2. LITERATURE REVIEW

Each material has an individual post-cure process that relies on raw materials. Post curing variables consist of temperature, time of duration of cure, the time between initial curing and post-curing, and temperature profile gradient. There are some ways to find out the cure state of a polymer. It can be assessed based on the mechanical and physical properties, glass transition temperature, etc.

In many polymeric materials, improvement and control of the manufacturing process require attention towards the degree of cure. Polymeric composite is assessed in a simple, rapid, and non-destructive way by heating a surface of the polymeric composite to significantly curing temperature, over a predefined period, and constantly observation with a contact type temperature sensor of the heated surface during the preset period of time.

This review is focused on 1) the concept of curing 2) concept of in-process curing and post-process curing and its effects on mechanical strength 3) concept of thermal conductivity 4) experimental methods for measuring the thermal conductivity of composite material, and 5) analytical/numerical methods for predicting the thermal conductivity of composite materials.6) effect of filler on thermal conductivity of composite materials. This section outlines some of the research work available on the mechanical behaviour of fiber-reinforced polymer composites with special emphasis on the effect of pressure (load), temperature, and time as one of the parameters during post-process curing.

2.1 Curing of Polymer Composites

Ray and Rathore (2014) stated that mechanical properties of Polymer Matrix Composites (PMCs) were considerably affected by heat i.e., variation in temperature. Curing was an irretrievable reaction where chemical covalent cross-links were produced which were thermally and mechanically substantial. The curing process acted a vital role to attain the end mechanical properties and chemical resistance of PMCs. For the fabrication of PMCs, resin, and curing agents (hardener) with correct ratios were used. During cross-linking, the state of the matrix changed from liquid to gel and then transformed into solid. Curing was generally be done at room temperature as well as at elevated temperatures. (Aruniit et al. 2012)

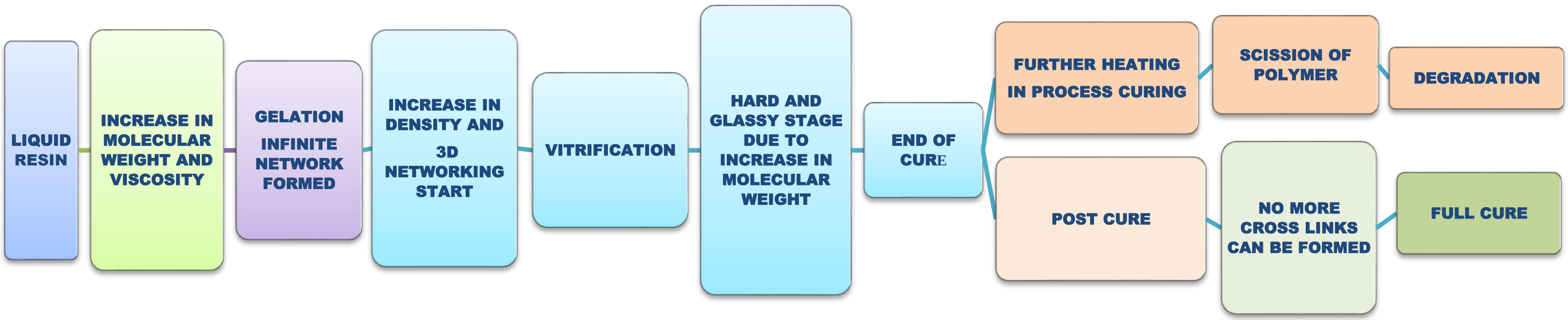


Figure 2.1 Different Stages of Curing

2.1.1 Stages of Curing

The stages of cure are shown in the line diagram in fig. 2.1. From the liquid resin stage, the start of the curing process is started either by heat, irradiation, or chemical reaction. Gillham J K, (1986) stated that as the exothermic reaction proceeds, polymer cross-links form incessantly and ultimately create an infinite network. This is known as the gelation point. At this point, the material transforms from the viscous liquid to the elastic gel or rubbery state and the polymer will stop to flow. As cure proceeds, the number of 3D crosslinks and the molecular weight of the polymer will continue to boost until the thermoset reaches the solid-state, this is described as vitrification. Vitrification has been termed as the point at which the glass transition temperature and cure temperature are the same. The polymer then proceeds to the end of the cure and no more new crosslinks can be formed at that temperature. Further heating can either result in a further cure of the material or degradation, in which the polymer chains are damaged. Vilas et al. (2001) concluded that generally, a higher cure temperature would increase the rate of reaction for a cure.

