General introduction

Highlights

This chapter encompasses a brief description of the different aspects of bio-based epoxy systems. It outlines the importance, preparation methodologies, and characterization techniques of epoxy resins and their composites, precisely emphasizing the possibilities of renewable materials as sustainable synthons for bio-based epoxy. Various preparation strategies for micro- or nano-reinforcing agents and their influence on improving the final performance of pristine epoxy systems have been described. The successive sections provide a description of the different analytical, spectroscopic, and microscopic techniques employed for the structural scrutinization of bio-based epoxies, different reinforcing agents, and their amalgamated forms as composites. Moreover, the chapter elaborates on various inherent attributes of these epoxy-based systems, including physicochemical, thermal, mechanical, biodegradable, chemical resistance properties, etc. Furthermore, the chapter highlights the special features such as antibacterial activity, biocompatibility, weathering resistance, corrosion resistance, etc., of the composites that extend their pertinency to multiple domains. Finally, the scopes, objectives, and plan of action for the present investigation are listed in the final part of the chapter.

1.1. Introduction

The inventions related to abstract science domains, that emerged during the inter-war years appear today everywhere, satisfying all the real-world requirements [1]. The discovery of synthetic polymers is a pinnacle example of such an innovation that guided us to many scientific and technological breakthroughs. Polymer symbolizes the macromolecular arrangement of tiny molecules (termed monomers) connected through covalent linkages to each other [2, 3]. Thanks to the pioneering works of the innovative thinkers, whose incremental developments over these years molded polymers with all their recognition and popularity. Today, the integral role of polymers can be realized in construction, transportation, irrigation, food and nutrition, health care, medication, and energy industries, with an endless list of products made for daily amenities [4]. Polymers can also convey sustainability to materials in different aspects, such as light-weight components of automobiles made up of polymers increasing fuel efficiency, plastic insulators boosting energy savings, plastic packaging materials improving shelf-life of food products, etc. [4]. Despite these exciting traits, the non-biodegradability of these synthetic polymers is an issue that cannot be sidelined at present, after all the environmental deformations coming to light on account of the overconsumption of polymeric products [7]. To ameliorate the same, the concept of biodegradable polymers was launched, and sustainable polymers were designed, especially by utilizing renewable resource-derived products as raw materials [8-10].

Thermosetting polymers are characterized by their ability to irretrievably crosslink from a liquid solution to a three-dimensional, robust solid structure [9, 11]. Some typical paradigms of thermosetting polymers presently available in the market include epoxy resins, phenolic resins, acrylics, alkyds, unsaturated polyesters, polyamides, vinyl esters, furans, etc. [11]. Among these groups, epoxy resins epitomize the most well-known thermosetting polymers with a history of more than 60 years that have become an indispensable element of modern civilization [12, 13]. Epoxy resins, on account of their inbred versatile characteristics-a combination of excellent mechanical strength and thermal stability, outstanding adhesion to substrates, favorable chemical, creep, and heat resistance, etc. have achieved commendable applicability in a broad spectrum of applications [14, 15]. The list embraces electronics to aerospace engineering, packaging to surface coatings, adhesives to high-performance composites [12, 16]. The commercial epoxies originate from bisphenol A (BPA) in the form of its

diglycidyl ether (DGEBA), which is specifically derived from fossil fuels that limits their prevalent practice. Additionally, BPA has been proven to be a toxic chemical and some developed nations have banned its use in food industries [17-19]. Moreover, its highly crosslinked structure prevents its degradation in a natural environment, causing contamination of the planet's biota [20-23]. All these concerns have guided the research in the field of epoxy resins toward embracing "sustainability".

Multitudinous studies have been reported over the past years that have engrossed on designing ecofriendly or "carbon neutral" epoxy resins using bio-based resources that can compete with DGEBA [24]. Some precedents of the leading contenders include vegetable oils (soyabean oil, palm oil, linseed oil, sunflower oil, and suchlike) [25-28], eugenol [29], tannins [30], lignin [31], vanillin [32, 33], furan [34, 35], isosorbide [36], etc. One latest report by Yang et al. exemplifies the synthesis of a series of bio-based epoxies by reacting epoxidized soyabean, cannabis, linseed, and rubber seed oils with a bio-based hardener to give epoxy elastomers [25]. The major commercial hydrolysable tannin, i.e., tannic acid (TA), possesses great potency as a feedstock for bio-based epoxies because of its rich functionalities [37]. Nevertheless, epoxies derived from these renewable resources are associated with some debits such as vegetable oil-based epoxies possess poor performance, renewable precursors demand expensive and laborious extraction conditions, etc. [38]. To add more, the rich aromatic structure in tannin-based epoxies induces unwanted brittleness that needs to be taken care of by critically optimizing the hard-to-soft fragment's ratio. The impression of these lacunae appears in the market statistics and their development seems inexpedient, demanding a long way off.

