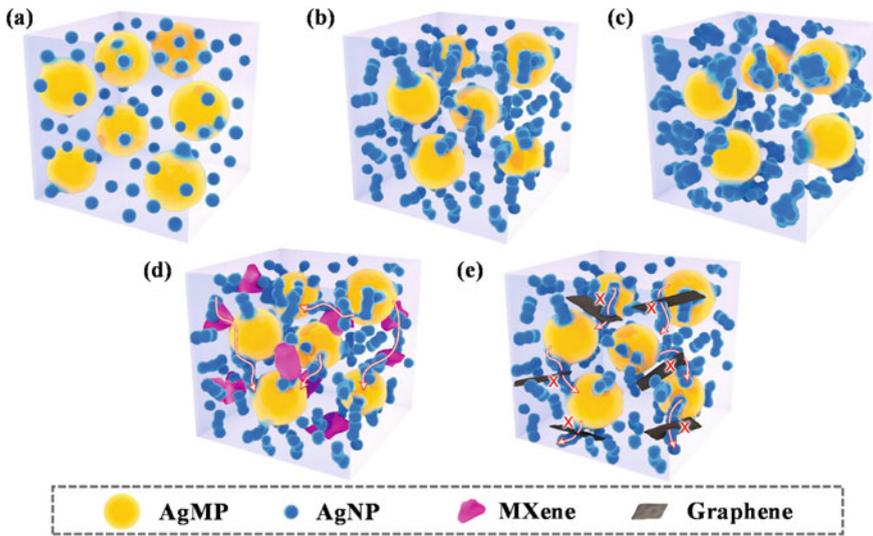
Fig. 2 Schematic figure of microstructural characteristics of composites. **a–c** The Ag/epoxy composites with an increment of AgNP. **d** The MXene/AgMP/AgNP composite. **e** The graphene/AgMP/AgNP composites [7]. (Reproduced with permission from Elsevier Ltd.)

pathway for heat transfer. In polymer composites, the thermal conductivity is determined by the thermal conductivity of the filler matrix [49, 50].

Interfacial thermal resistance is one important drawback of epoxy composites where phonon scattering causing rapid accumulation of heat inside the composite, reducing its stability [51, 52]. Similarly, excessive addition of fillers will not adequately improve the overall thermal conductivity of the composite over a certain point and large quantity of fillers will deteriorate the mechanical properties of the composite [53].

The filler aspect ratio, dimensions, and surface are important parameters that affect the resultant composite. Filler alignment and direction in the epoxy matrix also affect the overall thermal conductivity of the composite. Transfer of thermal conductivity at the filler-matrix is the biggest challenge that needs resolution to achieve superior thermal conductivity in polymer composites [54].

The thermal conductivity of a composite is explained by several models and equations. Maxwell model explains the composites with spherical filler and low volume fraction. Rayleigh model includes analytical expression for thermal conductivity of continuous matrix reinforced with parallel cylindrical fibres arranged in uniaxial simple cubic array. Hasselman–Johnson model states that the effective thermal conductivity of a composite depends not only on filler volume but particle size as well. The bruggeman theory gives formula for multicomponent systems in addition to the two components system.
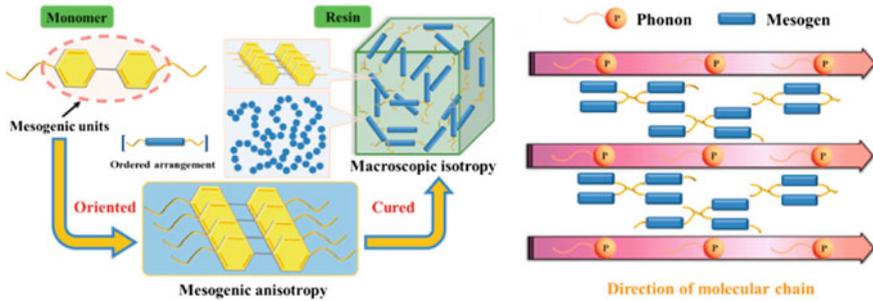
Fig. 3 Schematic diagram phase arrangement and heat flow transfer in liquid crystal epoxy [59]. (Reproduced with permission from Elsevier Ltd.)

