A Review on Thermal Properties of Hybrid Polymer Matrix Composites

Gurushanth B Vaggar¹*, S C Kamate², Rithesh Shetty³.

¹Research Scholar, Alva’s Institute of Engineering and Technology, Mijar, Moodbidri, Visvesvaraya Technological University, Belagavi, Karnataka state, India.
²Principal Hirasugar Institute of Technology, Nidasoshi, Visvesvaraya Technological University, Belagavi, Karnataka state, India.
³UG student, Alva’s Institute of Engineering and Technology, Mijar, Moodbidri, Visvesvaraya Technological University, Belagavi, Karnataka state, India.

E-mail: gvgr.aiet@gmail.com

Abstract. The requirement and demand of hybrid polymer composites increasing in every filed of applications day by day due to low weight high strength. Since the polymers have found low thermal properties and low strength to high temperature conditions, similarly glass fibre reinforced epoxy resin composites are high strength and stiffness but poor in thermal stability and easily degrades at high temperatures. Which encourages to enhance thermal properties to increase the thermal stability of glass fibre reinforced epoxy resin composites without compromising the strength and stiffness, solution of that is adding high thermal conductivity filler particles to glass fibre reinforced epoxy resin composites, increases the thermal stability and thermal resistivity.

1. Introduction
Most of the polymers are low thermal conductivity, low thermal and heat resistant and high coefficient of expansion, to improve their thermal stability and thermal properties, fibres and fillers are used in neat polymers to develop hybrid polymer composites. The complete review on hybrid polymer composites concentrated on enhancement of thermal property and thermal stability.

1.1. Polymers
Polymer matrix are of two types as given below.

a) Thermoplastics: Materials made by intermolecular linear polymer structures are called thermoplastics. Thermoplastics are excellent elastic property, poor strength to high load. Melting of thermoplastics gives the restructure to intermolecular polymer structures. The linear structure chemical bonds loses their strength to high temperature exposure. Thermoplastics soften or fuse when heated, harden and become rigid after cooling. Unlike thermosets, thermoplastics can be modified or reused upon the need. Thermoplastics have longer shelf life and higher fracture toughness than thermoset resins. Thermoplastic resins have high viscosity and less creep resistance when compared to thermosets. Examples of thermoplastics are Polyethylene, Polystyrene, Polyamides and Nylons.
b) Thermosets: Materials with more number of crosslinked structure made by polymer matrix with highly chemical bonds are called thermoset materials. Due to high crosslinked structure thermosets are stronger than thermoplastics and poor in elastic property. Once the thermosets are transferred from liquid to solid state during the solidification, can’t bring back to liquid form due to non-ability of recycle. Examples of thermosets are Epoxy, Polyester and Phenolic polyamide resins. Epoxy resin has excellent adhesion property and mechanical properties compared to other resins. Epoxies are expensive compared to polyester and less resistant to moisture. Polyester has the advantages of low cost, ease of handling, good chemical resistance with reasonable mechanical properties. Polyester and epoxy makes approximately 85% of the fibre reinforced polymer composites.

Polymer matrix composites have advantages, high strength in tensile, Stiffness more, Fracture due to toughness is high, Resistance due to abrasion is good, Resistance due to puncture is good, Good resistance against corrosion. Polymer matrix composites also have certain disadvantages, Resistance against thermal conditions is low, Thermal expansion coefficient is high, Methods of developing composite materials are slow in nature.

1.2. Resins
Thermoplastic materials are formed by addition polymerization. Thermoplastics soften or fuse when heated, harden and become rigid after cooling. Unlike thermosets, thermoplastics can be modified or reused upon the need. Thermoplastics have longer shelf life and higher fracture toughness than thermoset resins. Thermoplastic resins have high viscosity and less creep resistance when compared to thermosets. Epoxy resin has excellent adhesion property compared to other resins and have excellent mechanical properties. Epoxies are expensive compared to polyester and less resistant to moisture. Polyester has the advantages of low cost, ease of handling, good chemical resistance with reasonable mechanical properties. Polyester and epoxy makes approximately 85% of the fibre reinforced polymer composites. Vinyl ester offers good mechanical properties and excellent corrosion resistance. The bonding ability of vinyl ester is good to glass fibre but less efficient with carbon or Kevlar. Phenolic resin cures through condensation reaction, which produces water during the reaction.