A convincing strategy to fortify the comprehensive performance of bio-based epoxy resins is to fabricate composite systems by amalgamating these epoxies with suitable tougheners or reinforcing agents [39]. These multiphase composite materials provide the desired strength and toughness to the epoxy as well as convey some adventitious features that widen its pertinency without losing the structural integrity [40, 41]. Depending upon the anticipated performance and field of exploitation, a divergent range multifunctional reinforcing agents with dimensions varying from micro to nano ranges can be employed. Inorganic metal oxides in micro or nano sizes, glass and carbon fibers, nanoplatelets, clays, carbon nanotubes (CNTs), graphite or boron nitride (BN) nanosheets are some additives that are commonly employed as reinforcing agents in

epoxy composites [40]. However, because of their highly energy-intensive life cycles and delayed degradation profiles, attention has been drawn toward less energy-intensive and more sustainable reinforcing agents [39]. Microstructures like natural plant-derived fibers, biogenic metal oxide nanoparticles, waste biomass-derived cellulose nanofibers (CNFs), etc. claim special mention in the list of sustainable reinforcing agents. Natural fibers derived from jute, hemp, cotton, banana, pine, and suchlike plants, with or without suitable chemical modulations, have been utilized to fabricate light-weight, durable, and eco-friendly epoxy biocomposites for semi-structural applications [41-43]. Meanwhile, nanostructures like CNFs, metal oxide nanoparticles or their integrated nanohybrids deliver an ultra-large interfacial area between the epoxy and the reinforcing agent that is mandatory for attaining superior performance [41]. Competent barrier properties, bactericidal activity, stimuli-responsive release behavior, etc. are some additional credits offered by these nanostructures. Therefore, such ecofriendly epoxy biocomposites and nanocomposites have potential utility in multiple domains including anticorrosive coatings, sustainable biomaterials, structural composite, etc.

Consequently, bio-based epoxy thermosets and their integration with multidimensional reinforcing agents to result in sustainable epoxy composites for an assortment of focused applications seem to be an enthusiastic area of research with numerous foreseeable opportunities.

1.2. Background

After the 1920s, following the invention of the synthetic polymer "Bakelite" by Leo Baekeland and the groundbreaking research of Hermann Staudinger, the astonishing "polymer era" commenced with some revolutionary advancements standing out in the field of polymers [44, 2]. As the demands of polymer products started mounting with time, their debits started appearing, which triggered environmental pollution, resource scarcity, etc. Soon, the concept of biodegradable polymers was advocated, followed by the advent of the first biodegradable synthetic polymer, poly(glycolic acid), in the 1950s, unveiling new visions in the polymer industry [8].

Epoxy resins occupy a prominent position in the field of thermosetting polymers. The liquid resinous material contains low molecular weight prepolymers with two or more reactive epoxy functionalities in their structure [9]. Although the first synthesis of epoxy resin was reported in 1891 by the Russian chemist Prileschajev, the commercial

possibilities of epoxy were only realized after the novel inventions of Pierre Castan (year 1936) and Sylvan Greenlee (year 1939) from Switzerland and United States, respectively [1]. They individually inspected the polycondensation reaction between BPA and epichlorohydrin to obtain their own epoxies and patented their innovations in later years [1, 45-46]. In 1949, the commercial production of epoxy was commenced and soon it started becoming a household name, marking the rest as a golden history [46]. In the present scenario, the global demand statistics for epoxy achieved a value of 21.5 billion USD in 2016 and are projected to reach 37.3 billion USD by 2025, 90% of which is occupied by DGEBA [17, 47]. But the dependency of BPA, and hence DGEBA, on petrochemicals steadily surging the exploitation of these dwindling resources and consequently raising their extraction expenses [48]. Simultaneously, the studies suggesting the toxic traits associated with BPA and its noxious effects on living bodies added fuel to the fire, setting the stage for new developments centered on the search of renewable reactants [48].

