Review Article

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A review on allotropes of carbon and natural filler-reinforced thermomechanical properties of upgraded epoxy hybrid composite

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Abstract: The scarcity of nonrenewable resource motivated inclination towards the environmental-friendly novel materials and development of waste natural filler-based hybrid composite is encouraged to fulfill the material demand. Epoxy resins-based composites are high-performing thermosetting polymers and have outstanding blending properties, good machinability, and low cost. Due to these advantages, thermoset plastic is largely used in a broad range of engineering applications; however, thermomechanical properties of neat epoxy are low. Thus, to enhance the thermomechanical properties of epoxy, it is interfaced materials such as graphite, graphene nanoplatelet, boron, carbon fiber, aluminium, silver, etc. Among various substances, graphene has been deliberated as an acceptable novel filler because of its exceptional properties. In addition to inorganic filler inclusion, natural filler/fiber like hemp, sisal, flax, bamboo, jute, etc. can be utilized in a higher percentage as biodegradable material. The present article assisted to improve thermomechanical properties of neat epoxy. This work identifies and addresses (i) processes used for graphene modification; (ii) treatment utilized for enhancing the binding properties of natural filler; (iii) various natural filler extraction process employed; (iv) neat epoxy modification; and (v) influence of different dimensions of fillers.

Keywords: thermomechanical properties, waste product, natural filler/fiber, graphene, hybrid composite

1 Introduction

In the era of twenty first-century, advanced materials play a significant part in the area of technology such as engineering, medical science, power sector, aerospace, and many more. A rigorous development of current materials is essential with better-quality belongings, so that these advanced materials may be utilized further in various applications [1]. Plastics have lots of advantages, like low weight, low price, ease of machinability, and displaying decent erosion resistance compared to metal. However, their practical application is minimum because of low mechanical and electrical properties and poor thermal conductivity [2]. Among the existing diverse type of materials, plastic is one of them with specific physical properties, in relation to temperature polymer considerably divided into thermosetting and thermoplastic. Thermosetting polymer does not deform much with the influence of temperature. Formation of thermoset polymer is achieved due to the cross-connected reaction of two monomers. Thermoset polymer is found with better physical properties like mechanical strength, hardness, and thermal constancy when correlated to the thermoplastic [3]. Frequently, pure polymer shows very poor glass transition temperature and low thermal conductivity with the range from 0.1 to 0.5 W/m × K, due to its amorphous state of nature. There are three energy transport carriers in various materials: phonons, photons, and electrons. Phonons were leading heat carrier for improving thermal conductivity in polymers. Because of the amorphous nature of polymers, they have a proportion of defects that lead to phonon scattering, which contribute to low thermal conductivity in polymers [4]. Nevertheless, with the reinforcement of nanoparticle to polymer, it exhibits extraordinary properties in the polymeric composite material. Nano-sized reinforcement inclusion has been more traditional in the recent past years. Different high thermal conductivity filler materials have been added like copper, aluminum, diamond, silver, aluminum oxide, zinc oxide, boron nitride, carbon

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nanotube, natural graphite, graphene, and graphene nanoplatelet to the thermoset polymer. Among these different types of filler materials, graphene and various forms of graphene were found to be quite interesting substances that can be used to enhance mechanical and thermal properties of neat thermoset polymers. Micro- and nano-sized particulate filler reinforcement is found to be more attractive, as the addition of these particulates to neat polymer enhances the thermomechanical properties to new stage [5].

With the emergent environmental awareness, proper utilization of eco-friendly natural fiber and fillers is essential by replacing artificial filler/fibers. As a result of easy availability of natural filler/fibers, utilization of natural filler/fiber as a reinforcement mediator emerged in the application of science and technology [6]. The utilization of million tons of power form of natural dust produced as waste product can be utilized in useful work. The improved consciousness about the use of natural filler and fibers in the development of hybrid composite materials replaces and fulfills the novel materials' demand in the field of engineering application. Therefore, it's a matter of anxiety to the indication that evaluates status and put forward the struggle for additional sustainable and feasible use and further expansion of unique materials [7]. The properties of fiber and filler-reinforced composites differ significantly and depend upon their fundamental material constitution, fiber volume, orientation, and filler disproportion in the matrix. However, a precise information about material properties is required for obtaining desired materials that are to be implemented for developing hybrid composite. Thermal conductivity is the material property which describes capability to transfer heat and also helps to encourage the temperature deviation inside the composite materials during specific operations [8]. Enhancing the thermal property of this epoxy-based polymer at present is considered to be challenging. An attempt to improve both the mechanical and thermal properties of these epoxy-based hybrid composites is essential for replacing the outdated appliances for better efficient result [9]. The usage of high-density metallic material is exchanged by high-performance polymer-based composite in automobile, electronic and aerospace application, and marine industry for fulfilling the necessity.

Here, the state-of-the-art hybrid composite constituents are investigated to improve thermomechanical properties of composite materials.

- (i) Through considering and investigating various modifying treatments that can be suitable to implement different types of natural fiber/fillers, and different extraction methods for natural fiber, modified filler/

fiber creates a stronger chemical bonding with the neat epoxy for developing hybrid composite.

- (ii) Different modifying techniques are also discussed to enhance the crosslink bonding of virgin epoxy monomers that are suitable for preparing a hybrid thermosetting composite.
- (iii) The combined effect of treated filler/fiber and functionalized high thermal conductivity graphene in the modified epoxy resin improves thermomechanical properties of hybrid composite.
- (iv) Influence of micro- and nano-sized fillers is able to reach inside the interior spacing gaps of cross-linked fibers and improve the crosslinking bonding by minimizing the void content.
- (v) Effect of various dimensions, viz., 0D, 1D, 2D, and 3D nano-fillers' inclusion in epoxy and filler/fiber-based hybrid composite.

2 Graphene synthesis

Graphene synthesis is usually carried out with various processes; mostly, top-down and bottom-up methods are adopted during production. In top-down method, separation of graphene nanosheets from graphite or graphite oxide is done. Scotch tape approach is used to peel off single or multilayer graphene. This approach is not appropriate for mass production; investigators explored for mass production of graphene using different methods using chemical reduction, thermal reduction, mechanical exfoliation, and liquid phase exfoliation. For mass production, liquid phase exfoliation is suitable compared to thermal and chemical reduction. All these reduction methods of graphene have more or less structural defects [10,11].

In the bottom-up method of graphene making using building blocks, different bottom approach techniques include chemical vapor deposition (CVD), epitaxial growth on substrate, and carbon nanotube unzipping. Better superiority graphene can be produced over different metal substrates like Ni and Cu used for CVD. CVD yields graphene sheets without any flaw, but this approach doesn't have much potential for mass scale production [12]. The epitaxial growth method of graphene is carried out on the insulating material; on silicon carbide surface, single and multilayer extraordinary feature of graphene is produced. Epitaxial growth approach is a small yield, more costly, and processed under a higher temperature state [13]. Carbon nanotube unzipping method

is appropriate for graphene nanoribbon production. Nanoribbons have various application in the field of electronics, composite materials, solar cell, etc., at a nominal cost [14].

2.1 Surface modification of graphene

Graphene has extraordinary properties like high carrier electron mobility [15], unique electrical properties [16], mechanical strength [17], larger surface area [18], extraordinary transparency [19] and higher thermal conductivity [20]. It has various applications in the field of the electronic touch screen, fuel cells, sensors, high-frequency electronic circuit, toxic substance separator, and flexible electronics [21–25]. Graphene-based design of nanostructure is open to the new area of research in the field of biotechnology and DNA sequencing [26–28]. The functionalization of graphene is essential due to high demand in various fields of science and technology. Many researchers have carried out functionalization of graphene with organic, inorganic reaction and chemical treatment for enhancing the graphene surface area [29,30]. Also, the band gap of graphene layer can be improved from zero band gap to higher by the method of doping and intercalation, which will mostly help electron movement in the electronic and conductive devices [31,32].

Graphene shows essentially high thermal conductivity and better mechanical properties; however, properties

diminish when mixed with polymers, which can be chemically modified to boost up the agglomeration with polymer or epoxy [33]. The unmodified graphene does not have much better dispersion compared to modified graphene. Development of chemical treatment of graphene directly encourages the new era towards composite materials [34]. For treatment of graphene and graphene nanoplatelets, graphene oxide is prepared with diverse functional groups such as hydroxyl, carboxyl, amino, bromine, and long alkyl chains [35]. These chemically treated graphene substances have been providing well dispersion in different kinds of polymers, to upgrade material properties [36–39].

2.2 Covalent functionalization

Among the different approaches of graphene synthesis method, oxidation of graphite and subsequently chemical treatment was adopted for large-scale production. However, the presence of secondary van der Waals force is found in graphene reduction process; hence, reducing interfacial binding force between graphene and epoxy is also found. To withdraw these strong forces, chemical modification of graphene is required. Chemical treatment of graphene is accomplished by the covalent and non-covalent modifications shown in Figure 1, for improving properties of thermosetting-based nanocomposites

Figure 1: Classification of graphene modification.

application [40]. A different method has been attempted to attain a high rate of graphene distribution. The main motto of functionalization of pure graphene is the development of graphene-based nanocomposite. Attachment of chromophores' functional group to graphene leads in improvement of thermal conductivity of composite material. Organic group attachment on the surface of graphene spreads aromatic character is disturbed. Graphene sheets are functionalized with *p*-nitrobenzediazonium tetrafluoroborate and improve the surface roughness of pristine graphene sheet [41]. Organic covalent bond of graphene is formed by (i) covalent bond among free radicals or dienophiles and C≡C bonds of pristine graphene; and (ii) The covalent bond among organic group and graphene oxygen group. Addition of diazonium salt (free radicals) to the sp²-hybridized carbon of graphene forms a covalent bond. Graphene nanoribbons are treated with 4-nitrobenzene diazonium tetrafluoroborate, to give prominence to the electronic properties of functionalized graphene. Diazonium salt treatment results in declining the conductivity because of aromatic group transformation [42–44]. The graphene nanosheets' surfaces are covalently linked via diazonium salt with successive atom transfer radical polymerization (ATRP) bonding which improves glass transition temperature nearly 15°C, along with the tensile strength 70% improved and Young's modulus 57% increased [45]. Further at 18°C, improvement in the glass transition temperature of single-layer graphene nanosheets is observed with varying concentrations of diazonium salt succeeding ATRP in polystyrene-grafted graphene nanocomposite [46]. To the single-layer graphene sheet, free radical addition is carried out with the addition of benzoyl peroxide. Reduction in conductivity is found due to higher sp³ carbon bond after covalent bonding [47]. With free radical addition to graphene, dienophiles react to carbon bonds of graphene. Functionalization of graphene is mostly done with 1,3-dipolar cycloaddition. This modified graphene is found suitable in wide range of applications like polymer composites, solar cells, and flexible electronic device and in the field of biotechnology [48–50]. The graphene sheet is simply emulsifiable in polar aqueous solvent and water after chemically treated by 1,3-dipolar cycloaddition of azomethine ylide. The chemical reaction changes radical structure of graphene sheet which makes mixing and combination process easier. The AFM image indicates the increase in the graphene nanosheet owing to the presence of functional groups on the surface [51]. It's flexible to react with numerous aldehydes or amino acids as the predecessor consequently creates diversity in the functional group. Pristine graphene-TPP (tetraphenylporphyrin) and graphene-pdTPP (palladium

tetraphenylporphyrin) are easily finished by one-pot cycloaddition chemical reactions.

The TGA result of grapheneTPP and graphene-PdTPP showed weight loss around 18 to 20% in the temperature range 250 to 500°C, when compared to pristine graphene [52]. Few-layer graphene is treated with 1,3-dipolar cycloaddition of azomethine ylides which is greatly functionalized for the manufacture of nanocomposites. The existence of the organic group is confirmed by TGA and TEM analysis and indicates the attendances of Au-nanorods' homogeneously dispersion [53]. For covalent modification of pristine graphene, it is treated with perfluorophenylazide (PFPA); the functional groups with the addition of molecules create a good opening in the composite material, nanomaterial fabrication [54]. With anthraquinone (AQ) aqueous solution, graphene sheet is treated for oxygen reduction. TGA result confirmed the attachment of the functional group to a graphene sheet; weight loss is detected near about 300°C due to decomposition of the organic group [55,56]. To encourage a homogeneous distribution of graphene in poly(styrene-*co*-maleic anhydride) PSMA, graphite oxide (GO) is modified with 3-aminopropyltriethoxysilane (APTS). Functionalized graphene oxide is formed which is confirmed by FTIR, XPS, and TGA [57]. The conductivity is improved 4 times when graphene is covalently modified by Cr(CO)₆ and increases by 2 times with Cr(η⁶-benzene)(CO)₃ reagent. Organometallic chemistry has a good prospect in the new composite material production [58]. The surface modification of graphene oxide (GO) and reduced graphene oxide (rGO) is carried out with a carboxylic acid; this synthesized GO-COOH and rGO-COOH; further, these are catalyzed with molybdenum on the surface of carboxylic group. The catalyst reaction supports high rate dispersion in the hydrophobic nature of epoxy [59].