1.3. Additives
Additive materials are primarily used to modify and tailor material properties of the composite. By introducing additives into resin system it enhances the processability or durability of the composite. Additives help in increasing the performance or a specific property as well it increases the overall cost of the product. Various additives widely used to boost the thermal and electrical conductivity of the resin are graphite powder, chopped carbon fibre, carbon nano-tubes, SiC nanoparticles, Cu nanoparticles etc.

2. Composites by polymer matrix
Composites made by polymer matrix is the material comprising of a polymer matrix mixed with fibres dispersed by reinforcing method. Simple methods of fabrication with economical cost made polymer matrix composites more popular. Polymer matrix composites possess lightweight, have good mechanical strength and properties, reinforcement occur in wet well which leads to good adhesion. Polymer reinforced composites are low-density materials.

Matrix is the continuous phase and surrounds the reinforcements. The role of matrix is to transfer equal amount of stresses to fibres and fillers to protect them from surroundings and environment.

Reinforcement is the distributed fibres which enhances the matrix properties. In polymer matrix composite (PMC) materials the basic constituent (the matrix) contribute at least 45% by weight. The materials used as a matrix in PMCs are usually Epoxy resin, Polyester, Phenolic polyamide resins. Glass Fibre, Carbon Fibre, Aramid are used reinforcement materials in PMCs.

The widely used thermoset polymers are epoxy resin due to low shrinkage, less moisture absorption, excellent interface, quick curing, high strength stiffness, good mechanical properties and
Easy to process at RTP (room temperature and pressure). Epoxy resins are strong in bonding at low pressure curing [1].

The matrix used in FRPCs are continuous phase, may be metal, ceramic or polymer. Ceramics are high strength and brittle, polymers have low strength, metals matrices have moderate strength and ductile in nature. Glass fibre with chopped strand mat (CSM) are suitable for FRPCs due to intact held with matrix [2].

3. Polymer matrix composites manufacturing methods
Polymer composites are manufactured by various methods as shown below.

3.1. Hand Layup Method
It is one of oldest and simplest method to manufacture polymer composites. Polymer matrix, fibres are used in desired shape of moulding box, laid down the one by one layer of fibres into the mould box by applying the required amount polymer matrix on every layer of fibres. To avoid stickiness a non-stick material is applied on to the surface of mould box before placing the fibres and polymer matrix. Curing takes more time to settle down for solidification, accuracy in dimensions and shape lies on skill of worker.

3.2. Compression Moulding Method
This method of manufacturing composites is used for similar kind bulk composite materials by compression moulding technique. Compression moulding machine is designed in such a way that it consists of two parts one is male and another female, fibres and polymer matrix together placed in a female part of a mould box and male part is placed above the female part. Then apply the desired amount of pressure by using hydraulic press and allow cure at normal temperature and pressure. After curing remove the composite material from mould box. This method is more suitable for automobile applications.

3.3. Resin Transfer Moulding (TRM) Method
This manufacturing method uses a mould with an inlet to introduce resin/catalyst mixture and vent ports to allow air to escape. In this method, resin and catalysts are mixed proportionally in an injection head and then pumped into the mould. Dry reinforcement is placed inside the mould and is closed. Required amount of resin is pumped to the mould and allowed to cure under atmospheric condition. After composites are removed from the mould. RTM has been further modified by using vacuum to suck resin catalyst mixture inside. In this case, vacuum bags are used along with moulds enhances resin flow and reduces void fraction. RTM process is cleaner with less emissions of volatiles. The applications of this process includes manufacturing of auto body panels, swim pool panels, sandwich panels etc.