3.2 By Intrinsic Modification of Thermal Conductivity in Epoxy

Designing and modification of the epoxy molecular chain structure and orientation, to introduce crystalline characteristics to the naturally amorphous epoxy matrix, has widely become a popular topic in recent years. This method successfully eliminates many issues caused by the filler enhanced thermal conductivity of epoxy composites.

Liquid crystal epoxy resins are an important thermosetting polymer in this category. They are formed by curing liquid crystal epoxy monomers containing rigid rod-shaped mesogens, special flexible segments, and epoxy end groups [36, 55]. A highly ordered mesogen structure shows high thermal conductivity [56]. The liquid crystal epoxy resins form partial crystal-like structure so that the heat flow is conducted along the molecular chain direction which inhibits the scattering of phonons. The thermal conductivity of the liquid crystal epoxy resins can be further improved by preparing its composites by the addition of fillers [35, 57]. The highly aligned microstructure in the liquid crystal gives the composite high thermal conductivity [58]. Figure 3 is a schematic representation of phase arrangement and heat flow transfer in liquid crystal epoxy.

4 Factors Influencing Thermal Conductivity of Epoxy Polymers

4.1 Radius of Gyration—Amorphous State

The amorphous structure intensifies the phonon scattering resulting in lower thermal conductivity of epoxy resins [15]. The ratio of the thickness dz to the radius of gyration R_g of a polymer film is known as the chain coefficient indicator dz/R_g.

Fig. 4 Schematics of the chain structure as *dz/Rg* decreases. **a** Large *dz/Rg*, polymer chains entangle with each other; **b** Middle *dz/Rg*, polymer chains have less overlap; and **c** Small *dz/Rg*, polymer chains are isolated (limiting case) [60]. (Reproduced with permission from AIP publishing)
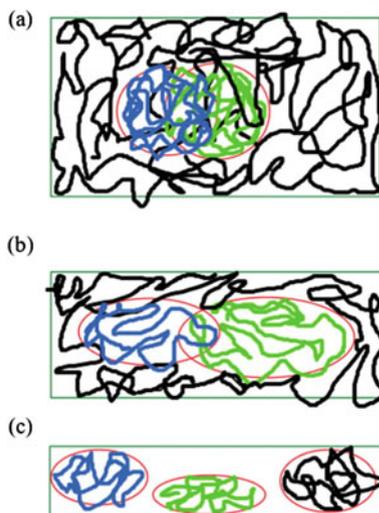
Thermal conductivity increases linearly with chain coefficient indicator for amorphous polymer films. Larger radius of gyration improves the thermal conductivity of amorphous polymer films by providing more space for heat transfer. Strongly confined and less entangled polymer chains in amorphous polymers will increase the thermal conductivity (Fig. 4) [60, 61].

4.2 High-Order Structure—Crystalline State

Phonon scattering caused by microscopic anisotropy reduces the thermal conductivity in epoxy polymers. In an anisotropic cross-linked polymer, thermal conductivity will also be anisotropic. Thermal conductivity values through the molecular chain direction could be higher than those of perpendicular direction [62]. The macroscopic isotropy can be achieved by the use of liquid crystal epoxy resins (LCEs) by disordering the domains of the crystal-like structure that is linked with the internal amorphous structure through covalent bond. This high order structure will suppress phonon scattering and enable the resin with high thermal conductivity. High density of covalent bonds and packaging of mesogenic groups lead to high thermal conductivity [63]. The covalent network of mesogenic epoxy can trap thermally conductive phase change material, polyethylene glycol, to achieve a homogenous solid state [64]. Formation of spherulites on the mesogenic resins enhances thermal conductivity by suppressing phonon scattering. Adjusting the initial curing temperature will have effect on the formation of larger spherulite structures further enhancing the thermal conductivity [15, 65, 66]. The spontaneous orientation of LCEs can be achieved by designing the molecules of LCE bringing diglycidyl moieties at the side position of the molecule to maintain the orientation after thermal curing [67].

4.3   Polymer Chain Orientation

The random chain orientation in amorphous epoxy polymers reduces the phonon mean path causing phonon scattering [68]. The orientation of epoxy molecular microchain in an ordered structure maximises the thermal conductivity path. Polymer chain can be oriented by applying external forces such as electrical, magnetic, or mechanical at low viscosity states [69, 70].