Under this pretext, a bulk of researchers started attempting the epoxidation of natural products, the very first candidates being plant-based oils. Interestingly, nature offers a set of plant oils containing long fatty acid chains with intrinsic unsaturation in their structure that are prone to epoxidation [49]. The very first instance of botanical oil epoxidation includes the work of Crivello and his group in 1992 exemplifying the photopolymerization of these epoxidized oils into thermosets [50]. The introduction of epoxidized oils to DGEBA with an aim to remove brittleness falls among the initial trials of removing the demerits of DGEBA by incorporating botanical resources. The study performed by Frischinger et al. in the later years demonstrated such an attempt to improvise the crack and impact resistance of DGEBA by using a classical mixture of epoxidized soyabean oil (ESO) and aromatic diamine [51]. But realizing the inferior performance of these pristine plant oil-based epoxies, the focus has quickly sifted to biomolecules possessing aromatic moieties that were supposed to impart rigidity to the epoxy [52]. Over the years, various naturally occurring phenol-containing bioactive compounds like lignin, cardanol, eugenol, TA, vanillin, gallic acid, etc. have been utilized to obtain bio-based epoxies [52]. TA, possessing twenty-five hydroxyl groups, offers an excellent platform for epoxidation [53]. A patent was filed by Tomita et al. in 1985 on the poly-glycidylation of TA by epihalohydrin in the presence of a phase transfer catalyst (PTC), reporting the first successful example of TA epoxidation [53].

After this report, in 2017, Esmaeili et al. studied the curing kinetics, thermal behavior, antioxidant activity, and cell viability of TA-based epoxy [54]. However, the literature lacks intensive reports on such bio-epoxies with newfangled attributes, indicating the field to be in its infancy, thus forming the basement for the present investigation.

To enhance the performance of these pristine bio-based epoxies for multidimensional applications, composite systems can be fabricated using different reinforcing agents. Composites have been actively associated with human civilization for millennia; back in 1500 BC, mud and straw mixtures were used for preparing huts and 1200 AD, Mongolians prepared bows for defense purposes that were made up of composites [55]. However, the first instance of composite fabrication emerged after the discovery of glass fabric: a commercial glass fiber laminate-based boat hull was prepared by Brandt Goldsworthy in 1946 lighting the lamp for the composite's era [55]. Bio-fibers derived from different plant components are nowadays in high demand for light-weight composites usable in the automotive and construction industries [42]. In 2001, Khot et al. attempted to fabricate a composite from acrylated epoxidized soyabean oil (AESO) using flax and hemp fibers [56]. O'donnell and his group, in their novel work, fabricated biocomposites using flax, hemp, cellulose, and pulp-based mats and a bio-based polymeric matrix: AESO [57]. However, as nano-ranged technologies started developing with fascinating progressions, polymer nanocomposite emerged as a potential area of research for material scientists. A tire compounded by incorporating carbon black into natural rubber in the early 1860s may be considered as the first example of a nanocomposite. Reportedly a century later in 1950, a nanocomposite fabricated using a synthetic elastomer and clay was filed as patent [58].

By tuning the type of nano-dimensional reinforcing agents used, bio-based epoxy nanocomposites can be practiced in a wide spectrum of applications. For instance, polyaniline nanofibers offer excellent anticorrosive performance; graphene, molybdenum disulfide (MoS_2), BN nanosheets-derived epoxy nanocomposites possess thermal and electrical insulating behavior; MXene is known for its exceptional electromagnetic (EMI) shielding ability, and nanoparticles like silver (Ag), copper (Cu), zinc oxide (ZnO), etc. are applied for achieving bactericidal activity [40, 59, 60]. Similarly, surface-modified CNFs are playing an integral role in bolstering pristine bio-based epoxies. Recently, a vanillin-derived bio-based epoxy was incorporated with lignin-modified CNFs to obtain a nanocomposite with 81% higher tensile strength and 185% high

toughness than the pristine, only with 1 weight percent (wt%) nano-content [61]. Silane-modified nanocellulose was again embedded into epoxidized linseed oil to obtain nanocomposites with anticorrosive properties [62]. Yet, noticing the promising attributes of CNFs, more research input is required to attain advanced applications. Designing propitious hybrid nanomaterials using CNFs and biogenic nanoparticles can be effective for achieving adventitious attributes such as antibacterial activity, drug release ability, etc. in pristine epoxy.