3.4. Pultrusion Method
Pultrusion is a continuous and highly automated moulding process used for manufacture of similar kind of composites in mass production. Reinforcement materials are arranged in such a pattern so that they match the profile of the die. The fibres are pulled through a resin bath and then to the heated metal pultrusion die. The die is maintained at a précised temperature so that it can transfer heat to polymer matrix and fibres. The heating process is used to carry on the polymerization of the resin to matrix. The cooled solid part is then pulled from the die and cut to desired length. Applications of this process are in the fields like construction, transportation, electrical etc. A detailed method of manufacturing hybrid polymer composites shown in figure 1.
4. Thermal property of hybrid polymer composite materials

4.1 Thermal Conductivity

For various applications designing and developing of hybrid composites, a study of thermal behaviour needs to be consider under varying conditions. The thermal property variations are nonlinear in hybrid composites, it is very difficult to identify and predict the temperature behaviour of these materials with unknown thermal conductivity. However, thermal conductivity measurement of hybrid composite materials is not an easy task due to temperature variations complexity [3]. Addition of Silicon carbide filler particles to the neat epoxy polymer composites increases thermal conductivity as the volume fraction percentage increases; 20% and 30% SiC filler particles have shown 0.41 and 0.51 W/m K thermal conductivity respectively. Thermal conductivity of silicon carbide alone is very high as compared to hybrid composites, silicon carbide epoxy resin composites exhibit low thermal conductivity due to size of filler particles are smaller. However, they are not useful in generating conductive paths [4]. Hence, electronic devices are going to fail because of inadequate cooling. Durability and performance of electronic devices depends on the limit of specified operating temperature range. The high performance of semiconductors depends on the accurate thermal management [5].

The advantage of using HPCs depends upon the filler materials which give highest thermal conductivity. Hybrid nano-filler modified polymer matrices have created wide opportunities in research to achieve excellent thermal and mechanical properties for advances in many fields of applications. The commonly used nanoparticle-fillers are carbon nanoparticle-filler, carbon nanotubes, nano clay and silicon carbide fibres [6]. Since polymers have low thermal conductivity, an effort has been made to increase thermal conductivity and electrical resistivity of polymers by adding boron nitride, silicon carbides, glass Fibre, mica, aluminum nitride, alumina and zinc oxide fillers [7]. Improved Fire resistance and more thermal stability is found in silica hybrid composites, due to high strength of interfacial bonding of silica particles and epoxy resin [8]. The addition of graphene nano-plates (1% weight) increased thermal conductivity and the enhancement was significant due to homogenous dispersion of graphene nano-plates in the epoxy polymer matrix and internal bonding. Thermal conductivity improvement is 33.3% for 1% graphene nano-plates compared to plain epoxy resin [9].

On comparison of experimental thermal conductivity for the particulate filled polymer composites with theoretical mathematical models, such as parallel thermal conductivity model, maxwell thermal conductivity model and rule of mixture thermal conductivity model, all the three mathematical models
and experimental results have been reported to be close to each other at low % fibre content. They observed that experimental thermal conductivity and theoretically calculated values increase with increase of fibre content; the errors associated with Maxwell model, Parallel model and Rule of mixture model compared to experimental values lie in the range of 31 to 75.2%, 28.5 to 73.2% and 33.25 to 79.2% respectively [10]. Further, thermal conductivity and thermal stability of polymers composites can be enriched by making them hybrid polymer composites by adding fillers such as CNT, graphene, copper powder, copper mesh in carbon fibre reinforced polymer (CFRP) [11].

4.2 Coefficient Thermal Expansion.
Coefficient of thermal expansion improves for 5% weight multi walled nanotubes added in polyurethane composites and thermal degradation temperature improves from 409°C to 421°C [12]. Hybrid composites prepared with epoxy resin, glass fibre, fly ash, stone powder and silicon carbide in a 50:50 matrix fibre and 5% & 20% fillers in weight proportionate. From thermal experiments it is observed that glass fibre epoxy resin (GFER), GFER + silicon carbide 5% and GFER + silicon carbide 20% shows high thermal conductivities compared to other composites, but GFER + fly ash 5%, GFER + silicon carbide 20% and GFER + stone powder 20% exhibits low CTE when compared with other composites [13]. Use of hybrid fillers (Aluminium nitride, Silicon carbide, Boron nitride) in polymer composites was found more effective in decreasing the coefficient of thermal expansion [14].