2.2 Effect of post-process curing (PPC) and in-process curing (IPC) on the mechanical behaviour of the composite plates

Uzay (2017) worked on the post-cure heat treatment on the impact toughness and tensile properties of fiber-reinforced composites. The laminates were made by utilizing hand layup vacuum bag moulding of woven carbon and glass fiber fabric plies. At three different temperatures (i.e. 25, 62.5, and 100°C), the post-curing was done for one hour. The impact (Charpy) and tensile tests were conducted along with the statistical analysis to know the impact of post-curing and different types of hybrid plies. The results reflected that post-curing had an encouraging effect on the energy absorption capacity and mechanical properties of FRC. This was because, during post-curing, the epoxy polymer matrix made the composite stronger due to improved formation of cross-linking.

Kumar et al. (2015) emphasized the effects of post-curing parameters on thermal and mechanical properties of the Glass Fiber Reinforced Polymer (GFRP) composite. Post curing was carried out at three different temperatures (80° C, 110° C and 140° C) for changed periods (2h, 4h, 6h, 8h, and 12h). It was revealed that post-curing at 140°C for 6 hrs shows better thermal and mechanical properties compared to post-curing at different temperatures and periods. The curing cycle had a strong influence on the thermal and mechanical behaviour of thermosetting polymers. The amount of cross-linking which was a strong function of curing temperature and time was directly correlated to the glass transition temperature (Tg) of the thermosetting polymer. This transition temperature determined the transformation of the polymer from the glassy phase to the rubbery phase, hence determined the applicability of the material at a certain temperature with a certain degree of safety and reliability.

Chavan et al. (2018) conducted experiments and examined the impact of post-curing on GFRP hybrid composites. The results availed show that the samples only with natural fiber had more challenging results compared with synthetic fiber. The synthetic fibers get crumpled due to post-curing whereas no such visuals in the natural fibers.

Furtos et al. (2012) investigated that mechanical properties were enhanced by post-curing and by increasing the content of glass fiber in the composites. SEM micrographs present strong interfacial interaction amongst glass fibers and polymer matrix.

Bourchak et al. (2013) revealed that preheating epoxy resin for extended duration could decline the material ultimate tensile strength and enhance its stiffness while post-curing the epoxy resin for two hours at 80°C to some extent increased ultimate tensile strength but made the material considerably stiffer due to a large decreased in the material ultimate tensile strain.

Elleuch et al. (1999) investigated that upon the post-curing by heat, it was established that the mechanical properties of the woven glass-polyester composites were improved moderately and the curing of the composite was also improved. Micro indentation tests were employed to study the quality of the fiber-matrix interface by using post cured and non-post-cured. The result of the micro-indentation test was similar to that of the monotonic and fatigue test and ensured that post-cure improves the resistance of the fiber-matrix interface.

Cao et al. (2007) investigated that the tensile properties of FRP composites had also been affected by curing temperature applied during the fabrication of composite materials. Usually, the specimens had been cured at room temperature. However, the increase in curing temperature improved the mechanical properties compared to curing at room temperature stated Joshi et al. (2003). Systematic research work based on in-process curing of a polymer-based composite was not observed in the literature.

2.3 Thermal conductivity

The hypothesis of thermal conductivity was projected by Fourier in 1822. According to Fourier, the primary heat conduction equation can be stated as “For a homogeneous solid, the local heat flux is proportional to the negative local temperature gradient”. For one-dimensional steady-state heat transfer, this statement can be reflected by Equation 2.1:

$$Q = -K\frac{dt}{dx} \qquad \text{(Eqn 2.1)}$$

Where,

-ve (negative) sign indicates the temperature reduction from a hot surface to a cold surface.

According to Equation 2.2, conductivity can be given as (assuming that heatis not lost in its plane)

$$K = \frac{(\frac{Q}{A})}{(\frac{\Delta T}{\Delta L})} \qquad \text{(Eqn 2.2)}$$

Thus, the thermal conductivity (K) of a material can be defined as a rate of/at which heat is transferred by conduction through a particular unit area of a particular material when the temperature gradient is perpendicular to the cross-sectional area. The thermal conductivity of a composite material relies on the fiber, resin materials, volume fraction of fiber, the arrangement of the fiber, the direction of heat flow, and operating temperature.