A new approach for the molecular welding fabrication is adopted to grow thermal conductivity of graphitized-graphene/polyimide (g-GO/PI) film. After the graphitization defect in graphene sheet is established, phonon transference is troubled. The functional group C–O–C or –COOH is decomposed and forms C–N–C or –CONH covalent bond when countered with an amine group in polyimide (PI). The presence of PI in a graphene sheet enhances the phonon transportation by increasing the grain size of graphene; thus, thermal conductivity is improved in the graphene sheet. The in-plane thermal conductivity of g-GO/PI-1% film improved around 21.9% then pristine graphene [60–62]. The chemical modification of graphene is of crucial importance to advance composite manufacturing. Graphene is covalently functionalized with porphyrins or phthalocyanines; the study was focused

on energy transfer and electron transfer is highlighted [63]. Functionalization of few layers of graphene is done under different arynes in microwave irradiation; this approach is a fast and efficient way of covalent modification as presented. TGA result displays the significant deviation in graphene functionalization subject to a number of cycles. Modified few-layer graphene with arynes is decomposed around 200°C; five cycle modification is accepted as a standard approach to achieve functionalization degree as per the experimental result [64]. rGO is treated with 3-amino-1,2,4-triazole (TZ) in potassium hydroxide (KOH). KOH acts as reducing agent and used as a catalyst between graphene oxide surface and TZ for nucleophilic addition. From TGA analysis, TZ functionalized GO (TGZ) showed 5% weight loss at around 250°C; it makes clear that oxygen functionalities are removed from GO during the chemical treatment [65]. To improve the lubrication of mechanical components, graphene quantum dots (GQD) are produced. Dodecyl amine was used to modify the few layers of graphene oxide. These functionalized quantum dots are highly soluble in organic solution, ethers, methanol, toluene, and heptane and also have thermal stability of nearly about 220°C. GQD is applied as spray on the steel surface, resulting in a reduction in the coefficient of friction from 0.17 to 0.11 and also improves the corrosion of materials [66]. Graphene oxide nanosheets (GONs) of different sizes of 0.85, 8.2, and 38 μm were covalently treated with *p*-phenylenediamine (PPDA). These functionalized graphenes are mixed with polyamine epoxy for composite material production. The result showed GONs particles less than 1,000 nm in epoxy prominently increase mechanical properties, anticorrosion. The thermal stability does not depend much on the lateral size of graphene oxide. The increase of storage modulus was observed from the dynamic mechanical analysis, as modified GONs fill the free space, void, and pores [67].

Graphene oxide nanosheets are covalently treated with (3-glycidyloxypropyl) trimethoxysilane and characterization of both treated and untreated is carried out. TGA, dynamic mechanical thermal analysis (DMTA), and tensile test were executed. The results of tensile stress, storage modulus, and energy at break were improved significantly with treated graphene oxide (TGO). Also, stability, interfacial bonding, and dispersion rate TGO were improved in polyurethane (PU) thermoplastic polymer [68]. Graphene nanoplatelets (GNPs), when covalently treated with xylitol and citric acid, GNPs' dispersion rate improvement is observed in different aqueous solutions like in water, methanol, ethanol, ethyleneglycol, and 1-hexanol. Thermal conductivity improvement is reached up to 34% with tetrahydrofurfuryl polyethylene

glycol-functionalized GNPs (TFPEG-treated GNPs) at 60°C. Also, treated GNPs with diverse concentration behave like Newtonian fluid [69]. Tetrahydrofurfuryl polyethylene glycol is used to modify the GNPs and zirconium(IV) oxychloride octahydrate is used as a catalyst and to improve the dispersion stability in water and other organic solutions. Highest thermal conductivity is found at 0.1 wt% GNPs in water and can be used as heat transfer working fluid. It will be very useful for mass production of functionalized graphene being simple, cost-effective and eco-friendly [70]. Hyperbranched polyether epoxy (HBPEE) is used for functionalization of graphene oxide sheets named as GO-HE. The composite material prepared with benzoxazine (BOZ) with GO and BOZ with GO-HE, BOZ, and GO-HE is observed with improved flexural strength, thermal stability, and impact strength at 0.05 wt% of GO-HE. The flexure modulus is also enhanced 10% when compared to neat BOZ. The significant improvement is because of the higher distribution rate of GO-HE and stronger interfacial-bonding neat BOZ and GO-HE [71]. It was clear observation that, mostly, covalent functionalization of graphene generates defects and declines intrinsic properties of pristine graphene [72].

2.3 Non-covalent modification of graphene

Non-covalent modification of graphene improves intrinsic properties without formation of any defect [73]. Non-covalent modification includes (a) cation π type interaction; (b) anion π type interaction; (c) hydrogen bonding; (d) surface assisted functionalization; and (e) π - π stacking interaction. Graphene is modified non-covalently with sodium alginate (SA); the formation of anion- π interaction is observed among SA and graphene. Modified graphene with SA improves the desorption rate in polyvinyl alcohol (PVA). Prepared nanocomposite with PVA and modified graphene ensued in substantial upgrading in mechanical properties. Tensile strength enhancement up to 103 ± 2 MPa and Young's modulus 2.8 ± 0.05 GPa with 0.5 wt% modified graphene in PVA composite [74]. Graphene nanosheets are non-covalently functionalized with sodium dodecyl sulfate (SDS) and SA. These modified graphene nanosheets are used in PVA for composite material production, and effects of mechanical properties, thermal, and crystallinity were studied. Tensile modulus and tensile strengths were 385.1 and 111.6%, respectively, improved from neat PVA with 0.5 wt% modified graphene. The SA and SDS treatment enriches thermal stability remarkably in the nanocomposite [75]. Non-covalent functionalization of graphene was

set by poly-*o*-phenylenediamine (PoPD) named PoPD-G reinforced in PI. PoPD-G showed tremendous dispersibility in different organic solvents. Raman spectroscopy observation indicated π - π interaction observed among PoPD-G. With 0.5 wt% of PoPD-G in PI nanocomposite improved 20.8% hardness, 84% storage modulus, and decreased wear rate 72.8% [76]. Graphene flakes are non-covalently treated 1-pyrenebutyric acid (PBA). These functionalized graphene flakes (f-GFs) are blended with epoxy to enrich thermal conductivity of the composite. These F-GFs are more effective with low flaw rate of graphene flakes. Addition of 10 wt% of F-GFs into epoxy matrix enriched thermal conductivity up to $1.53 \text{ W/m} \times \text{K}$ [77]. Graphene nanoplatelet is covalently treated with 1-aminopyrene prepared with the hexafluoro-2-propanol solution. Modification of graphene increased dispersion rate and interfacial bonding in the polyketone matrix [78]. Surfactant modification of graphene is an effective way to progress dispersion rate during epoxy composite fabrication. Triton X-100 (polyoxyethylene octyl phenyl ether, POPE) is utilized to improve graphene sheet compatibility in epoxy resin. Triton-treated graphene with epoxy composite improved tensile strength by 57% with 0.1 wt% loading. TGA showed a slight improvement in thermal stability when related to neat epoxy, which might be a graphene sheet barrier that reduces volatilization of composite material. Besides, composite with non-covalently treated graphene improved reinforcement and a better interface between the matrix and functionalized graphene [79]. GNPs are non-covalently treated with melamine aromatic molecule using a mechanochemical ball-milling processing. Melamine is a cost-effective non-covalently π - π stacking interaction functionalization method for graphene to progress the interfacial bonding and dispersion rate in epoxy. F-GNPs improved Young's modulus of 94.3% and tensile strength of 35.3% with 0.2 wt%. F-GNPs/epoxy nanocomposite has application in a lightweight and high-strength industrial structural uses [80].

3 Natural filler modification

3.1 Alkali acid pretreatment

Many researchers have done alkali pre-chemical treatment before doing mechanical fibrillation process. An initial alkaline treatment of natural fibers for solubilization of lignin, pectins, and other carbohydrates also helps to fragment the structural linkage between them [81,82].

During alkaline pretreatment, hemp and flax fiber of length 2 to 3 mm are shocked in 17.5 wt% sodium hydroxide (NaOH) for 2 h duration. With an aim to raise the surface area of lignocellulosic substance in order to make polysaccharides additional inclined to hydrolysis. After that, fiber is cleaned with distilled water subsequently with 1 M hydrochloric acid at 60 to 80°C for solubilizing hemicellulose content. Again, it is neutralized in distilled water followed by treatment with NaOH solution with 2 wt% for 2 h at 60 to 80°C. This dilute concentration treatment brakes the linkage of carbohydrate and lignin [83].

3.2 Enzyme pretreatment

This enzymatic treatment is used to transform and/or destroy lignin and hemicellulose with balancing cellulose content. This enzymatic treatment also reduces the rate of energy consumption with endoglucanase enzymatic treatment and exhibits better structure in wood nanofiber compared to acid hydrolysis treatment [84]. For degradation of cellulose, single enzyme is not sufficient; rather a group of enzymes is involved, as these fibers are made up of dissimilar organic compounds [85]. These degraded cellulases are classified as type A and B, also named as cellobiohydrolases, which have the potential to attack high crystalline cellulose substance. However, type C and D cellulases, similarly termed as endoglucanases, are basically desired for making disorder in the structural linkage. Plenty of researches are focused on the use of cellobiohydrolases and endoglucanases enzymatic treatment [86–88].

When softwood kraft is treated with cellulases, type A and type B enzymes improve the solids' level, which then easily pass through a high-pressure homogenizer. Also, with varied concentration of cellulases enzyme, best fibrillation of nanofiber is obtained [89]. Similarly, with OS1 biotreatment, kraft wood nanofiber is extra different than that being untreated. After doing fibrillation, nanofiber is obtained with below 50 nm diameter [90].

3.3 Liquid electrolytes pretreatment

Liquid electrolytes pretreatment is called ionic liquids treatment in which different organic salts like 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl) are used. A large amount of chloride

content in BMIMCI is highly active in breaking the hydrogen-bonding linkage present in fiber. The existence of water in the BMIMCI reduces the solubility of fiber cellulose. These cellulose content in the BMIMCI can be simply precipitated by the addition of H_2O , C_2H_5-OH , and C_3H_6O [91]. Various studies are undertaken with this ionic liquid treatment before the fibrillation process. It has been used widely for dissolving cellulose content of nanofiber [92–95]. Sugarcane bagasse is treated with BMIMCI ionic liquid to dissolve cellulose content successively by high-pressure homogenization. This results in minimization in the cellulose content to escape the clogging in the homogenizer passing. The effective result of solubilization is obtained at $130^\circ C$ with 400 microwave power supply at a ratio of 1% (g/g) cellulose to ionic liquid [96].

3.4 Mechanical modification

After the pre-chemical treatment, the treated fiber is mechanically processed to obtain micro- and nano-sized particulate. Different mechanical treatments like high-pressure homogenization, microfluidization, grinding, cyro-crushing, high-intensity ultrasonication, ball-milling, etc. during mechanical processing of nanofiber structure modification are detected. Mechanical fibrillation approach is carried out for purifying and standardizing [97–99].

3.5 High-pressure homogenization

In the mechanical high-pressure homogenization, cellulose fiber slurry moves at high pressure inside the chamber through a small nozzle. High pressure and velocity along with impact and shear force creates a shear load in the nanofibers and reduces the fiber size to micro and nano sizes [100]. High-pressure homogenization is an effective process for fiber refinement without any use of organic solution [101]. High-pressure homogenization application is suitable for different raw materials with varying nozzle diameter, pressure, and number of cycles. Clogging is a critical issue in high-pressure homogenization, in order to eradicate reduction of fiber size is carried out before allowing for homogenization. Many experiments were performed using kenaf bast, kenaf core, and kenaf stem fiber as raw materials to produce nanofibers [102–104]. Homogenization process is also used to produce nano-fibrillation from wheat straw, wood, and cotton fibers [105,106]. Refining and milling pretreatment

is done before high-pressure homogenization. Milling operation increases the inflammation properties of natural fibers in water with reduced fiber size. During refining, diluted fibers are allowed to pass through stator and rotor disks. Refining and homogenization at 50 MPa is applied to fibrillation of hard and softwood pulps [107]. Atomic force microscopy (AFM) result showed that achieved diameter of nanofibers was approximately 10–25 nm. They revealed that increasing the cycle number leads to reduction in the failure strain and softwood strength. However, scanning electron microscope (SEM) showed that refining was more proficient and faster for softwood when related to hardwood, as after 25 cycles most softwood broke where hardwood remains unbroken up to 75 cycles. Because of inner and outer fibrillation phenomenon. Internal fibrillation occurs due to the breaking of hydrogen bonds by mechanical action. And external fibrillation happens upon surface due to abrasive load [108].

3.6 Microfluidization

Microfluidization is another mechanical treatment for modification of natural fiber similar to high-pressure homogenization. In the microfluidization process, a high intensifier pump is used to raise the pressure inside the chamber for fibrillation of fiber by the application of an impact and shear load [109]. The outcome of several passing time 1 to 20 of microcrystalline done at 137.9 MPa on the morphology of nanofiber was observed. With 10 to 15 time allowing through the microfluidizer, aspect ratio enhanced in the fiber; later, increasing more than 20 passes creates a cluster of fibrils. These fibrils cluster formation is owing to the improved surface area and a higher concentration of hydroxyl group is also detected [110]. This indicates a higher number of passing through the microfluidizer greater than the surface area obtained in the cellulose fibrils. The morphological character revealed regular size dispersal of natural nanofiber achieved by microfluidization treatment.