4.3 Thermogravimetric Analysis.
The composites made by polyester resin, glass fibre and jute fibre undergone thermogravimetric analysis and found that the composite PO77-JU23-V10 (polyester 77% + Jute 23% + glass fibre 0%) without glass fibre lost more mass in function of temperature and the composite with more percentage of glass fiber PO56-JU21-V12 (polyester 56% + Jute 23% + glass fibre 23%) lost less weight with increasing temperature[15]. The TGA comparison of glass fibre composite, Carbon fibre composite and hybrid polymer composites, the thermal stability of hybrid composites found better [16]. The TGA of PMMA toughened glass-epoxy composite shows higher mass loss whereas SiC addition retains the temperature stability [17]. Several graphene-based nanomaterials including graphene oxide (GO), reduced graphene oxide (rGO), graphene nanoplatelets (GNPs) and multi-walled carbon nanotubes (MWCNTs) were used to modify the epoxy matrix and the surface of glass fibres. The results indicate that the introduction of GNPs, GO, rGO, and MWCNTs enhance thermal conductivity. The thermal conductivity of two-phase epoxy/nanoparticle composites was increased by up to 6.0% for 1.2 wt. % of GNPs in GFER composites [18].

4.4 Effect of filler materials on glass transition temperature of polymers.
Micro and Nano filler particles using in epoxy resin glass fibre (ERGF) composites are the reason in glass transition temperature (GTT) rise of hybrid polymer matrix composites. As the GTT of polymers lies in the range of 90°C to 120°C, and thermogravimetric analysis tests are conducted at a temperature range from 200°C to 300°C or more and is much higher than the epoxy resin glass transition temperature (GTT), filler particles thermal conductivity values are higher compared to glass fibre and epoxy resin, which causes the polymer hybrid composites bear higher temperature than that of GTT of neat polymers, individually no effect on GTT of polymer matrix in addition of percentage volume fraction of filler particles and fibres but as a whole polymer hybrid composites GTT improves in comparison with neat polymer matrix.

Adding higher thermal conductivity value fillers to epoxy resin glass fibre (ERGF) leads to delink the covalent bonds of polymer matrix and allows fillers to disperse evenly in epoxy resin Fibre reinforced composites, which in turn increases the thermal conductivity and thermal stability. Fillers are added in small percentages either in volume fraction or weight fraction 5%, 10%, 15%, 20%, 25% and 30% so on. The shape of fillers may be in spherical, flakes, tubes, and whiskers. Minimum size of fillers added in microns and advanced study of composites shows Nanoparticle fillers more effective in hybrid polymer composites. The effect of thermal properties varies with respect to the use of fibres and filling materials. The orientation of fibres, additives, size of fillers and type of resins will affect the Thermal conductivity, Coefficient of thermal expansion and thermal stability with respect to high temperature. Some composite are also tested for low temperature for structural stability.
Table 1. Thermal Characteristics of glass fibre epoxy resin reinforced hybrid composites

| Matrix | Type of fibre | Powder filler | Powder filler Vol.% | Mixing method | Technology | Improved properties | Reference |
|--------|---------------|---------------|---------------------|---------------|------------|---------------------|-----------|
| Epoxy / PMMA | E-Glass | SiC | 0.5% and 1.0% | Mechanical stirred with epoxy | Hand layup | Thermal stability increases | [17] |
| Epoxy / LY556 | E-Glass | Al₂O₃, Mg(OH)₂, SiC | 10% and 15% | Mechanical stirred with epoxy | Hand layup | Thermal conductivity, Coefficient of thermal expansion and fire resistance | [18] |
| Epoxy / Hardener | E-Glass | MWCNTs, GO, rGO, GNPs. | 1.1% to 5.5% | Mechanical Stirring at 400 rpm | Vacuum Assisted Resin Transfer Moulding (VARTM) | Thermal conductivity and thermal stability | [19] |
| Epoxy resin(L12) / Hardener | E-Glass | Fly ash, Stone powder, SiC. | 5% and 20% | Mechanical stirred with epoxy | Hand layup | Thermal properties (Thermal conductivity, CTE, Specific heat) Overall thermal properties | [13] |
| polypropylene | --- | CNT, SND, BN, Cu. | 4% | Mechanical stirred with polypropylene | Compression moulding using mould box | | [20] |
| HDPE | --- | Silicon particulates | 5%, 10%, 15% and 20% | Mechanical stirred with HDPE | Compression moulding using mould box | Thermal conductivity, CTE, TGA | [21] |
| E-51 Matrix / MeHHPA / DMP-30 | --- | GNPs, | | Mechanical Stirring | Compression moulding using mould box | Thermal conductivity. | [22] |