1.3. Materials and methods

1.3.1. Materials

1.3.1.1. Epoxy

The structure of the resinous epoxy prepolymer, prior to curing, is characterized by two or more epoxy rings in its backbone. These epoxy rings are unfolded during the curing process upon exposure to heat or ultraviolet (UV) radiation by reacting either with themselves through anionic or cationic homo-polymerization or with secondary components known as hardeners [9, 63]. These hardeners are compounds possessing multiple functionalities in their system, such as amines, anhydrides, acids, thiols, polyols, etc. [11]. The synthesis of epoxy resins can primarily be achieved by two typical pathways: (a) O-glycidylation of active hydroxyl compounds and (b) peracid oxidation of olefinic compounds. However, the most commercially efficient way of producing an epoxy resin is through O-glycidylation, reacting a polyhydroxy compound with epichlorohydrin in the presence of a basic catalyst [52]. However, by varying the type of polyhydroxy compound chosen, an epoxy resin with the desired functionality can be prepared which would offer some exciting features.

(a) Polyhydric phenols

The productively abundant fuel-derived epoxy DGEBA is obtained by reacting bis(4-hydroxyphenylene)-2,2-propane (BPA) and 1-chloroprene-2-oxide i.e., epichlorohydrin in a theoretical 1:2 ratio in the presence of sodium hydroxide (NaOH), as shown in **Scheme 1.1**. The resin is obtained as a white, transparent, viscous mass with a molecular weight of 340 g/mol and a viscosity of 5-15 Pa.s at ambient temperature. However, by varying the stoichiometric ratio of the synthons, the molecular weight and viscosity of the resin can be appropriately altered [9]. Apart from BPA, some other petro-based

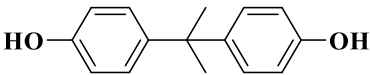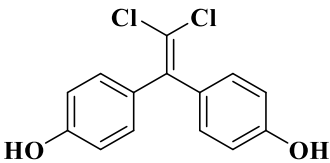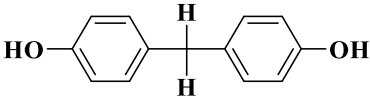synthons used for the synthesis of epoxy resin are listed in **Table 1.1** along with their typical features.
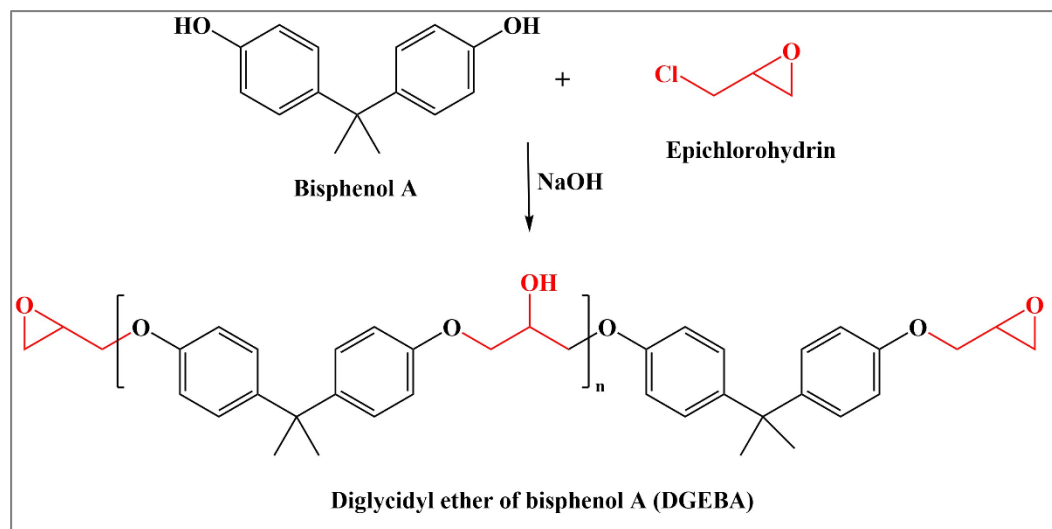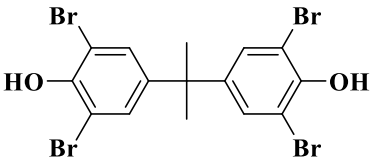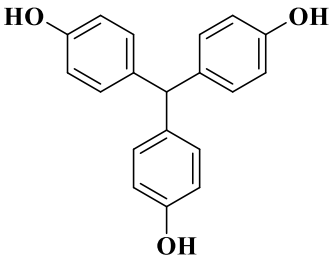