3.7 Grinding

Grinding is an alternative approach to obtain nano-sized fiber. In grinding, mechanical modification of natural biomass is carried out by the breakdown in between static and moving grinding stones. The grinding mechanism of fibrillation is to breakdown hydrogen bonds and cell wall

structure with the shear force and individualization of fibers to nanofiber. Eucalyptus is used to produce nanofiber, by using a stone grinder, where the electrical energy input affects the degree of polymerization and crystallinity. Heat generated by friction during the fibrillation process leads to evaporation of water content and also increases the specific fibrillation energy [111]. They established that extended fibrillation may form nanowhiskers with better crystallinity from untwisted nanofibers. Furthermore, from rice straw and bagasse, nanofibers are produced by passing through the shear grinder and high-pressure homogenizer 30 to 10 cycle [112]. They observed that smaller and uniform size nanofiber can be obtained by high-pressure homogenization. However, it's incomplete to do fibrillation process using a high shear grinder and high-pressure homogenization. The significant parameter which affects the natural fiber characteristics is the number of passing through the high-pressure homogenization and grinder. After 14 cycles through homogenizer, further passing through homogenizer is not encouraged for fibrillation. Also, it is established that 10 reiterations of mechanical grinding nanofiber with regular dimension 50 to 100 nm were obtained. They also evaluated with varying the number of passing 1 to 30 in the grinding with fixed 1,500 rpm. After passing 5 times, nanofiber of 20 to 50 nm was achieved; further passing did not find many variations in the size [113,114].

3.8 Cyrocrushing

Cyrocrushing is another strategy of mechanical fibrillation of natural cellulose. During this method, water enflamed fibers are submerged in liquid nitrogen and then crushed in mortar and pestle. Production of nanofibers forms natural soybean by cyrocrushing with liquid nitrogen and high-pressure defibrillation [115]. Under transmission, electronic microscope diameter of nanofiber was found around 50 to 100 nm. The X-ray diffraction result shows 48% crystalline [116].

3.9 High-intensity ultrasonication

In high-intensity ultrasonication fibrillation process, oscillating power helps to isolate the cellulose fibers by the application of a hydrodynamic force of ultrasound. Throughout this practice, cavitation creates a powerful oscillating energy [117,118]. Numerous researchers also

worked with high-intensity ultrasonication for fibrillation from natural cellulose [119–121], with varying temperature, concentration, power, dimension, and time duration and distance from the probe tip. Improved fibrillation result was obtained by high power and temperature, whereas long fiber had a lower rate of fibrillation [122]. The combined process of high-intensity ultrasonication and high-pressure homogenization process gives enhanced fibrillation and regularity of nanofiber. Cellulose nanofibers from different kinds of plant, mined from wood, bamboo, and wheat straw, compared and characterized the chemical composition, morphology character, crystallinity performance, and thermal behavior. The extracted cellulose nanofibers from wood, bamboo, and wheat straw fibers have uniform diameter of 10 to 40 nm. However, flax fibers were irregular in dimension due to their high cellulose content. With the chemical treatment, crystallinity of fibers improved. This nanofiber was extracted by ultrasonication treatment for 30 min with 1,000 W power and 20–25 kHz [123,124].

3.10 Chemical treatment of filler/fiber

Natural fiber contains lignin which forms unproductive interfacial adhesive. Alkali chemical treatment called mercerization removes the lignin content and other unwanted materials from the natural fiber. Besides, it also reduces the amorphous content from the natural fibers bundles and makes the cellulose fiber surface rough and rigid which leads to the formation of cellulose nano-sized or micro-sized crystals. The mercerization process improves the mechanical strength like tensile and flexure of composite material and also boost fiber and matrix interlocking due to the higher surface area [125]. However, when the alkali treatment of bamboo fiber was done, more than a 15% reduction of mechanical and thermal characteristics was found in the composite materials [126]. The incompatibility nature of natural fillers with the hydrophobic matrix can be compatible with introducing an interlinking substance. This interlinking substance creates an intermediary between the filler and matrix. Technically, this intermediary substance is known as a coupling agent. Different coupling mechanisms create bonding by the formation of a weak edge, deformed boundary, wettability, and chemical-bonding reaction. Understanding the bonding mechanisms, with the use of coupling agents, is a great challenge in the composite materials. Apart from the chemical reaction between the filler and matrix, understanding the concept of morphological characteristics of the substance in the

interface, acid-based chemical reaction in interphase, interfacial free energy, and wettability also plays a significant role for enhancing the composite material features.

3.11 Mercerization treatment

Mercerization or alkaline treatment, mostly in the alkaline treatment sodium hydroxide, is used at different weight percentages to eliminate the lignin, oils, and wax from the surface of the fiber. Before using natural filler in thermosets or thermoplastics matrix, alkaline treatment can be considered for better agglomeration. With the mercerization process, disorder of hydrogen atomic bond takes place, thus increasing the surface unevenness. The consequent result of mercerization process for improving the thermal conductivity of natural fiber reinforced composite material. Abaca fiber treatment is done with 1.0 to 5.0 wt% of aqueous NaOH solution with time 5 and 30 min, respectively. Thereafter, fibers are washed with water to eliminate excess NaOH subsequently dried at 70°C. From chemical treatment, it is clarified that crystalline percentage of abaca fiber is boosted. With alkaline 0.5 wt%, sodium hydroxide solution sisal fiber is soaked for understanding the effect of wetting ability and coherence. The treatment upgraded the adhesive properties and increased density. Due to the increased surface interface, the composite material has higher compressive and water confrontation. Along with removal of intercrystalline lignin and extra waxy substance takes place. Considerably increased the mechanical and chemical bonding [127]. Pineapple leaf fiber was immersed in 5% w/v of NaOH solution for 2 h at room temperature. The treatment removed impurities and improved the natural fiber adhesive nature and coarsened topography [128]. Ramie natural fibers were treated with 15% sodium hydroxide solution with an applied load method to rise the mechanical strength of the natural fiber. The result showed 4 to 18% upsurge in tensile strength compared to untreated fiber. It was also found with increased fracture strain and decreased Young's modulus. It was considered that variation of morphological and chemical bonding occurred due to mercerization [129]. Sisal fiber was soaked in 2M sodium hydroxide under tension load from 0 to 100 g weight per fiber. Natural fiber shrinkage is reduced by the application of a load to individual fibers; during the alkaline treatment, it also reduces the microfibril angle. Mercerization process upgraded young's modulus and fracture stress, while the reduction in fracture strain and toughness was found in natural fibers. SEM image of composite sample

surfaces exhibited tinier fibrils projecting in the treated fiber. Reinforced sisal fiber and soy protein resin displayed better bond due to changed fiber surface [130].

The effect of alkali treatment on bamboo filler, when bamboo fillers were treated with 5 wt% NaOH solution for 8 h at a temperature of 48°C for the reaction to be done. They used both treated and untreated fillers as reinforcement in bamboo filler epoxy composites. The properties like tensile, flexural strength, and storage modulus showed tremendous improvement compared to untreated bamboo filler. They concluded that alkali treatment of bamboo filler causes excellent interfacial bonding between hydrophilic filler particulates and hydrophobic epoxy matrix [131]. The influence of different chemical treatments on sisal fiber is studied. At first, sisal fibers are treated with 10 wt% NaOH solution and stirred for 1 h. Then the solution is washed to eliminate the NaOH from fibers and then dried at room temperature. The treated fibers showed increments in the tensile properties of the composites. Even the scanning electron microscopic images of the fracture surfaces of the treated specimens showed the extent of interfacial adhesion between hydrophilic fiber and hydrophobic matrix, which is LDPE [132]. The chemical treatment effect on flexural properties of Alfa-reinforced polyester composites is investigated. Alkali treatment at different concentrations of NaOH like 1, 5, and 10 wt% for a time period of 0, 24, and 48 h, respectively, is performed. After the experimentation, he found that 10 wt% alkali treatment of fibers led to the improvement of flexural modulus and strength of the composite about 62 and 60%, respectively. Greater the time period of chemical treatment, stiffer the fiber and this reduces the properties [133]. The alkali treatment effect on kenaf fiber and their epoxy composites is examined. An alkali treatment of 6 wt% NaOH on kenaf natural fibers at different time periods of 48 and 144 h is performed. The properties of the composite showed a negative effect when it is exposed for 144 h. On the other hand, chemical treatment for 48 h showed enhancement in the mechanical properties of the composite. It is also found that rubbery region of the storage modulus was greatly affected by alkali treatment than plastic region. Moreover, the mechanical properties of the composite were greatly influenced by the chemical treatment which was the reason for the enhancement of fiber-matrix interfacial bonding [134]. Flax fibers were treated with alkali and silane agents with certain concentrations and the time periods of the properties like flexural strength and flexural modulus were found to be increased by 40 and 60%, respectively. The increment in bending strength in the transverse direction was up to 200% and stiffness increased by 500% [135]. The mechanical properties of

the natural fibers are controlled by the bonding strength between fiber and matrix. Treating the hemp fiber chemically, the hydroxyl group which is present in the constituents of natural fiber is completely removed. According to the results of different mechanical testings, the treated natural fibers showed better strength than the untreated fiber composites. It was also explained that acetylated fibers showed a decrement in their mechanical properties due to their brittle nature [136]. The consequences of alkali treatment and elevated temperature on bamboo fiber-incorporated polyester composites were investigated. Composite was prepared with both untreated and alkali-treated bamboo fiber at different temperatures of 40, 80, and 120°C. The alkali treatment was performed with different concentrations of NaOH from 4 to 8 wt%. The best mechanical results were found for 6% alkali-treated bamboo fiber. All the mechanical properties of 6 wt% alkali-treated bamboo fiber-reinforced polyester composites exhibited greater results than the untreated composites [137].

The effect of alkali treatment on coir fiber-incorporated polymer composites was studied. In this experiment, an aqueous NaOH solution was prepared at a concentration of 5 wt% and coir fibers were added and stirred for 30 min at a temperature of 20°C. The surface roughness of the fibers was increased and resulted in greater bonding strength among fiber and matrix. The tensile strength and flexural strength of the treated coir fiber-reinforced polymer composites were improved by 17.8 and 16.7%, respectively, compared to untreated composites [138]. The effect of chemical treatment on the mechanical properties of the banana reinforced epoxy composite. The lack of interfacial adhesion between hydrophilic filler and the matrix is the reason for the decrement of mechanical properties which can be overcome by the alkali treatment which results in the increment of surface roughness of the fibers. In this experimentation, the banana fiber was treated with different concentrations of NaOH which varies from 0.5 to 20% and their effect on mechanical properties was studied. It was found that the mechanical properties of 1% treated bamboo fiber-reinforced epoxy composites showed better properties than the other treated and untreated composites [139]. The effect of chemical treatment on woven kenaf reinforced hybrid composites. The natural kenaf mat was treated with 6% aqueous NaOH solution and showed how the properties of the treated hybrid composite are better than an untreated hybrid composite. Chemically treated woven mats showed improved bonding strength with the matrix, which increases the interfacial adhesion, thereby improving the strength of hybrid composite material [140].

3.12 Carboxymethylation treatment

Nanofiber surface can be furnished more hydrophobically by carboxymethylation processing. During this treatment, the pH value remains more than 3.5 because of the release of carboxylic acid. The surface is highly negatively charged, promotes constant suspension in aqueous solution, and also helps in fibrillation mechanism. Using carboxymethylation and high-pressure homogenizer, fibrillation of fiber can be produced with a diameter of 5 to 15 nm having length 1 μ m. At too low pH and/or very high salt concentration, there will be quick agglomeration of fibrils. So pH and concentration level of salt are significant parameters [141]. With the alternation of mechanical disintegration (m) and carboxymethylation treatment (c) sequence, fiber effect was estimated in the route 1 as follows: Fiber effect was estimated in the route 1 as follows: bleached beech pulp (RBP) followed by mechanical disintegration (RBP-m) and RBP subsequently mc (RBP-mc); and in route 2: RBP followed by c (RBP-c) and RBP followed cm (RBP-cm). Following route 2 has been found to have better dispersion effect of nanofibers compared to route 1. However, the effect of crystallinity index is less for route 2 when related to route 1. From the thermal gravity analysis, it was confirmed that thermal stability degraded for carboxymethylated samples. Fourier transform infrared spectroscopy (FTIR) obtained a clear difference for treated and untreated chemical modification. The FTIR spectrum for modified treatments of RBP with carboxymethylation (RBP-mc, RBP-c, and RBP-cm) reached an intensity around 1,595 cm^{-1} [142]. The signal intensity for route 1 was lower than route 2. The crystallinity is maximum for raw RBP having 71%, and eventually, RBP-m (68%), RBP-mc (65%), RBP-m (63%), and the lowest among these is RBP-cm (49%). From the assessed thermal gravity analysis, it was very clear that carboxymethylation treatment decreases thermal stability. To understand the stable suspension of nanofibers, scanning electron microscopy test was conducted for both the treated and untreated conditions of the fibers. The results showed RBP forms a higher aggregation, which indicates the rate of sedimentation is higher. RBP-m did also form the aggregation, but it was found that there were fibrils having below under micrometer range. When compared to the carboxymethylation treatment samples, RBP-mc did not have a much important change in the morphology charters. However, RBP-c created cellulose fibrils linkage under diameter 1 m, while RBP-cm formed higher messy interlinked nanofibers, having a diameter under 100 nm. This makes clear that low agglomeration rate of nanofibers is formed by route 2

treatment process. From softwood pulp, microfibrillation was produced through high-pressure homogenization and carboxymethylation treatment. Similarly here also, the crystallinity value remained around 60% as like carboxymethyl-treated fibers and there is not much crystallinity change found due to the passing number of times through high-pressure homogenizer [143]. However, the AFM result conforms to fiber dimension reduction happened due to the homogenization treatment [144].