Conclusions
Thermal property characterization of polymer hybrid materials provides the information about withstanding and sustainability of polymer hybrid composite materials under steady, transient temperature conditions it may be low or high temperature exposure conditions. Thermal properties and thermal characterization study of hybrid polymer composites with various fillers volume fractions.
navigates importance of decomposition temperature, increase or decrease of thermal conductivity value and CTE variations. Without altering the basic strength of composites, improve or enhance the thermal properties of composite materials by adding fillers to make them hybrid composites. The failure analysis of advanced composites are having more complexity due to various reasons, failure may takes along or across the fibre, failure may occur micro level cracks in Fibre or matrix, fibre debonding with matrix due to environmental and high range of temperature variant conditions makes difficulty of identifying and finding the solution to micro level failure of advanced composites, encourage to work more in improving the thermal stability and thermal properties of composite materials to reduce the failure percentage.

References
[1] M. K. Gupta, American Journal of Polymer Science & Engineering, (2018) ISSN 2572-5734, Volume 6, Issue 1.
[2] R Ambigai and S Prabhu, Materials Science and Engineering 402 (2018) 012136
[3] Dilek Kumlutas et al. Composites Science and Technology 63 (2003) 113–117, Elsevier.
[4] Krishnamuchar Srinivas and Mysore Siddalingappa Bhagyashkehar, Journal of Minerals and Materials Characterization and Engineering, 2015, 3, 76-84.
[5] Th. Schubert, et al, Advanced Materials Research Vol. 59 (2009) pp 169-172.
[6] Naveen Jesuarockiam et al, Polymers 2019, 11, 1085.
[7] Watthanaphon Cheewawuttipong et al, Energy Procedia 34 (2013) 808 – 817.
[8] Dongho Kim et al, Fibers and Polymers 2013, Vol.14, No.12, 2141-2147.
[9] Minh-Tai Le and Shyh-Chour Huang, Materials 2015, 8, 5526-5536.
[10] Daniel J. Thomas, J Fail. Anal. and Preven. (2016) 16:513–514.
[11] Rakesh S et al, International Journal of Advance Research, Ideas and Innovations in Technology, Volume 4, Issue 5, ISSN: 2454-132X, 2018.
[12] Dinesh Kumar and Prashant Jindal, Materials Research Express 6 (2019) 105336.
[13] Ravi Kumar B N et al. International Journal of Mechanical Engineering Research & Applications. ISSN: 2347-1719, Vol. 1 Issue 4, September – 2013.
[14] Geon-Woong Lee et al, Composites: Part A 37 (2006) 727–734, Applied Science & Manufacturing, Elsevier.
[15] Braga, R. A et al. Int. Journal of Engineering Research and Applications, ISSN: 2248-9622, Vol. 5, Issue5, (Part -2) May 2015, pp.113-118.
[16] Bhasker Bommarra, et al, International Journal of Mechanical Engineering and Technology, International Journal of Mechanical Engineering and Technology, ISSN Print: 0976-6340 and ISSN Online: 0976-6359.
[17] V Ravi Raj and B Vijaya Ramnath, Springer Nature B.V. 2020, doi.org/10.1007/s12633-020-00580-5.
[18] K.Devendra and T. Rangaswamy, International Journal of Computational Engineering Research (ijceronline.com) Vol. 2 Issue.5, ISSN Online: 2250-3005. (2012).
[19] M. Rafiee et al, Composites Part B (2018), https://doi.org/10.1016/j.compositesb.2018.11.051.
[20] MS Nurul and M Mariatti, Journal of Thermoplastic Composite Materials, 26(5) 627–639, DOI: 10.1177/089270571427345.
[21] T.K. Dey and M. Tripathi, Thermochimica Acta 502 (2010) 35–42, doi:10.1016/j.tca.2010.02.002.
[22] Junwei Gu et al, International Journal of Heat and Mass Transfer 92 (2016) 15–22