Scheme 1.1: Synthetic route to diglycidyl ether of BPA; DGEBA

However, the increasing environmental concerns, finite reserves, and volatile prices of fuels have urged scientists and engineers to seek green renewables [20]. Meanwhile, the most alarming issue originates from the harmfulness of BPA, which has been relentlessly pressurizing epoxy manufacturers to increase bio-content in starting materials [1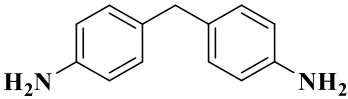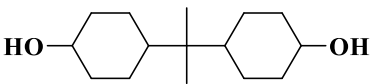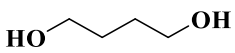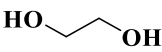1, 23]. Most of the studies have found that food products stored in DGEBA-based packages contain BPA, which is released during the processing and storage of the product, making its ingress inside the body [64]. Scientists have proven BPA to have estrogenic properties because of its mimicking structure to estrogens and its ability to act as an endocrine disruptor [17]. In mammals, it can cause complications like attention deficit hyperactivity disorder, obesity, infertility, genital tract abnormalities, prostate and breast cancer, etc. Exposure of human fetuses, infants and neonates to BPA is extremely dangerous as these stages involve the development of sensitive organs, including the brain, and BPA can affect their functions [18]. The United States Federal Drug Administration has ordered a prohibition on using BPA-based products in packaging baby products [19].

To resolve all these complications, nature-derived polyhydroxy phenols are extensively utilized for preparing epoxies. Such polyphenols own multiple functionalities that can be epoxidized effortlessly to obtain eco-friendly epoxies. A very recent example of such an attempt by Miao et al. showcased the synthesis of a fire-safe, fully bio-based
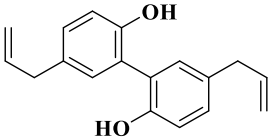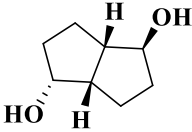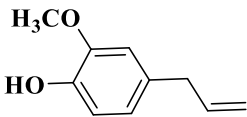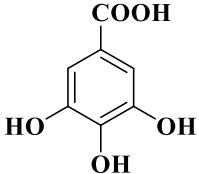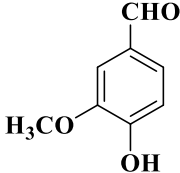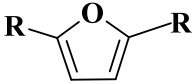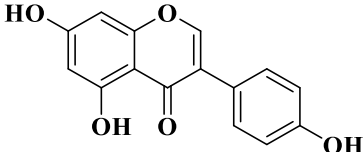
epoxy from vanillin and 2-furfurylamine using vitrimer chemistry [65]. Another interesting work by Faggio et al. demonstrated the synthesis of a fully bio-based epoxy
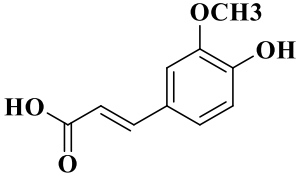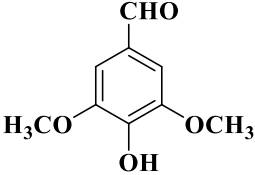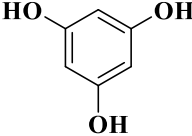
Table 1.1: Structure of renowned, petro-derived synthons for epoxidation and unique features of their epoxies

Name	Structure	Unique features of epoxy
BPA		High-performance commercial epoxy
Bisphenol C		High-performance, flame-retardant epoxy
Bisphenol F		Low viscous, high-performance epoxy as diluents
Tetrabromobisphenol A		Flame-retardant epoxy for electronic insulators
Trihydroxyphenyl methane		High thermal stability for electronic encapsulation
Methylene dianiline		Highly crosslinkable, temperature-resistant epoxy
Hydroginated bisphenol A		Flexible epoxy with tunable shape memory attribute
Butane diol		Low viscous, flexible epoxy
Ethylene glycol		Low viscous epoxy

from 2,4-(dihydroxymethyl) furan and cured with maleic anhydride for high-performance adhesive applications [66]. **Table 1.2** showcases some other renewable polyhydric compounds utilized for deriving different eco-friendly epoxies.