3.13 TEMPO-oxidized treatment

The surface modification of natural nanofibers, TEMPO-oxidation, is a suitable approach. In this treatment process, NaClO is added to the 2,2,6,6 tetramethyl-1-piperidinyloxy (TEMPO) blended with the natural fiber in the presence of NaBr and pH level is maintained 10 to 11 at normal room temperature [145]. After adding NaOH, pH level reduces; at a certain state, the pH level remains almost constant and then we consider the chemical reaction is over; by adding HCL, the pH level is brought back to the neutral state. With the consumption of NaBr and NaOH, the hydroxyl group of natural fibers transferred carboxylate group [146,147]. Many researchers have conducted the surface modification with TEMPO-oxidation treatment and TEMPO-electro-mediated treatment [148,149].

3.14 Effect of natural filler/fiber in hybrid composite material

The development of composite material based on consumers demand increased, while environmental awareness has made an effort to develop novelty materials for satisfying market demand. Natural fiber/filler-based polymeric composite improved research interest to bring considerable progress in polymeric composite materials. Nevertheless, an addition of natural fiber/filler in the polymeric matrix is very challenging due to opposite polar nature. As the end-user application, demand increased for lightweight and energy proficient. The inclusion of fibers to epoxy shows high tensile strength increase when compared to filler addition. Fiber orientation and prepetition method also play a vital role to improve properties of hybrid composite materials. Larger acceptable material is mostly based on renewable resources in present day scenario [150]. Ecological anxiety and environment protection and sustainability issues have ensured a growing interest in renewable materials. There are outstanding improvements

in renewable materials in the development of polymeric composite materials [151]. These environmental apprehensions forced governments and private organizations to invest huge amount in the research and development. Natural cellulosic filler/fibers are used as a viable alternative to synthetic fiber-based polymer composites and to produce environmentally gentle composite materials. Properties such as lightweight, low cost, availability, and environmental friendliness make these fibers perfect replacement to conventional or synthetic fibers. The main substances of natural fibers are cellulose, hemicellulose, lignin, pectin, and wax, and classification diverse of natural and man-made fibers is shown in Figure 2.

A natural fiber-based composite can be a feasible substitute over synthetic fibers for lightweight applications [152,153]. Substituting synthetic fiber with natural filler/fiber can be more economical and environmentally suitable. Natural filler/fiber is also a suitable alternative replacement to overcome exhausting nonrenewable resources [154]. Natural fiber and filler-based composite material exhibit decent mechanical, thermal, and electrical resistance and greater resistance to fracture [155,156]. Composite and hybrid composite materials are explored for the various end-user applications in domestic product, automotive industry, agricultural product, packaging items, shelves, aerospace, sports instrument, etc., to cut the buying and maintenance price [157]. The natural filler/fiber-based hybrid composite is focused to replace the man-made fiber-reinforced composite materials; mostly to swap wooden fittings, domestic products like furniture, insulating panels, etc. [158]. An attempt is made to study mechanical and morphological characteristics of the hybrid composite produced from jute, hemp, and hemp in an epoxy matrix using the hand-lay-up technique. The tensile, flexure, impact, and hardness of composite material are examined. Results of hybrid composites is observed with improved mechanical properties. Jute, hemp, and flax-mediated hybrid composite exhibited highest tensile strength of 58.59 MPa, Young's modulus 1.88 GPa, and impact strength 10.19 kJ/m². Similarly, jute/hemp-based hybrid composite exhibited highest flexural strength of 86.6 MPa, caused by the inclusion of unlike natural fibers, and synergetic effect of fibers in the epoxy matrix led to stronger bonding [159]. Performed structural and mechanical analysis of fly ash and jute epoxy added hybrid composite by hand-lay-up method followed by compression molding. Mechanical properties increased linearly with the reinforcement of fly ash, at 2 wt% maximum tensile and flexural strength, and wear resistance is achieved. As the particulates of fly ash could enter into the interstitial position, it helped to fill the voids in the existing jute

Figure 2: Classification of natural and man-made fiber.

epoxy network. With the experimental investigation, they confirmed 2 wt% of fly ash is more suitable for better thermal and mechanical strength [160]. Epoxy-based hybrid composite by utilizing agricultural waste is fixed at bean pod at 3 wt% and calcined kaolin is varied weight percentage from 0.5 to 5 wt%. Tensile strength and elongation break of hybrid composite obtained maximum value of 39.8 MPa at 2 wt% of calcined kaolin, might be due to the enhanced compatibility of hybrid filler and neat epoxy. However, further higher addition of filler decreased the strength, due to poorer interfacial bonding among matrix and fillers. The rate of corrosion resistance enhanced with the inclusion of 5 wt% calcined kaolin; hybrid composite showed chemical resistance to NaOH, NaCl, and HCl solution. The combination of kaolin leads to declining sorption by increasing hydrophobicity of composite [161].

The mechanical properties of hemp/Kevlar and jute/Kevlar were reinforced in epoxy to prepare a hybrid composite. The relationship between them has been established, considering tensile, compression, and three-point bending test. Hemp/Kevlar-based hybrid composite has the maximum tensile strength of 123.45 MPa and jute/Kevlar hybrid composite has maximum compression of 33.81 MPa and flexural strength of 5.06 MPa. Combination of natural and synthetic fiber can be established for improving the mechanical properties [162]. Graphite flake (NGF) and

basalt fiber (BFs) were reinforced in the epoxy matrix; NGF wt% is varied from 10, 20, 30, 40 wt%. The hybrid composite exhibited maximum thermal conductivity at 40 wt%, with a 252% improvement from neat epoxy. With increasing the NGF, phonon transfer improved between epoxy due to the increased thermal conductivity path [163]. Natural fiber-based hybrid composite consists of jute fiber (J), kenaf fiber (K), and fiberglass (FG) which were reinforced in epoxy. The hybrid composite is configured as FG-J-J-J-FG, consisted of five layers of fibers, and exhibited higher tensile strength of 124.05 MPa, Young's modulus 7.79 GPa, and high energy absorption potential, as the improving lamination process improved the synergetic effect of hybrid composite [164].

A biodegradable hybrid composite with sisal/glass fiber and MWCNT into the epoxy resin was developed. MWCNT incorporation with weight percentage varied as 0, 0.5, and 1%; however, this small variation gave rise to a large variation in mechanical properties. Tensile strength value corresponding to 0, 0.5, and 1 wt% was 234.5, 198.6, and 155.7 MPa, respectively; it is very clear that the resulting effect of adding nano-filler in the hybrid composite was better strength [165]. Effect of bamboo fiber reinforcement in natural rubber composite was examined. Mechanical properties showed better results with the inclusion of bamboo fiber. The presence of silane

treatment further increased its mechanical properties owing to improvement in the fiber matrix; interfacial adhesion which upgrades the bonding strength. They have also examined the effect of cure time and scorch time on bamboo fiber-reinforced natural rubber composite and concluded that presence of silane agent significantly improved all the mechanical properties with improved interfacial strength [166]. Short bamboo fiber composite had investigated the effect of fiber–matrix interaction; fiber presence affected density of the composite and reduced the weight of the composite. At first, the bamboo fiber was treated chemically by using NaOH to improve its surface roughness and to provide better fiber–matrix interactions. Different tests had been conducted to see the effect of the bamboo fiber on the mentioned objectives and it has been concluded that the increment in the fiber content provided better fiber–matrix bonding strength, thus reduced void content, and density of the composite decreased with increase in the percentage of the fiber. The percentage weight reduction is also found to be increasing linearly with an increase in fiber content [167]. Fabricated bamboo fiber added epoxy composites where fibers were treated chemically with altered percentages of NaOH to see its effect on mechanical properties of bamboo fiber-based composites. Bamboo fibers were soaked at 0, 1, 2, and 3% in aqueous NaOH for twenty minutes followed by cleaning with distilled water and oven-dried at 60°C for 8 h. Bamboo fibers were reinforced into the matrix in transverse and longitudinal direction and its effect on flexural properties was studied. Flexural strength of longitudinally arranged bamboo fibers was found to be decreasing with rise in NaOH percentage. However, when bamboo fibers were arranged in the transverse direction, the properties were found to be increasing with rise in NaOH percentage. This revealed that sometimes interfacial strength of untreated fibers is adequate to reinforce into the matrix and also the process of alkali treatment can be eliminated [168]. Bamboo fiber/filler-reinforced epoxy composites were developed by using press molding. Bamboo fibers were extracted with steam explosion method which provided better surface roughness compared to other extraction methods. Composite was prepared with different variations in filler/fiber content at different molding and temperature conditions to see their effect on mechanical properties like tensile strength and flexural strength. The results concluded that increase in fiber content improved both tensile and flexural properties tremendously with better interfacial adhesion and better reinforcement and matrix. It has also been concluded that molding temperature has a negative consequence on the properties of composite

material [169]. The impact behavior of hybrid composite is examined by using MWCNT as nano-filler with flax and carbon fiber enhanced the impact energy to 20 J. Similarly, CNT filler is used with bamboo and glass fiber for impact and compression analysis [170,171].

4 Modification of epoxy resin

The habit of using low weight materials and decline of parts in composite material and its improvement is a conception that has been surviving since materials were designed. Combination of monomers produces polymeric plastic materials. Polymers are classified in different ways depending upon the structure and source of origin, molecular, and polymerization are shown in Figure 3. Epoxy-based polymeric composite materials are mostly attracted because of high strength to weight ratio. Epoxy thermoset polymers are produced by adopting different process-ing techniques. The petroleum-based epoxy polymer has higher mechanical properties like tensile strength, better stiffness, and superior electrical resistance. Polymers are macromolecules, together with numerous small repeating unit of monomers. Among the existing polymers, thermosetting polymer is more beneficial to play as a matrix due to low viscosity in nature, high strength, and modulus and it's most suitable for long fiber/filler fabrication. More the degree of interlinking, polymer will exhibit more rigidity. Thermosetting polymers are usually robust than thermoplastic polymers because of strong covalent bonding. Epoxy is a thermosetting polymer that is easily feasible, which has actual strength, toughness, resistance to moisture attack, and chemical reaction. The epoxy resin can be fused to most kinds of the substance of natural fiber/filler and inorganic materials. These are cured at room temperature with added hardener either in the presence of ambient temperature or presence of heat source within a nominal time. Thermosetting epoxy shows negligible or no shrinkage after being solidified. The chemical structure of epoxy group is also named as glycidyl or oxirane group. These glycidyl group monomers are blended with different kinds of curing agents like aliphatic amines, anhydrides, phenols, polyamides, aromatic amines, and other ring opening compounds, forming rigid thermosetting materials. Epoxy becomes highly brittle in nature and is of low impact strength due to a high degree of crosslinking. To improve the thermomechanical properties of polymer, it is necessary to adopt different modification methods shown in Figure 4.

Figure 3: Classification of polymers.

Figure 4: Different methods for polymer modification.

(i) Thermoset toughening epoxy; (ii) the addition of inorganic, organic filler, and fibers; (iii) elastomer toughening; (iv) thermoplastic modification; and (v) miscellaneous modification methods.

The present review modification focused on thermoset epoxy and modification by the addition of inorganic and organic filler/fibers for enhancing thermomechanical and reducing brittleness nature of epoxy resin.