2.4 Thermal properties of Fiber Reinforced Polymer Composites

The heat transfer property of polymer composites is one of the most significant parameters for material design in thermal applications. Normally, the thermal conductivity of natural fiber is lower than that of conventional mineral fibers like glass fiber and carbon fiber. Therefore, better thermal insulation is effortlessly attained by mixing natural fibers in polymer composites. In addition, the thermal properties of the fiber composites can be varied not only by changing the thermal conductivity values of the matrix but also by varying the internal microstructure of the fiber. The thermal utility of natural fiber is mainly derived from its internal physical and chemical nature. There is an empty cavity in natural fibers, which is known as 'lumen' because of that thermal conductivity of natural fibers is lesser than that of glass and carbon fibers, which are solid. (Takagi et al.2014).

A natural fiber-reinforced polymer composite has advantages like low density, less expensive, and reduced solidity when compared to synthetic composite products, thus provides utilities in the area of the automotive industry, buildings, and constructions. The objective of this literature study is to look into the thermal properties of the fibers and polymers and its effects on variation in thermal conductivity, specific heat capacity, thermal diffusivity, and thermal expansion, etc. of natural fiber polymer composites (Mohammed et al. 2015).

2.5 Thermal Conductivity Measurement of Fiber Reinforced Polymer Composites

Increasing in the use of composites makes space in engineering systems and emphasizes its importance/significance in various applications through thermal property analysis. The thermal conductivity of a composite can be measured by investigational methods. Analytical equations are necessary to predict the thermal conductivities of a composite material. Knowledge of the thermal properties of composite materials would facilitate the design of an engineering system made from FRPs.

Published literature is loaded with investigations of mechanical properties of composites. Fewer publications concentrated on thermal properties. quite a few publications like Hashin (1979), Caruso et al (1986), Muralidhar (1990), Springer and Tsai (1967) are covering different theoretical approaches to predict the thermal conductivity of composite materials. A non-linear increase in the thermal conductivity was described with the increase of fiber volume fraction of plain weaves (Gowayed, 1995).

Measurement of thermal conductivity (K) of materials is generally classified into two methods: steady-state methods and non-steady state (transient methods) mainly differ from each other from an equilibrium point of view. In steady-state methods, assessment is done when the temperature of the system becomes constant with time (i.e. equilibrium or steady-state condition). Where as in transient methods assessment is done during the heating process and no need to wait for the system to reach a steady-state. Hence the method is rapid but less accurate compared to the previous.

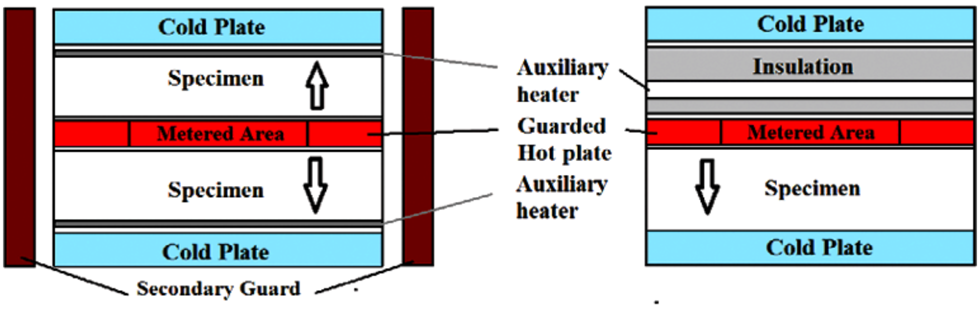
2.5.1 Guarded Hot Plate Method (GHP)

The guarded hot plate, also recognized as the Poensgen apparatus, Itis the most frequently used and most effective method for evaluating the thermal conductivity of insulative materials. The GHP depends on a steady temperature difference against a known thickness of a specimen and its primary function is to control the heat flow through the material. The experimental setup of the guarded hot plate (GHP) applies a steady-state heat transfer between a hot plate and a cold plate. The standardized GHP method is the ideal method for researchers and scientists in the field of thermal testing material and it is considered as a perfect measurement method. Another benefit is that the GHP method is standardized in countries such as the United States (ASTM C 177-63), U K (B.S. 874:1965), and Germany (DIN 52612). The details of the method are provided by the ASTM (American Society for Testing Material) Standards associated with the method and materials (Yüksel, 2016).

2.5.1.1 Construction of the GHP

The guarded hot-plate set-up consists of cold plates, a hot plate, a guard heaters system, and thermal insulation. A hot plate is heated electrically and the cold plates are liquid-cooled heat sinks. The composition of GHP is symmetric, with guarded hot plates located on the sides while the heater unit is sandwiched between two.