Table 1.2: Renewable-resource based synthons and properties of their epoxy

Name	Structure	Unique features of the epoxy
Magnolol		Higher performance than DGEBA, low viscosity for processibility, intrinsic flame retardancy
Isosorbide		Water soluble, comparable performance to DGEBA
Eugenol		Flame retardancy, dynamic linkages with shape memory, self-healing, reprocessable attributes
Gallic Acid		High-performance, flame retardancy
Vanillin		High-performance, flame retardancy, shape memory, self-healing, reprocessablity, degradation
Furan derivatives	R = -COOH, -CH$_2$OH, others	Versatile performances, fire-resistance, recyclability
Genistein		Higher performance than DGEBA, intrinsic flame retardancy

Ferulic acid		High-performance, fire-resistance, degradable and recyclable
Stringaldehyde		Comparable performance to DGEBA, inherent flame retardancy, antibacterial activity
Phloroglucinol		High glass transition temperature, high strength, dense crosslinked structure

(b) Epichlorohydrin

Epichlorohydrin is a prime reactant required in the O-glycidylation process of polyhydroxy compounds for introducing the oxirane ring in them, driven by a polycondensation mechanism. The industrial production of epichlorohydrin involves reaction between allyl chloride and hypochlorous acid, while propylene and chlorine in a multistep reaction also generate epichlorohydrin [67, 68]. However, in an urge to promote "green techniques", to achieve very low emissions of volatile organic compounds (VOCs) and to consume low energy, epichlorohydrin is nowadays produced from glycerol. Glycerol is obtained as a byproduct in the process of biodiesel production from renewable biomass [69]. This renewable glycerol is converted to epichlorohydrin (the GTE process) in a two-step process, as shown in **Scheme 1.2**. The world's largest epichlorohydrin producer, Dow Chemical Company, is using this acid-catalyzed hydrochlorination process of bio-based glycerin to produce epichlorohydrin [68]. Solvay Chemicals is also producing epichlorohydrin form glycerol obtained during biodiesel production from rapeseeds via the EPICEROL® technology [70]. This bio-based epichlorohydrin is effectively being employed for the glycidylation process.

(c) Catalyst

For the discussed polycondensation reaction between a di- or polyhydroxy compound and epichlorohydrin, a basic reaction medium is necessary to remove the generated

hydrochloric acid (HCl). Otherwise, the HCl present in the reaction mixture will again open up the epoxy rings in the product and adversely affect the efficiency of the reaction.
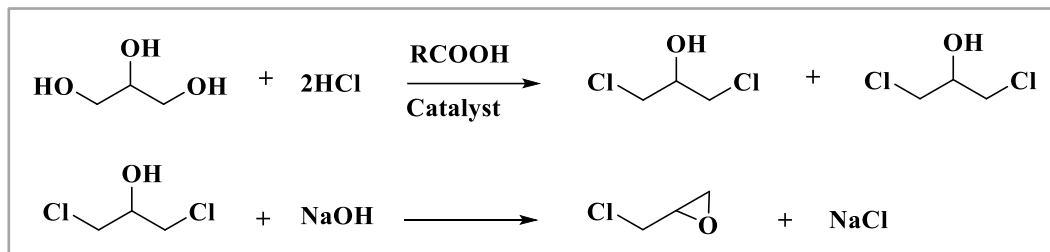
Scheme 1.2: Synthesis of epichlorohydrin from glycerol: the GTE process

Some catalysts such as NaOH, potassium hydroxide (KOH), calcium hydroxide (Ca(OH)$_2$), sodium carbonate (Na$_2$CO$_3$), potassium carbonate (K$_2$CO$_3$), calcium carbonate (CaCO$_3$), etc., are prevalently used to provide a basic environment in the O-glycidylation process [71]. In some cases, to control the epoxy content and by-products formed during the O-glycidylation, a PTC is also used. Quaternary ammonium salts such as benzyltriethyl ammonium chloride [72], tetrabutyl ammonium bromide [54], tetrabutylammonium hydroxide [73], cetylmethyl ammonium chloride, etc. are prevalently utilized as PTC for epoxidation through O-glycidylation. The active, mechanistic role of the PTC catalyst was studied by Aouf et al. for the O-glycidylation of some natural polyhydric phenols [72]. A study by Kou et al. also investigated the role of solvents in the epoxidation reaction, which showed the presence of single or bi-phasic solvent systems differently affected the end product. Using a biphasic system generated the need for a PTC to obtain epoxy with low molecular weight, narrow polydispersity, high purity, and high yield [73].