4.1 Thermosetting toughening epoxy modification

Diglycidyl ether of bisphenol A (DGEBA) is the most marketable epoxy with lower molecular weight, higher reactive functional group, and more crosslinking density. Hydroxyl group's presence is found in their backbone and helps to provide better adhesion when mixed with

hardeners. Bisphenol-A (DGEBA), phenolphthalein (DGEPP), and 9,9-bis(4-hydroxyphenyl)fluorene (DGEBF) resins are called di-functional epoxy monomers which were blended with trimethoxyboroxine (TMB) curing agent. It was observed that DGEBA–DGEBF have higher thermal resistance [172]. 3,6-Dihydroxyspiro-[fluorene-9,9-xanthane] (DGEFX) and 10,10-bis(4-hydroxyphenyl)anthrone (DGEA), DGEBA, DGEBF epoxy monomers, cured with diaminophenylsulfone (DDS) and trimethoxyboroxine (TMB), exhibited high flame resistance and better heat resistance, owing to the presence of the higher aromatic ring. However, the glass transition temperature (T_g) of these monomers in decreasing order under-cured and uncured with DDS/TMB is DGEFX > DGEA > DGEBF > DGEBA [173]. The cured Diglycidylether sulfone (DGES) monomer is higher thermally stable than DGEBA, as DGES was prepared from bis(4-hydroxyphenyl)sulfone and epichlorohydrin. The presence of a sulfate compound in DGES makes it more thermally stable. The glass transition temperature of DGES ($T_g = 163.81^\circ\text{C}$) is higher than DGEBA ($T_g = 111.2^\circ\text{C}$); T_g of DGEBA enhanced is from $T_g = 111.2^\circ\text{C}$ to $T_g = 139.1^\circ\text{C}$ with the addition of DGES. This helps to develop hydrogen bond among sulfone and hydroxyl group [174]. The epoxy matrix toughness has been enhanced by the establishment of interpenetrating polymer links (IPNs). The lower viscosity nature of unsaturated polyester resin increases mechanical and fracture properties of the resin. IPNs showed incredible compatibility and interaction with the monomer epoxy, as regard the chemical reaction amid hydrogen bonds of cured resin and the carbonyl group of unsaturated polymer. However, the glass transition temperature declined with rise of IPNs in polymer. As chain mobility increases, interpolymer hydrogen bonding decreases [175]. To improve the fracture property of DGEBA resin, hydroxyl-terminated polyesters are introduced during hardening the matrix [176]. The epoxy composite was toughened with the addition of 5, 10, and 15 wt% of unsaturated polyester (UP) to the resin matrix. The combination of UP to resin monomer, thermal stability, and impact strength is enhanced. Further increasing the UP addition led to percentage degradation in the properties of epoxy resin, due to chain entanglement between UP and resin matrix. The glass transition temperature epoxy was found to be degraded with increasing UP wt%, which led to flexibility nature of unsaturated polyester epoxy, and crosslink density is decreased. The few researchers also reported that they have blended vinyl esters to modify the epoxy to increase the toughness without reducing the thermal and mechanical properties. Enhancement in mechanical properties is reported with addition of 5, 10, and 15 wt% of vinyl ester into the epoxy monomer. The thermal properties of monomer are reduced as the chain

length and flexural behavior of ester reduce the effective crosslink density [177,178]. Polyurethane (PU) is a largely used industrial polymer material adopted to enhance the toughness of polymer and impact strength, flexibility, wear resistance, and other properties [179,180]. Cross-linked-based siliconized polyurethane/epoxy was developed. Toughness, thermomechanical, and corrosion resistance properties were enhanced. With the addition of hydroxyl, terminated polydimethylsiloxane is cured with dibutyltin dilaurate catalyst. Mechanical properties' improvement was achieved at 10 wt% higher with the PU and silicone toughening the brittle epoxy composition. Thermal stability is also improved with 10 wt% silicon incorporation into the PU-modified epoxy resin. PU addition enhanced thermal stability owing to ionic nature, higher bond energy, and thermal stability among $-\text{Si}-\text{O}-\text{Si}-$ bond [181]. Ester added with epoxy resin monomer cured in the presence of acetylacetone cobalt(II) for cryogenic science application because of outstanding mechanical properties, better radiation absorption, longer pot life, low rate moisture absorption, and low price [182].

For improving properties of petroleum-based DGEBA, epoxy used in renewable sources like plant oil, natural rubber, bio-based copolymers, tannic acid, CO_2 , natural filler, and cardanol has been accepted as toughening substance [183]. The soybean oil is used to produce epoxidized soybean oil (ESO) and epoxy methyl soyate (EMS) by transesterified. ESO and EMS bio-resins were combined with DGEBA by varying the composition percentage and compared with commercially available glycidyl ether (AGE)-based epoxy blend. Improvement in thermal and mechanical properties of EMS-based bio-resin is found to be enhanced. The EMS bio-resin percentage increment effectively improved the toughness of the DGEBA epoxy matrix [184]. Experimentally employed naturally available castor oil was blended to commercially based epoxy resin DGEBA. 20 wt% of epoxidized castor oil (ECO) showed better impact and flexural properties than commercially available DGEBA. Thermogravimetric analysis (TGA) showed the improved thermal stability of neat epoxy at high temperature with the bio-resin-based mixture; also, the loss modulus and storage modulus ratio are improved with ECO presences [185]. The use of bio-based block copolymers (BBP) for toughening epoxy resin is negligible. Hence, for the preparation of bio-based copolymer ATRP, nitroxide mediated polymerization (NMP) and reversible addition-fragmentation transfer (RAFT) [186,187]. These BBP can be derived from different natural resources constituents like starch, sugar, lignocellulose, pine resin, fatty acid, and essential oil [188].

Natural-based block copolymer was introduced for toughening thermosetting epoxy; they overcome encounter from chemically rGO to the tri-blocked bio-based copolymer. By adding 30 wt% of PCL–PPC–PCL, tri-blocked copolymer improved fracture toughness $1,099 \text{ J/m}^3$ from neat epoxy 688 J/m^3 [189]. Prepared bio-based aromatic methacrylate vanillyl alcohol (MVA) was used for toughening epoxidized soybean-oil thermosetting resin. The addition of MVA influenced viscosity, curing time with low volatility. The glass transition temperature improvement was observed by increasing the percentage of MVA blending to epoxy. The tensile properties from neat epoxy tensile were enhanced from 23.7 to 31.5 MPa with 40% addition of MVA copolymer [190]. Utilizing carbon dioxide for toughening DGEBA epoxy is of great interest. Cyclic carbonate was synthesized by CO_2 fixation chemical reaction; demonstrated to increase transparency, toughness, and binding strength of epoxy resin. Monocycle carbonate (MCC) was prepared by chemical reaction among CO_2 and epoxy. The adhesive strength was improved from 17 to 22 MPa and glass transition temperature was enhanced by H-bonding collaboration [191]. Epoxy resin with poor thermal conductivity is enhanced around 0.3 to $0.80 \text{ W/m} \times \text{K}$ by aligning the amorphous molecules parallel-linked; the electro-spinning method was adopted to align the linearly. Moreover, applying tensile stress along intra-chain direction, conductivity is improved $6.45 \text{ W/m} \times \text{K}$ [192]. The accumulation of filler to the epoxy polymer increases thermal conductivity; however, the viscosity rises at the same time. Thus, improving thermal conductivity of itself is also essential. A synthesized epoxy polymer with two 2,7-naphthalene benzoate as mesogens were attached by 4 carbons alkyl chain (TME2,7-NB4). Higher order structural changes were obtained because of alterations in the alkyl chain. The thermal conductivity of polymer TME2,7-NB4, where NB4 stands for naphthalene benzoate with 4 carbon spacing. TMEPB4 (phenyl benzoate as mesogen) shows better thermal conductivity value $1.02 \text{ W/m} \times \text{K}$. Thermal conductivity of TME2,7-NB4 is higher than TME2,7-NB8, but lower than TMEPB4 [193].

4.2 Thermomechanical properties of hybrid composite materials

Hybrid composites exhibit an orbital interaction between two or more different types of natural and synthetic filler/fibers of varying sizes in a common matrix. That leads to reform innovative material with excellent properties

which are not achievable by individual filler/fiber reinforcement [194]. Hybrid composites with natural fillers become more attractive due to biodegradable and eco-friendly aspects for utilizing in the thermosetting matrix. Hybrid fiber composite is diversified based on type of fibers used, fiber length, alignment, and fiber–matrix bonding attachment. The extent of intermixing of fiber and rule of mixing can determine mechanical, thermal, chemical, and physical properties of the successful hybrid composite development. Researchers worked using different natural and synthetic fibers with varying natural oil or petroleum-based epoxy resin like poly-urethane, rooflite, phenolic, epoxy vinyl ester, polyester, and resin [195,196].

Hybridization of two or more dissimilar types of filler/fibers of varying dimensions offers a wide range of material properties and exhibits more advantage than using single filler alone in the epoxy matrix. Hybrid composite material development demands increase with greener and decomposable-based filler/fiber materials' inclusion. The epoxy matrix with suitably treated filler/fiber shows higher interaction rate and filler distribution in the matrix will be more homogeneous. The presence of organic and inorganic filler/fibers-based hybrid composite offers commencement application in advance material technology and provides a business opportunity in the different commercial sectors such as building construction, home interior decoration, automobile sector, aerospace industry, material packaging industry, electronic appliances, medical science, fire-retardant, optical industry, and biotechnology industry. The bio-based hybrid composite polymer also improves the material properties along with focusing on minimizing environmental plastic consumption rate. Improving the use of bio-based epoxy with the addition of natural filler/fiber increases the usage of pure biodegradable hybrid composite for specific applications, which would lead any community towards a greener environment and socioeconomic development [197]. However, the pure natural fiber-based hybrid composite uses have been restricted to a limited application due to unexceptional material properties. Hence, researchers are motivated to improve thermomechanical properties of hybrid composite to rise to new level.

The effect of nano-silica inclusion on reinforced carbon, Kevlar epoxy resin, is investigated with different filler content. Nano-silica weight percentage is varied from 0.5 to 3 wt% in the hybrid composite and result of the analysis showed that, at 3 wt% filler addition, the highest tensile strength is obtained around 444.89 MPa, with 46.8% improvement. With the increasing nano-silica weight percentage, the interfacial bonding has been enhanced,

resulting in improving the load transfer in hybrid composite [198]. A hybrid composite material is developed which consists of two natural fibers, banana and flax, along with glass fiber. Epoxy resin LY556 and hardener HY951 were used as matrix materials, which give better binding properties even at room temperature conditions. The developed hybrid composite consists of banana fiber in the middle of the composite which is surrounded by flax fiber at the immediate top and bottom layers which are sandwiched between glass fiber-reinforced polymers at top and bottom faces of the total composite to give better surface properties. Mechanical tests like tensile, flexural, and impact were performed, which showed that total hybrid composite has better properties. Scanning micron electroscope (SEM) test showed the presence of voids due to imperfections caused by hand-lay-up process that reduced the bond strength between the fibers. It has also been concluded that the arrangement and orientations of fibers affect the fiber strength of the composite [199]. A hybrid composite material is fabricated using three different kinds of fibers, namely, sisal, jute, and glass fiber. Three different kinds of hybrid composites using these fibers were developed and different mechanical testing on these composites performed. Three different kinds of composites are made, which are sisal/jute/glass, sisal-glass fiber-reinforced polymer (GFRP), and jute-GFRP. Tensile test results showed that among the three hybrid composites, jute-GFRP composite has better tensile properties and sisal-flax-GFRP has the greater flexural strength than the other two hybrid composites. Void formation, incomplete distribution of fiber, matrix, breakage of fiber, and some other things were clearly explained through SEM results [200]. Developed hybrid composite materials consist of glass fiber, carbon fiber, graphene, and multiwalled carbon nanotube fillers. One hybrid composite consists of glass/carbon fibers, the second hybrid composite of glass/carbon fibers with graphene filler, and the third hybrid composite is made up of glass/carbon fiber with MWCNT. Hand-lay-up technique is the common method used to develop these hybrid composite materials. Results exhibited that Young's modulus and hardness of the graphene-filled hybrid composite exhibited better properties than the other two hybrid composites. However, the modulus of bending and toughness of multiwalled carbon nanotubes-filled hybrid composite is greater than the other two hybrid composites [201].

Hybrid composite material with graphene nanoplatelet (GNP) and carbon nanotubes (CNT) is prepared and compared with both GNP-neat epoxy composite and CNT-neat epoxy composite. It is proved that larger size of the GNP flakes enhanced the results of the composite

properties and there is 82% increment in the fracture toughness for 2 wt% graphene composite over neat epoxy composite. Even the synergistic effect is found excellent for the CNT and GNP mixture samples when their ratio is 9:1 and 5:1. Even the toughening mechanisms such as deflection of crack and bridging of crack are affected by flake size of fillers [202].

The effect of graphene nano-pellets reinforcement on mechanical properties of BF thermosetting composites was investigated. Mechanical behavior was studied with three different graphene percentages like 0.1, 0.2, and 0.3 wt%. Hand-lay-up method was the manufacturing method used to fabricate the composite material. Among all the samples, samples with 0.1 wt% graphene loading showed enhancement in the mechanical behavior under different testing conditions. The interfacial adhesive strength between graphene nano-pellets and basalt epoxy composites reduced at 0.2 and 0.3 wt% filler loading, which results in decrement in mechanical properties [203]. Mechanical strength variation due to carbon nanotubes and graphene nanoplatelet dispersion in epoxy composites at different ratios were investigated. Among different ratios, the ratio with 8:2 between carbon nanotubes and graphene nanoplatelet showed better flexural properties. FTIR test conducted for carbon nanotubes and graphene nanoplatelet epoxy composites revealed that presence of oxygen moieties in graphene nanoplatelet is responsible for bond strength with epoxy composites. Optical microscope tests showed that the presence of GNP improved dispersion ability and stability of carbon nanotubes in epoxy composites [204]. The fabrication of hybrid composite material is dealt with and its mechanical properties with other composites compared. The natural fibers are used in this paper abaca and jute along with artificially made glass fiber. Hand-lay-up fabrication method is used during sample preparation. Three different types of composites are fabricated, jute-abaca-GFRP, jute-GFRP, and abaca-GFRP. Different mechanical testings like tensile, flexural, and impact are conducted. The results concluded that tensile strength of jute-abaca-GFRP is more than that of the other two composites. The withstanding ability of the hybrid composite is comparatively higher than single natural fiber-reinforced hybrid composite. However, the flexural strength of the abaca-GFRP hybrid composite is higher than that of the remaining composites. Interestingly, the shear strength of all the three composites is almost the equivalent [205].