The most general types of guarded hot-plate apparatus are shown in Fig. 2.2. In the single-sided system state, the heat flow passes through one specimen, while the top of the main heater acts as an insulating guard, thus ensuring an adiabatic environment (Yüksel, 2016).



2.2 Schematic Diagram of Guarded Hot Plate (GHP)

Table 2.1 Comparison of Some of The Steady-State Methods and Unsteady-State Methods (Transient Method) for Measuring Thermal Conductivity [Czichos et al.(2006), Tong X C (2011), Yüksel (2016), Evitherm (internet)]

Sr.No.	Methods	Temperature Range	Uncertainty	Materials
Steady-State Methods				
1	Guarded Hot Plate (GHP)	80K–800 K , 80K–1500 K	2% 2–5%	Insulation Materials, Composite Materials and Solid, Opaque, Insulators
2	Cylinder	4K–1000 K	2%	Metals
3	Heat-Flow Meter	Normally −100C–200C 90K–1300K (Axial Heat Flow) 298K–2600K (Radial Heat Flow)	3–10% 0.5–2% (Axial) 3–15% (Radial)	Insulations, Plastics, Glasses, Ceramics Metals and Solids
4	Comparative	20K–1300C	10–20%	Metals, Ceramics, Plastics
5	Direct Heating	400K–3000K	2–10% 2–5% and 10–200 W/(m K)	Tubes of Electrical Conductors ,Metals Wires, Rods,
6	Pipe Method	20K–2500C and 50C–800C	3–20% and 0.02–2 W/(m K)	Solids Calcium Silicates,
Transient Methods				
1	Hot Wire, Hot Strip	20C–2000C , 298K–1800K for hot wire	1–10 % 5–15%	Liquids, Glasses, Refractory Materials
2	Hot Disk (TPS technique)	30K–1200K	--	Liquids, Pastes, Solids and Powders
3	Laser Flash	−100K–3000C and 100K–3300K	3–5% 1.5–5 %	Solids, Liquids, Powders, Liquid Metals, Ceramics
4	Photo-Thermal(PT), Photo-Acoustic(PA)	30K–1500K for PT,200K–800K for PA	1–10 %	Solids, Liquids, Gases, Thin Films, Small Solid Parts

2.5.1.2 Principle of working of GHP

It is presumed that the measured heat power rate is transferred through the specimen from guarded heaters. After acquiring thermal equilibrium, the heating and cooling plates are kept in stable temperatures, the thermal conductivity can be accessed from the input values. The input values are the heat power (*Q*), the temperature difference across the specimen (Thot − Tcold), the specimen thickness (Δx), and the heat transfer area (A). The thermal conductivity is calculated by measuring the quantity of heat input under the steady-state temperature condition in the entire specimen. From the measured input values, the effective thermal conductivity can be computed using the following unidirectional steady-state heat transfer equation. The heat flow Q is derived by measuring a power P (or half power for two specimens) from an electrical heater

$$Q = k * A * \frac{dt}{dx} \qquad \text{(Single − sided GHP)}$$

$$\frac{Q}{2} = k * A * \frac{dt}{dx} \qquad \text{(Double − sided GHP)}$$

2.6. Effect of fiber properties on Mechanical and Thermal Behaviour of composites

The thermal conductivity of composites is anisotropic. The knowledge of the thermal conductivity of composites is needed for accurate design. Mutnuri (2006) stated data regarding thermal conductivity of resin facilitates to reduce stresses related to shrinkage and also to find a mismatch of thermal expansion coefficients of the composite during cure. The heat conduction mainly depends on thermal transport property called thermal conductivity. The measured numerical value of thermal conductivity gives an idea about the use of the material as a heat conductor or insulator. Various investigations on the thermal properties of polymer-based composites with varying core materials and fillers have been published. A primary correlation between various composites is not so easy as different manufacturing technique is used by each researcher. Also, the correlation between the same materials, base, and filler might be useless as there might be a difference of crystal structure, size, and shape between the same type of filler. Before conducting experiments to determine the thermal conductivity of various composites, knowledge about the effect of different parameters influencing thermal conductivity is essential. Some of the properties of fibers affecting the mechanical and thermal properties of the polymer composites are discussed in table No.2.2.