In epoxy composites, the thermal conductivity along the filler orientation increases the thermal conductivity of the composite [71]. However, the interfacial thermal resistance between the filler and the polymer matrix remains large. The interfacial thermal resistance (R_{int}) is defined as the ratio of temperature discontinuity ΔT occurring at the interface to the heat rate Q per unit area A flowing across the interface between two phases in contact [72, 73] and is given by the equation

$$R_{int} = \frac{\Delta T}{Q/A}$$

In epoxy composites, interfacial thermal resistance is caused by the lack of continuous thermal conductive paths between the polymer matrix and fillers [74]. Poor interfacial adhesion creates voids between the filler and epoxy matrix [75], whereas improved interfacial affinity between the filler and epoxy matrix decreases the resistance and reduces the number of voids in the composite [76] resulting in high thermal conductivity. The interfacial compatibility between filler and epoxy matrix requires effective methods that ensures a strong interfacial bonding [77]. The polymer–filler interfacial adhesion can be improved by modification [78] or functionalisation of the filler to generate or enhance van der Waals interaction or hydrogen bonding between the binder and the filler [79]. Functionalisation of the fillers will increase the thermal conductivity of the composite by reducing interfacial thermal resistance even though the intrinsic thermal conductivity of the filler itself is negatively affected by the functionalisation. Uniform dispersion and close contact of the fillers reduces the interfacial thermal resistance and provide a continuous thermal pathway. Unfortunately, some of the modification methods such as strong acid etching or high temperature ablation will destroy the crystal structure of the filler resulting in reduced thermal conductivity [80].

5   Thermal Degradation and Thermal Conductivity of Epoxy Polymer

Thermal degradation of a polymer is influenced by heat and may undergo either chain end degradation mechanism or random degradation mechanism. The chain end degradation mechanism results in generating monomers of the original polymer, whereas the random degradation mechanism results in producing smaller polymer

with a lower molecular weight. Thermal degradation mainly depends on the stability of carbon–carbon bond, substituent atoms on the carbon, presence of aromatic ring or oxygen in the polymer backchain, and formation of free radicals by breaking of the substituent groups on a polymer chain. A polymer with highly stable carbon–carbon bonds with high dissociation energy will have high thermal stability. When hydrogen atoms in a polymer chain is replaced with highly electronegative atoms such as fluorine, the polymer becomes thermally stable. Presence of aromatic rings increases the thermal stability of a polymer, whereas presence of oxygen decreases the thermal stability of a polymer. Thermal degradation or thermal stability of a polymer depends on the heat conducting properties of the polymer. As a matter of fact, thermal stability of a polymer increases proportionally with thermal conductivity.

The concept of reactive block copolymers where reactive groups are incorporated to promote covalent linkage with epoxy network in the resulting blend improves the thermal stability of the epoxy thermoset [81]. The ordered connections with covalent bond encourage efficient phonon transport [82]. The thermoset epoxy polymers when cross linked with ionic liquid system can also deliver flexible thermal behaviour. The material becomes soft and flexible when heated up to a certain temperature without thermal degradation [83].

6 Conclusion

The basic theories of thermal conductivity of epoxy resins have historically been revised to accommodate previously unidentified challenges. Based on those theories, several techniques have been evolved to improve the thermal conductivity of epoxy resins. Composites of epoxy resins prepared by inserting highly thermally conductive nanoparticles has gained popularity in research and application due to the variety of nanomaterials incorporated in the epoxy matrix resulting excellent improvement in thermal conductivity. Molecular chain modification and the use of mesogens such as liquid crystal epoxy significantly added crystallinity to the naturally amorphous epoxy structure. This change in the molecular chain significantly enhanced the heat transfer through the epoxy chain due to the reduced phonon scattering.

To expand the field of application for thermally conductive epoxy resins, the current state of molecular level nano-engineering should be expanded to address issues such as interfacial thermal resistance, deteriorated mechanical properties, failure strength, and processability. It is evident that the interfacial thermal resistance causes lack of continuous path for heat transport. Addressing these issues with the help of machine learning and numerical simulations will fast track the process when ultra-high thermal conductivity is targeted for epoxy resins. Thermal conductivity fostering fire retardancy of epoxy resins is identified as an appropriate characteristic improvement in fire retardant epoxy applications. Heat carried away from the surface of an epoxy coating is deemed ideal for fire retardant structural coating applications. Considering the definite application environment, the thermal conductivity of epoxy resins shall be a major research topic for years ahead.

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