Hybrid composite material was fabricated and effect of hybridization on mechanical properties of natural fiber-added composite was examined. The natural fibers

used in this study were pineapple leaf fiber and sisal fiber and synthetic glass fiber was included with natural fibers to see the variation in mechanical properties. Reinforcement of glass fiber with both pineapple leaf fiber and sisal fiber improved the tensile and flexural strength of the hybrid composite material at greater proportions compared to single fiber-reinforced composite materials. Results of the composites also proved that surface modification of natural fibers enriched properties of final composites. Scanning electron microscope images revealed that the treated natural fiber and glass fiber have better interfacial adhesion compared to untreated composites [206]. Unidirectional flax/glass fiber inclusion hybrid composites were fabricated and their mechanical characteristics studied. Tensile test results showed that rising the content of glass fiber improves tensile properties of flax/glass added fiber hybrid composite. The sequence with which hybrid composite material is fabricated also played a crucial role in influencing mechanical properties of the hybrid composite. Addition of glass fiber improved water resistance ability of the total composite. Fracture properties and shear properties of hybrid composite were higher than those of single glass fiber-reinforced composites [207]. Hybrid composite materials which are also known as modern age materials and can be developed with low cost and improved mechanical properties have been discussed. Different combinations of hybrid composite materials and their effect on properties have been explained. Improved thermomechanical properties of the epoxy-based hybrid composite are listed below in Table 1 [208–216].

4.3 Thermal conductivity description and physical mechanism in hybrid composite polymers

Conduction, convection, and radiation are three modes of heat transfer. Where conduction is the main mode of heat transfer in the solid material, thermal conduction occurs by the transmission of particles' vibration energy from end-to-end particles collision. This intricacy thermal conductivity mechanism in the solid material arises from many different parameters. Certainly, nature of the material is an important factor for thermal conductivity among other different parameters like morphological factor, size, and external factors [217].

Higher thermal conductivity is found in extremely crystalline materials like aluminum, gold, silver, and copper [218]. The basic structure of polymer consists of

crystalline and amorphous domain shown in Figure 5. The crystalline domain polymer chains are aligned in regular sequence, whereas random order polymer chains in case of the amorphous domain are observed. In most polymers, amorphous domain is dominant; heat energy transfer in polymer is localized in vibration mood. Energy flow is restricted which leads to low thermal conductivity in nature. Proper alignment of polymer chains is essential for improving thermal conductivity and glass transition temperature in polymeric materials.

The physical mechanism of thermal conductivity in crystalline material starts with the heat energy transfer to the atoms of the vicinity layer. Once the atomic layer gets sufficient heat energy, energy starts converting into vibrational, rotational form of energy. Due to the variation in the temperature gradient among the local layers, adjacent molecules strike each other; as they are constantly striking, transfer of energy from higher energetic to lower energetic level takes place [219]. Vibration and wave-like features of phonon help to transfer heat in crystalline materials. The rate of heat transmission depends primarily on thermal conductivity properties of materials. Thermal conductivity is theoretically estimated by Debye equation [220].

$$\lambda = \frac{C_p \nu l}{3} \quad (1)$$

where λ is thermal conductivity, C_p is specific heat capacity, ν is average phonon transport velocity, l is phonon mean free path. Some parameters like defects, dislocation, or grain boundary have a bad impact on thermal conductivity. Other aspects like atomic packing fraction, hardness, crystalline structure, and interatomic collaboration play a significant factor in thermal conductivity improvement [221]. Thermal conductivity in the polymeric material is different from crystalline materials. Heat conduction through the polymer is a complex process and depends on the various parameters, crystallinity, temperature, orientation of molecules, and other factors [222]. The different heat diffusion mechanism is observed between amorphous and crystalline polymers. The polymer is amorphous in nature with the disordered atomic structure having no dense lattice structure. The heat transfer mechanism in polymers is reasonably slower when compared to crystalline material. Reasonably, polymers are not good thermal conductor in nature, due to the unmannered distribution of polymeric links. The transporters of thermal conductivity in composite material mostly depend on molecules, electrons, phonons, and photons. The thermal conductivity mechanism comprises of molecular conductivity, electron conductivity, and phonon

Table 1: Thermosetting-based hybrid composite material properties

Matrix	Synthetic or natural filler/fiber	Mechanical properties	Method	Reference
Epoxy resin (A 062)	Oil palm empty fruit bunches//jute	Flexural strength 49.0 MPa Flexural modulus 3.07 GPa	Hand-lay-up	[208]
Epoxy resin and hardener	Kenaf/glass	Tensile strength ~150 MPa Young's modulus ~7.5 GPa Flexural strength ~230 MPa Flexural modulus ~12 GPa	Sheet molding compound	[209]
SuperSap bio-epoxy monomers CLX(S) and the cure inhibitor INH	Flax/carbon	Tensile strength 518.91 MPa Young's modulus 23.71 GPa Flexural strength 213 MPa Flexural modulus 35.24 GPa Glass transition temperature 59.8°C	Resin transfer molding	[210]
Vinyl ester resin and unsaturated polyester	Glass and bamboo	Flexural strength 60.8 ± 8.5 MPa Flexural modulus 3.96 ± 0.47 GPa and Flexural strength 35.5 ± 5.7 MPa Flexural modulus 3.66 ± 0.23 GPa		[211]
Araldite LY1564/Aradur 3486	Montmorillonite-carbon nanotube	Tensile strength ~58 MPa Young's modulus ~1.25 GPa Storage modulus increased 21.2%	Solution intercalation method	[212]
AW 106 and HV 953IN	Graphene and carbon fiber	Tensile strength ~1,000 MPa Flexural strength ~3.0 GPa	Vacuum mold chamber	[213]
Bisphenol A	Hexagonal boron nitride (h-BN), graphene oxide	Thermal conductivity $0.72 \text{ W/m} \times \text{K}$		[214]
Epoxy-terminated dimethyl siloxane	Boron nitride nanosheets and multiwalled carbon nanotubes	Thermal conductivity $4.7 \text{ W/m} \times \text{K}$		[215]
DER-331 and modified cycloaliphatic amine hardener	Bamboo fiber mat (B) and kenaf fiber mat (K)	Complex modulus 3,678 and 3,610 MPa		[216]
Epoxy LY556 and HY951	Rosewood, Padauk wood, jute fibers	Decomposition Temperature 448°C Flexural strength 4,356 MPa		[217]

Figure 5: Schematic diagram of polymer representing crystalline and amorphous domains.

conductivity. However, in most polymers, phonons are a mode of leading thermal transferors [223,224]. Thermal conductivity in crystalline polymer material is owing to lattice vibration. Schematic representation of heat transfer in perfectly organized crystalline domain is shown in Figure 6. The crystalline zone carries heat rapidly, which spreads in the form of waves at a faster rate. During the heat transfer from one layer to another layer, partly heat is transmitted and radiated to the surrounding. Illustration of the heat transfer mechanism in the amorphous domain of material is shown in Figure 7. Heat energy extends towards the surface boundary atoms from one layer to another layer after a certain time interval. The rate of heat diffusion is very slow in case of the polymeric material. During the heat transfer process, boundary atoms form unsystematic vibration and rotation to propagate heat among neighboring layer of atoms. Heat transfer doesn't propagate as faster wave mood like in crystalline material.

Thermal conductivity mechanism of filler added polymeric composite material is focused on based on conductive path, percolation, and thermoelastic coefficient theory

[225]. Filler added to matrix builds a conductivity path in the polymeric composite. The thermal resistance of matrix material is very poor, with inclusion of conductive filler materials providing the suitable path for the heat transfer mechanism due to low resistance [226].

Advancement of nanotechnology helped a lot to provide diverse unique filler/fibers and understanding its topological and morphological condition is essential. Whether the inclusion of nano-fillers in the polymer forms thermal conductivity chain or not is also matter of concern. Generally, when the conductive filler concentration is low, the formation of the conductive chain is most difficult. However, understanding the filler matrix bonding, i.e., interfacial resistance, filler concentration quantity, and morphology of filler, helped to improve thermal conductivity path. When the rate of filler concentration is too high, the chance of better thermal conductivity path is expected. The inclusion of a single conductivity filler in the matrix hasn't shown much significant improvement because of.

- (i) Larger inter-filler thermal contact resistance between filler and matrix.

Figure 6: Crystalline domain.

Figure 7: Amorphous domain.

- (ii) Inappropriate filler distribution in the matrix.
- (iii) Presence of more voids observed, a single kind of filler forms 3D network after inclusion in matrix [227].

The inclusion of optimal hybrid filler concentration may not ensure maximum thermal conductivity. However, high filler concentration may also reduce the synergetic effect of hybrid filler as it fails to form a stronger thermal conductivity chain [228]. To enhance the properties of the composite material, hybrid filler inclusion can be preferable because of synergetic effect. Most of the fillers are available in 0D, 1D, 2D, 3D, for example, fullerene, SiC (0D), carbon nanotube, MWCNTs (1D), graphene, boron nitride (2D), graphene foam, and carbon foam (3D). Considering if the nature of filler is either organic or inorganic, and based on the dimension, i.e., 0D, 1D, 2D, 3D, by considering two fillers' inclusion in epoxy resin, there can be set of possible combination. To understand the heat transfer mechanism of the hybrid filler sample Figure 8, a representation is shown considering 3D + 2D combined nano-filler in the matrix composite. One surface of hybrid composite is open to the heat source. The most vicinity layer gets heated, as the temperature inside the conductivity fillers increases. Hybrid fillers help to produce superior conductive path inside the matrix. With the increasing temperature, heat flows from high concentration to low concentration temperature gradient. The dimension of filler also enhances surface area of conductive path. It's complicated to recognize proper heat transfer mechanism, with combined consequence of micro and nano-filler mixed in the polymer matrix. The improvement of hybrid composite properties due to synergetic effect by varying filler dimension is achieved by experimental analysis in various papers.

Experimentally determined is the synergetic effect of the silane-treated MWCNTs (1D) + dodecylamine modified

graphene nanosheets (2D) hybrid filler added to cyanate ester resin. The hybrid composite with 3 wt% filler exhibited 185% increase in thermal conductivity than the neat resin. However, the composite individually exhibited 158% thermal conductivity with modified graphene and 108% with treated MWCNTs. The concentration of hybrid fillers employed a large effect in enhancing thermal conductivity value of hybrid composite. Individual and hybrid filler at optimal concentration ratio 3:1 modified graphene and treated MWCNTs exhibited maximum conductivity value [229].

The synergetic effect in the epoxy resin hybrid composite was recognized, filled with graphene nanoplatelet (GNP) and multiwall carbon nanotube (MWCNTs). The conductivity of the hybrid composite with 20 vol.% MWCNTs and GNP exhibited $6.3 \text{ W/m} \times \text{K}$, which is much higher than individual filler inclusion on epoxy matrix. Maximum thermal conductivity is obtained with 25 vol.% of MWCNTs and GNP showed $7.30 \text{ W/m} \times \text{K}$. This makes very clear that cross-linked hybrid filler is much better than individual filler inclusion to improve thermal conductivity [230]. The synergetic influence of graphene nanosheets (GNSs) and carbonyl iron–nickel alloy hybrid filler (CINAP) was studied, blended with cyanate ester (CE). Hybrid composite with 5 wt% of GNSs and 15 wt% of CINAP exhibited the maximum thermal conductivity value of $4.13 \text{ W/m} \times \text{K}$. The establishment of active heat flow 3-D percolating network is done by the synergetic effect [231]. The thermal conductivity value of highly anisotropic graphene (2D) with boron nitride (BN) hybrid aerogels (3D), the thermally annealed hybrid aerogel is greatly effective in improving conductivity of neat epoxy. The resulting hybrid composite showed a thermal conductivity of $11.01 \text{ W/m} \times \text{K}$ with 277% enhancement, due to aligned graphene nanosheets [232].

After investing various review papers, a set of possible combinations of hybrid filler is proposed as shown in Table 2, based on different filler dimensions; where D stands for the dimension of the filler or fiber.

For the clear understanding of synergetic effect, possible set of filler/fiber can be made. From the Table 2, ten possible combinations, as: 0D + 0D, 1D + 1D, 2D + 2D, 3D + 3D, 1D + 0D, 2D + 0D, 3D + 0D, 1D + 2D, 1D + 3D, and 3D + 2D, are taken; these are the suggested combinations pair for two types of filler/fibers inclusion potential in epoxy matrix.

Heat transfer rate of hybrid filler may increase under structured thermal filler network potential.

- (i) One conductive filler gets homogeneously distributed, while other filler forms a thermal conductive chain.

Figure 8: Symmetrically represent hybrid filler heat transfer mechanism in the polymer matrix.

Table 2: Possible hybrid filler combination sets

Filler dimensions	0D	1D	2D	3D
0D	0D + 0D	1D + 0D	2D + 0D	3D + 0D
1D	0D + 1D	1D + 1D	2D + 1D	3D + 1D
2D	0D + 2D	1D + 2D	2D + 2D	3D + 2D
3D	0D + 3D	1D + 3D	2D + 3D	3D + 3D

- (ii) Both the fillers will form a thermal conductivity path to transfer heat in the hybrid composite materials.