2.7 Use of Fillers in Composites

Fillers are the least expensive of the major ingredients, in comparison to resins and reinforcements. These materials are however very significant in establishing the performance of the composite laminate for the following reasons:

- Fillers reduce the shrinkage of the composites part.
- Fillers influence the fire resistance of laminates.
- Fillers lower compound costs by diluting more expensive resin and may reduce the amount of reinforcement required.
- Fillers can influence the mechanical strengths of composites.
- Fillers serve to transfer stresses between the primary structural components of the laminate (i.e., resin and reinforcement), thereby improving mechanical and physical performance.
- Uniformity of the laminate can be enhanced by the effective use of fillers.
- Crack resistance and crack prevention properties are improved with filled resin systems. This is particularly true in sharp corners and resin-rich areas where smaller particles in the filler help to reinforce the resin in these regions.
- The combination of small and medium filler particles helps control compound rheology at elevated temperatures and pressures, thereby helping to ensure that compression moulded parts are uniform.
- Low-density fillers are used extensively in marine putty and the transportation industry. They offer the lowest cost of filled systems, without an increase in weight that affects the performance of the final product.

Table No. 2.2 Effect of Fiber Properties on Mechanical and Thermal Properties of Composites

Sr.No	Study	Author/s	Materials	Remarks
1	Volume Fraction (V_f)	Sair et al. (2018)	Composite made from polyurethane (PU) and hemp fibers at different loading rates.	Around 15% in fiber content is better than other compositions for thermal insulation.
2		Gudapati et al. (2018)	Areca Palm fibers extracted from its stalk reinforced with polyester resin.	Thermal conductivity was inversely proportional to the volume fraction of the fiber.
3	Size of the Fibers (SF)	Das (2016)	Composite made from epoxy and short fibers of banana. Teak wood dust is used as filler material	TWD particles reduced the strength and thermal conductivity of epoxy. SBF enhanced the mechanical strength but reduced the thermal conductivity of epoxy.
4	Cross-sectional Shape of the fibers and weave pattern(CSF)	Karaca et al. (2012)	Polyester multifilament yarn produced from semi-dull polyethylene terephthalate by melt spinning process.	The Thermal conductivity increased in the fabrics woven with hollow fibers compared to those woven with solid fibers.
5	Fibers' Particles Size(FP)	Raju and Kumarappa (2012)	Specimens prepared from randomly distributed groundnut shell particles in a polymer matrix.	The particle size had a major effect on thermal properties.
6	Fibers 'Length (FL)	Supreeth et al. (2014)	Specimens from Bisphenol-A (BPA) as a matrix and the short PALF fiber of different length were prepared by hand lay-up technique.	Thermal behaviour of PALF reinforced Bisphenol-A composites greatly depends on fiber length.
7	Fibers 'Orientation (FO)	Gudapati et al. (2018)	The results are achieved at different volume fraction, temperature and fiber angles (0^o,45^o,90^o).	The thermal conductivity of the composites increases with increasing fiber angle
8	Surface Treatments of Fibers (STF)	Ravi et al. (2018)	Various natural and synthetic fibers	Fiber surface treatments improve interfacial adhesion between fiber surface and matrix

9		Adekunle (2015)	Natural Fibers	which enhances good mechanical properties of polymer-based composites.
10	Effect of Agglomerations	Teja et al. (2016)	Fabricated sisal fiber polymer composites by hand lay-up method. Three different samples with 0%, 5%, 10% SiC powder were considered .	Addition of SiC filler powder, thermal conductivity increased, specific heat capacity gradually increased
11		G.U. Raju and S. Kumarappa (2012)	Composite boards were fabricated with the different weight percentages of groundnut shell particles (the combination of smaller particle size of 0.5 mm with a higher weight (%) of filler material 80%)and epoxy resin.	Thermal conductivity of composite specimens ranges from 0.07638 to 0.3487 W/m-K and linear thermal expansion varies from 0.725×10^{-6} to 1.296×10^{-6}/°C.

2.8 Effect of Filler Material on Mechanical and Thermal Behaviour of Composites

Polymer matrix composites are prepared as per requirement by adding filler in a matrix material. These fillers' enhance the various properties like wear-resistance and hardness, cost reduction, control of thermal expansion, density control, etc. Recently ceramic or metal particles are used as hard fillers while glass is used as the fiber filler to improve the wear resistance up to two to three times stated by Sawyer et al. (2003) In the various industrial applications such as heaters, electrodes, thermal durability at high temperatures, polymer matrix composite with metal particles as filler are used (Kim et al. 2004). Silica particles are used to form a composite to improve thermal, electrical, and mechanical properties of the fabricated composite Nielsen L.E and Landel R.F.,(1994), Srivastava et al. (1988), researched the fracture toughness of the epoxy resin and concluded that by adding fly ash particles as filler, enhancement in the toughness of composites was observed. It also affected the tensile properties according to size and interfacial bonding.