4.4 Organic and inorganic graphene filler and natural fiber/filler influence in epoxy

Addition of nanomaterial to epoxy resin is found with better advantages, as properties like Young's modulus, mechanical strength, toughness, durability, heat resistance, and electrical properties, etc. were improved. The inclusion of nano-filler has a dimension usually from range 1 to 100 nm. These nanoscales fillers were considered with varying dimensions termed as nano-particulates, nanoplatelets, and nanofibers. Used are nano-particulates of different materials like aluminum oxide, boron, boron carbide, carbon nanotubes, graphene, graphite, calcium carbonate, multiwall carbon nanotubes, single-walled carbon nanotubes, cellulose, nanofibers, clays, silica, aluminum, gold, copper, silver, tungsten disulfide, nanostructured oil palm ash, aluminum nitrate, zinc oxide, silica, and so on [233–242].

Among various existing organic and inorganic filler/fibers, the review was focused on graphene and graphene-based materials. Graphene comes under carbon family, where carbon atoms are organized in a honeycomb structure. While relating to other fillers, graphene and allotrope of graphite exhibit high thermal conductivity, better thermal stability, and show improved resistance to corrosion with epoxy resin. Graphene is two-dimensional sp^2 -hybridized carbon atom. The properties of epoxy can be enriched with the crosslinking factor, as the crosslinking bonding of epoxy polymer is directly related to higher tensile, bending, and lower corrosion resistance and provides satisfactory electrical properties. However, the neat epoxy has a low thermal conductivity value and can be improved with the incorporation of high thermal conductivity filler. With 20 wt% silane-treated graphene into the epoxy, $5.8 \text{ W/m} \times \text{K}$ thermal conductivity value was found in the prepared composite [243]. Thermal conductivity of the prepared composite material, with multilayer

graphene and epoxy, exhibited conductivity $33.54 \text{ W/m} \times \text{K}$. High thermal conductivity is achieved due to aligned MLG in epoxy resin [244]. Hybrid composite is prepared with commercially available epoxy, and at very low wt% filler, i.e., 1 wt% of double wall nanotube and 0.01 wt% of graphene, is able to obtain thermal conductivity value $11.8 \text{ W/m} \times \text{K}$ [245]. The inclusion of graphene nanosheets and carbonyl iron–nickel hybrid filler in epoxy E-51 improved thermal value to $4.13 \text{ W/m} \times \text{K}$ [246]. Addition to these graphene and other high thermal conductivity nanofillers supports to increase the thermal conductivity of neat resin as shown in Table 3 [247–282].

4.5 Functionalization of filler/fiber

Reinforcement of natural fiber in the polymer matrix is not suitable due to less compatibility found between the matrix and natural filler. As natural fiber is hydrophilic, matrix is hydrophobic in nature. Consequently, surface alteration of natural filler is preferred to increase the interconnection link between the natural fiber and epoxy resin [283]. The high moisture content of natural fiber is relatively formed less interconnection when compared to synthetic fibers. With modified surface, thermomechanical properties are examined. In order to overwhelm this concern, various surface alteration methods are attempted. Such alternation improves the wettability of the polymer matrix and also decreases moisture absorption and increases the ease of machinability. Surface alternation basically includes chemical treatment (alkaline treatment, silane treatment, acetylation, etc.), physical-chemical treatment (solvent abstraction), physical treatment (steam explosion, use of rays like plasma), and mechanical method (rolling, swaging, etc.). Physical modification of natural fiber includes corona-discharge, plasma treatment, steam explosion with chemical treatment, laser, vacuum UV treatment, X-ray bombardment method, high radiation impingement, and autoclave treatment [284]. All these methods are implemented to increase the adhesion among fiber and matrix by reducing interlinking gap of hydrophilic fiber to the hydrophobic matrix.

There are two serious basics that need to be concerned with while using natural fiber for producing the composite material. First is about the fibrillation of fiber and second is problem in the dispersion of fiber with the polymeric matrix. Owing to incompatibility of natural fiber surface with matrix and different polarity nature of fiber and matrix, interfacial bond is weak [285,286].

Table 3: Thermomechanical of thermosetting polymer and filler-based composite

Epoxy and hardener	Filler	Filler wt%	Mechanical properties	Thermal properties and thermal conductivity ($W/m \times K$)	Reference
DGEBA and TETA	Graphene and bamboo filler	0.2 to 1 and 5 respectively	Tensile strength 52.48 MPa and elastic modulus of 1.28 GPa. Flexural strength and flexural modulus 56.8 MPa and 5.19 GPa	Glass transition temperature 90°C, thermal conductivity 1.21 $W/m \times K$	[247]
Epoxy resin (Epon 862)/curing agent (Epikure w.) ratio = 100/26.4	Few-layer graphene (FLG) composite TIMs (FLGTs) and copper	5 and 10 vol.%		Glass transition temperature 50 K, thermal conductivity 2.8 ± 0.2 ($W/m \times K$) and 3.9 ± 0.3 ($W/m \times K$) Thermal conductivity 0.71 ($W/m \times K$) Heat release rate 387 kW/m^2 Thermal conductivity 2.2 ($W/m \times K$) Thermal conductivity 2.27 ($W/m \times K$) Thermal conductivity 0.51 ($W/m \times K$)	[248]
Epoxy resin LY556 (RT cure)/amine hardener HY951 ratio = 10:1 Bisphenol-A liquid epoxy monomer/curing agent of methyl hexahydrophthalic anhydride (MHHPA)	Micro particulates of graphite (Gr) particulates of silicon carbide (SiC) Al_2O_3 , GNPs, $Mg(OH)_2$	10% to 40% (maximum) in steps of 10%, 20 Gr + 20 SiC + 60 epoxy epoxy/68% Al_2O_3 /7% mGNP/5% $Mg(OH)_2$		Thermal conductivity 0.71 ($W/m \times K$) Heat release rate 387 kW/m^2 Thermal conductivity 2.2 ($W/m \times K$) Thermal conductivity 2.27 ($W/m \times K$) Thermal conductivity 0.51 ($W/m \times K$)	[249]
Epoxy resin (DGEBA), Curing agent (MeHHPA), curing accelerator (DMP-30, CP) EPIKOTE 828LVEL (bisphenol A and epichlorohydrin)/aromatic di-amine, EPIKURE 3402 = 100:24 Epon862	AlN, graphene oxide (GO) Amine functionalized expanded graphene nanoplatelets (EGNPs)	50 wt% 5 μm -AlN + 6 wt% graphene oxide 0.1 to 2		Thermal conductivity 2.2 ($W/m \times K$) Thermal conductivity 2.27 ($W/m \times K$) Thermal conductivity 0.51 ($W/m \times K$)	[251]
	Graphene oxide (GO) sheet >1 nm, graphite, SWNT	1 to 5		Thermal conductivity 0.51 ($W/m \times K$)	[252]
Bisphenol A, EPON 862/curing agent (diethyltoluenediamine, EPI-CURE W) Bisphenol A (EPONOL resin 53-BH-35, MW = ca. 26,000)/methyl ethyl ketone and propylene glycol monomethyl ether Diglycidyl ether of bisphenol F, EPON 862, hexion/diethyltoluenediamine, EPIKURE = 4:1	Graphite nanoplatelet (GNP_{ox}) Carbon-nanosheet Aligned multilayer graphene (AG)	10 wt% 2–8 nm 11.8		Glass transition temperature $140 \pm 2.1^\circ C$ Thermal conductivity 1 ($W/m \times K$) (at 5% GO) Thermal conductivity 2.08 ($W/m \times K$) Thermal conductivity 6.7 ($W/m \times K$) Thermal conductivity 33.54 $W/m \times K$	[253]
Diglycidyl ether of bisphenol A (Epon128)/poly(oxyalkylene)amines	1. Multi-graphene platelets (MGPs) 2. 0.1 wt% GD400-MWCNTs/0.9 wt% MGPs Graphene nanoplatelets	1% 1% 6	Tensile strength 64.55 $\pm$ 42 MPa Tensile modulus 3361.4 $\pm$ 32 MPa	Thermal conductivity 0.161 $W/m \times K$ and 0.321 $W/m \times K$ Thermal conductivity 1.06 $W/m \times K$	[254]
Bisphenol A/curing agent				Thermal conductivity 1.06 $W/m \times K$	[255]
				Thermal conductivity 1.06 $W/m \times K$	[256]
				Thermal conductivity 1.06 $W/m \times K$	[257]
				Thermal conductivity 1.06 $W/m \times K$	[258]

Table 3: Continued

Epoxy and hardener	Filler	Filler wt%	Mechanical properties	Thermal properties and thermal conductivity ($W/m \times K$)	Reference
Epoxy resin	Reduced graphene oxide (RGO) sheets 5 layer	20	Ultimate stress 13 MPa	Thermal conductivity $6.1 W/m \times K$	[259]
Epoxy resin (E51)	Synthetic graphene films ($1.798 g/cm^3$)	44 vol. %	Tensile strength 12.33 MPa Young's modulus 910.77 MPa	Thermal conductivity $384.9 W/m \times K$	[260]
Epoxy-Mount Resin/(mount hardener) = 10:3	Self-aligning magnetic graphene	1		Thermal conductivity $1.25 W/m \times K$	[261]
Diglycidyl ether of bisphenol A, EPON 862/(diethylenediamine) = 100:26	Non-covalently functionalized GFs (f-GFs)	10		Thermal conductivity $1.53 W/m \times K$ Glass transition temperature $93.9^\circ C$	[262]
Epoxy resin E-51 bisphenol-A/methylhexahydrophthalic anhydride (MeHHPA)	Copolymer VCz-GMA-GNS	1	Tensile strength 55.8 MPa Tensile modulus 2.25 GPa	Thermal conductivity $0.45 W/m \times K$	[263]
Epon 828/m-phenylene diamine (m-PDA, flakes C99%, Aldrich)	Graphene nanoplatelets (GNPs)	5	Flexural strength 145 MPa	Glass transition temperature $158.2^\circ C$	[264]
CY 228-1 (bisphenol-A)/HY 918 hardener	GNPs-silica	2	Tensile strength 62 MPa	Thermal conductivity $0.45 W/m \times K$ 1.54	[265]
Epoxy resin (E-51)/650 polyamide	Natural graphite, copper, aluminum, zinc oxide, boron nitride, aluminum oxide, diamond, and silver powders	44.3, 68.2, 69.69, 66.3, 35.5, 67, 29.4, and 35, respectively	Tensile strength 67.33 MPa Young's modulus 14.42 GPa Fracture toughness $2.58 MPa m^{1/2}$	Thermal conductivity 1.68, 0.75, 1.11, 0.81, 0.59, 0.57, 0.35, and $0.3 W/m \times K$ respectively.	[266]
Bisphenol-A liquid epoxy resin (E-51)/650 polyamide = 1:1	Graphene sheet, graphite nanoflake, graphite	10.1		Thermal conductivity $4.01 W/m \times K$	[267]
Araldite LY556/Araldite XB3473	Graphene nanoplatelets (GNPs)	10	Lap shear strength $7.77 \pm 0.4 MPa$	Thermal conductivity $0.65 W/m \times K$	[268]
Silver-epoxy	Graphene	5 vol. %		Thermal conductivity $9.9 W/m \times K$	[269]
Epoxy-51/curing agent (MHHPA)/curing accelerator (2E4MZ-CN)	Reduced graphene oxide encapsulated copper sphere (Cu@rGO)	80	Lap shear strengths 23.04 MPa	Thermal conductivity $7 W/m \times K$	[270]
Epon 828/methyltetrahydrophthalic anhydride (MTHPA)	Surface modification of silver fillers	85	Shear strength 17 MPa	Thermal conductivity $13.5 W/m \times K$	[271]

Table 3: Continued

Epoxy and hardener	Filler	Filler wt%	Mechanical properties	Thermal properties and thermal conductivity ($W/m \times K$)	Reference
Diglycidyl ether of bisphenol F, EPON 862, Hexion/diethyltoluenediamine, EPI-CURE) = 100:26	Graphene-MLG-nanocomposite	10 vol. %		5.4	[272]
DGEBA-based E-51 epoxy/curing agent (EMI-2,4)	Silica-coated multiwalled carbon nanotubes	0.5, 1	Storage modulus 3 GPa	Glass transition temperature 149.2°C Thermal conductivity 0.24 $W/m \times K$ Thermal conductivity ~7 $W/m \times K$	[273]
Epon 828/DGEBA	MWCNTs + micro-SiC	5 + 55		Thermal conductivity 1,500 $W/m \times K$	[274]
Bisphenol-A liquid epoxy monomer	Anisotropic graphene/boron nitride (BN) hybrid aerogels GBA-2000	1.05		Thermal conductivity 11.1 $W/m \times K$	[275]
Aeronautical grade epoxy (MVR444), based on a resin (MVR444R) and hardener (MVR444H) = 10:5:8	CNT/GNP hybrid coating			Thermal conductivity 1,500 $W/m \times K$	[276]
Epoxy resin hardener (hexahydro-4-methylphthalic anhydride	3D microscale Ag flakes, 1D multiwalled carbon nanotubes (MWNTs), and OD silver nanoparticles (Ag NPs). MWNTs decorated with Ag NPs (nAgMWNTs) Secondary fillers (nAgMWNTs, MWNTs, Ag NPs, Ag NWs)	Primary filler (Ag flakes) fixed at 7.9 g (36.7 vol. % without secondary fillers), and the concentration of secondary fillers varied (0–3.5 vol. %)		Thermal conductivity 160 $W/m \times K$	[277]
Epoxy resin is a mixture of DGEBA and 3,4-epoxy cyclohexylmethyl-3,4-epoxy cyclohexyl carboxylate/hexahydro-4-methyl phthalic anhydride and 1-cyanoethyl-2-ethyl-4-methylimidazole were used as curing agent and catalyst	Polyimide (PI)-modified aluminum nitride (AlN) fillers, AlN@PI	40		Thermal conductivity 2.03 $W/m \times K$	[278]
Epon (R) resin 813 and EPI-Cure (R) 3,234 = 100:13	Boron nitride and aluminum nitride	57 & 60 vol. %		Thermal conductivity 10.3 and 11.0 $W/m \times K$	[279]
Diglycidyl ether of bisphenol A, EPON 862/(diethyltoluenediamine, SEIKA-S, 36 wt% to epoxy)	Hexagonal boron nitride (h-BN), graphite, carbon	10		Thermal conductivity 0.57 $W/m \times K$	[280]
Bisphenol A epoxy resin E51/curing agent D230	Carbon nanotubes and TiO ₂	2 to 8		Thermal conductivity ~0.37 $W/m \times K$	[281]
Diglycidyl ether of bisphenol A (DGEBA) epoxy NPEL-128/4,4-diaminodiphenyl sulfone (DDS)	Functionalize graphene nanosheets (GNSSs)			Thermal conductivity 1.19 $W/m \times K$	[282]

A different tactic is adopted to improve the interfacial adhesion quality. Proper identification is highly essential for surface variation of different natural fibers. It involves treatment without hampering base fiber cellulose structure; along with this, optimization is needed for various properties like impact resistance, elasticity modulus and breaking strength, etc., before filler/fiber dispersion in the matrix for better result [287].

4.6 Extraction methods for natural filler/fibers

Different methods were implemented for natural fiber/fillers' extraction from various parts of the plant. Retting is a process that facilitates separation of fiber from plant stem by the action of microorganisms and with time exposing to moisture. Also, mechanical decorticator was used for fiber extraction. There were generally four different types of retting techniques available that are biological, mechanical, physical, and chemical. The method of fiber extraction has an influence on the fiber quality and grade. Biological retting is divided into two parts, natural and artificial; the natural retting includes dew retting, water retting, and enzymatic retting. Under dew retting process, mostly *Rhizomucor pusillus*, *Fusarium lateritium*, and *Mycelium* fungi are used; found to be best active in their capability to attack the noncellulosic substances and isolate the fibers from the core. Also, they depend upon the environmental dew condition of the region. The crops are trimmed and left on the ground until atmospheric microorganisms isolate fibers from the core. Dew retting requires longer time duration and it's difficult to stop the process at right time to control the quality of fiber [288]. In the process of water retting, anaerobic bacteria such as *Bacillus*, *B. pumilus*, *B. subtilis*, and *Clostridium* are used to remove lignin, pectin, and wax from the core fiber bundle; these core fibers are submerged in water. Depending on the climatic condition and type of bacteria, this process usually takes one to two weeks. However, the contaminated water is a big problem to obtain a high-quality fiber. This fiber can also be extracted artificially by soaking the core fiber bundle in warm water to produce high-quality fiber within 4 to 5 day [289]. Enzymatic retting process was accomplished to remove pectin and other noncellulosic substance from plants by an enzymatic reaction. Enzymes such as Flaxzyme and Texazym BFE are introduced into the mechanically separated core fiber. The enzymes start reacting with the tissues of core fibers and help in fiber extraction [290]. Comparative analysis of different

biological retting methods is done for producing flax fiber. Results exhibited that water retted fibers were found to be good in quality, fineness, and strength [291].

Mechanical retting or decortication technique is a most simple way to separate fiber from core fiber of plant. The steam of the plant is longitudinally passed through crushing roller blades. Applied shear force ruptures and disrupts fibers. Impact stress was applied by using a thin hammer with speed around 60 m/s. The process continues until the required fiber fineness is achieved. Fiber extraction by using decortication method produces an uneven surface structure as compared to biological retting method. The produced fiber needs extra cleaning for removing the impurities [292]. In chemical retting process, core fiber is submerged in a heated chemical aqueous solution for 1 to 8 h. Chemicals that are used include sulfuric acid, sodium hydroxide, potassium hydroxide, nitric acid, sodium sulphide, and chlorinated lime to dissolve pectin and unwanted noncellulosic constituents [293,294]. Clean fibers are produced by removing waxy substance in short time period compared to water retting method [295]. Physical retting involves two steps; first step consists of chemical modification by alkali solution and mechanically defibrillated to enlarge surface to volume ratio. The second step involves plant stems to stem explosion; plant stems are treated in steam temperature from 180 to 240°C pressure from 0 to 12 bar for a time duration of 1 to 30 min [296]. Under high temperature and pressure condition, stem enters the opening spaces of the fiber core, which afterward results in an extensive decomposition into fiber production [297]. Different retting processes are compared and it is summarized that water retting method is a most inexpensive way to produce a fiber with good tensile strength. However, other retting processes consume less time period, but are expensive and produce low-quality fibers. Water retting process method was carried out in open water bodies like a river, pond, and lake; as a result, contamination of water takes place. To avoid this concern, tank retting was adopted to avoid water contamination, which also reduces time duration and stem to water ratio 1:30 [298,299].

Developing natural fiber/filler-based hybrid composite and understanding the natural microstructure and composition are highly essential. The important constituents of plant fiber are cellulose, pectin, lignin, and hemicellulose; their percentage occurrence fluctuates from plant to plant [300–303]. Cellulose is hydrophilic, semi-crystalline in nature, and main constituents of the plant. Hemicellulose is amorphous in nature and moderately soluble in alkaline and water. Lignin is hydrophobic and acts as a good cementing mediator to improve the

stiffness [304,305]. Pectin is polysaccharide which helps to bind fibers together, where lignin is complex hydrocarbons it is mostly insoluble in the various solvent. The glass transition temperature and melting point temperature are around 900°C and 1,700°C, respectively [306,307]. Presence of high cellulose content exhibits higher tensile strength and modulus [308].

The potential of natural filler inclusion in thermosetting epoxy is exploring due to homogeneous distribution; high aspect ratio helps to produce an improvised hybrid composite. Producing micro- and nano-sized natural filler/fiber, i.e., cellulose nanocrystal (CNC), nanofibrillated cellulose (NFC), microfibrillated cellulose (MFC), and micro-sized powders, mechanical processing is high energy consuming method [309]. With the increase in the energy consumption rate, it becomes a challenge to overcome. Besides, without the use of mechanical energy, the rate of fibrillation is also low. The rate of energy consumption per ton of natural fiber fibrillation was found to be 20,000 to 30,000 kW h/ton which can be reduced to 1,000 kW h/ton with suitable pre-chemical treatment [310]. To produce nano- and micro-sized filler/fibers requires rigorous mechanical treatment depending upon the raw material and chemical pretreatment. Usually, mechanical processing like high-pressure homogenization, cryocrushing, grinding, and pre-chemical treatment like alkaline acid, enzymatic, liquid electrolytes, and oxidation are adopted. Pre-chemically treated natural fiber extraction helps in energy saving along with chemically modify and also clean the surface. Hence, a variety of pretreatment is adapted for enhancing the natural fiber/filler composite strength, aging, and fiber–matrix bonding [311].

4.7 Environmental influence

Influence of plastic material use has been increased from last few decades and research development has been driven due to limited fossil fuel resources, hike in petroleum-based price, and anxiety over environment factor. To minimize the petroleum-based polymer usage, various efforts were undertaken by the past researchers for developing an environment-friendly epoxy resin. Preparing a hybrid composite material with natural filler/fiber, bio-based resin, and hardener can be taken care of in the coming future. Influence of better utilization and natural-based resources can protect the environment and reduce the pollution level. Composite materials' machining process consumes less power, which has a direct and indirect impact on the energy reduction and lowers the manpower.

Nevertheless, still, this is challenging to reduce energy consumption during the natural nanofiber/filler fibrillation, various treatment, and recycling process.

4.8 Observation and recommendation

In this review paper, more than 300 journal papers are reviewed to improve the thermomechanical properties of epoxy composite using natural filler/fiber with superior graphene material. Different techniques to improve the quality of graphene and natural filler/fiber were studied and different epoxy modification methods were recognized. Also, the influence of size and dimensional effect in epoxy matrix was understood. After observed thoroughly, various alternative actions are recommended for improving the thermomechanical properties of epoxy hybrid composite.

Improving the quality graphene combined covalent and non-covalent technique can be implemented. Also, large-scale production of graphene can minimize the high cost of graphene. However, utilization of large amount of natural filler/fiber with improved properties will have more environmental influence. Replacing natural fiber with natural filler will be preferred in order to improve the binding rate in epoxy. As the filler particulates are micro- and nano-sized, it is easy to intercept void positions available in the matrix. However, the natural fillers are hydrophilic and amorphous in nature and minimize the properties of composite material. In order to enhance properties of natural filler, chemical treatment like mercerization can be implemented for improving the crystallinity and remove impurity from the natural filler. The most advantage of using natural filler is to eliminate problem associated with fiber alignment, delamination, anisotropic property, and ineffective binding of fibers in the thermoset composite. Effect of conductive hybrid filler for improving thermal conductive path can be identified by ten possible combinations of altered dimensions of filler as: 0D + 0D, 1D + 1D, 2D + 2D, 3D + 3D, 1D + 0D, 2D + 0D, 3D + 0D, 1D + 2D, 1D + 3D, and 3D + 2D; these can be taken to identify the impact in thermomechanical properties. Also, the influence of different natural filler fibrillation was not studied thoroughly.

5 Conclusion

In the present review, various governing factors have been underlined and focus was given on their mechanism

for improving thermomechanical properties of graphene and natural filler-based epoxy hybrid composite. The most research works over last few decades were summarized as:

1. Hybrid composites were developed from epoxy matrix with carbon allotrope-based graphite, CNT, MWCNT, and SWCNT, graphene, along with different metal and ceramic-based micro and nano-sized filler as a inclusion material.
2. The synergetic behavior of matrix polymer in cooperation with natural or synthetic filler and/or fiber is the main cause for improving the thermomechanical properties of hybrid composite.
3. Graphene has excellent thermal and mechanical properties, but the poor dispersion rate and high cost of graphene minimize its area of application. Hence, in order to improve its dispersion rate, surface modification of graphene is done by implementing covalent and non-covalent methods.
4. Developing hybrid composite with inclusion of natural/synthetic fiber creates problem like fiber delamination, alignment, and ineffective binding of fiber with epoxy matrix. Large number of papers are found with natural fiber as incorporation material in epoxy matrix.
5. Enhancing the thermal property of hybrid composite crystallinity of composite and formation of heat transfer path inside the polymers play a significant role. So, formation of polymer heat transfer path and crystallinity were studied widely.
6. Thermomechanical properties of neat epoxy polymer may be improved by increasing inter-kinking polymer chains such as covalent cross chain, electro-spinning, and hydrogen bonding. This improvement might be due to minimizing the polymer chain rotation and enlargement of polymer links. However, in many papers, result exhibits lower thermal conductivity value due to phonon scattering of epoxy matrix.

Although major progress has been made over last few years in improving the thermomechanical properties of epoxy polymer for developing hybrid composite materials, there is lot of progress in work that need to be carried out; technically, the significance of micro- and nano-filler-based epoxy hybrid composite might be fruitful for further assessment.

1. The theoretical and experimental review provides more alternative modification methods to improve graphene desparation rate by combining both covalent and non-covalent modification techniques. Also,

controlling temperature and time duration of sonication process with neat epoxy can be implemented for better result.

2. Improving thermomechanical properties hybrid filler inclusion was carried out; however, the influence of combined effect of different shape of filler such as 1D, 2D, and 3D in epoxy needs to bring in examination. Further, for improving the thermal conductivity of virgin epoxy polymer, use of 3D conductive foam will be more attractive. These 3D foam of graphene or high conductive metal foam builds stronger conductive heat transfer path.
3. However, improving the mechanical properties of use of agricultural waste-based natural fiber addition in epoxy increased from last few years. This showed a positive result in the properties of developed composite material, but the hydrophobic characteristic of natural fiber minimizes its bonding effect and maximizes the void formation in the composite. An initiative can be taken to utilize these waste natural dust products in micro- and nano-sized form for achieving improved result as this will reduce the void formation after thorough sonication.
4. For enhancing the thermal conductivity properties of neat polymer, higher crystallinity nature of polymer is essential. Moreover, most polymers are amorphous in nature; from the experimental result, it is well-understood that after chemical treatment of natural filler crystallinity of filler increases. So this treated natural can be a substitute material to reduce amorphous nature of polymer.
5. Combining technique of improved polymer species and modified graphene filler together may achieve new level to improve the thermomechanical properties of developed hybrid composite. Mechanical stretching of epoxy polymer when blended with graphene foam exhibited higher thermal conductivity result.
6. To understand load transfer and conductive heat transfer path, theoretical and computational analysis is deeply essential. To evaluate the polymer's physical and chemical mechanism, effect of natural and graphene filler dimension, size, distribution, and bonding with polymer species is necessary. Influence of hybrid filler for developing composite material is exploring from time to time.

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