For epoxidation via double bond oxidation using peracids, a wide variety of catalysts can be utilized. The list varies from homogeneous catalysts like sulfuric acid (H$_2$SO$_4$), phosphoric acid (H$_3$PO$_4$) [74], hydrochloric acid (HCl), etc. in the presence of transition metal catalysts like Re [75], Mo [76], to heterogeneous catalysts like amberlite [77], polyoxometalates [78], zeolites [79], alumina [80], silica-supported Ti [81], Nb [82], catalyst, etc. Nowadays, even enzymatic catalysts are efficiently epoxidizing olefinic double bonds as greener alternatives to these inorganic catalysts [83].

(d) Curing agents

Epoxy resin in its native viscous form contains moieties with epoxy rings. These

monomers need to be tied together to form crosslinked thermosets that are rigid and can free-stand in the desired structural form. Curing agents or hardeners are these crosslinkers that link the epoxy rings to each other. Structurally, these curing agents are bi- or poly-functional compounds with nucleophilic groups that are prone to attack the oxirane rings of epoxy prepolymers and open up the same [71]. To accelerate the curing process, external stimuli (like heat and light) are required. However, curing agents can be broadly classified into three different types: (a) active hydrogen compounds and their derivatives (amines, amides, hydroxyls, acid, acid anhydride, etc.); (b) ionic initiators (tertiary amines, imidazole, alkoxides, halides, or fluoroborates of transition metals, and suchlike); and (c) latent catalysts (boron trifluoride-amine complex, dicyandiamide, benzylsulfonium, benzylpyridinium, benzylammonium, phosphonium salts, etc.) [46, 84, 85].

The structure of the curing agent, the degree of the curing reaction, and the density of cross-linking determine the final properties of epoxy thermosets [45]. In this context, aliphatic amines are excellent candidates for room temperature curing, while aromatic amines, although they require high temperatures for curing, are unequivocally best for bringing high rigidity to the epoxy. Nowadays, sustainably derived curing agents are receiving commendable attention, including aromatic amines derived from cardanol and furan; amino acids in their native or modified forms; polyphenols like TA, rosin, lignin; anhydrides derived from terpenes; carboxylic acids like citric acid, sebacic acid, etc. [86, 87]. Polyamides obtained from a reaction between dimer acid and a polyamine are exceptionally good hardeners for shock-resistant, high-compressive, and sturdy epoxy thermosets [46]. Recently, Huang et al. prepared a novel poly-carboxylic acid-based curing agent using vanillin and hexachlorocyclotriphosphazene to obtain a DGEBA-based flame-retardant epoxy thermoset [88]. Another recent study has illustrated the curing effect of myrcene and castor oil-derived hardener for the commercial epoxy to get highly tough, flexible thermosets [13]. Again, chitosan, a polysaccharide with lots of amine functionalities has been used as a curing agent for a resorcinol diglycidyl ether [89].

1.3.1.2. Micro and nano-reinforcing agents

In the present era, the use of composites has upsurged explicitly as energy-efficient light-weight, robust materials for multitudinous applications. Thermosetting epoxies are

widely used over other polymers as a matrix in composites owing to their versatility and good performance. Epoxy-derived composites have earned a respectable position in the aviation and construction industries, the manufacturing of wind turbines, automobiles, sporting goods sectors, etc. [90]. Epoxy can effortlessly form bonds with any foreign material like stone, glass, wood, plastic, ceramic, and metals which makes it the best candidate for composite manufacturing [42]. Additionally, although bio-based epoxies have sustainability as bonus, their unfortunate underperformance makes them more preferable to be used as composites rather than in pristine form, with a set of additional attributes credited by the reinforcing agents.

(a) Nature-derived microfibers

Counting on the prophesied behaviors or properties, numerous synthetic or nature-derived materials can be considered as reinforcing agents. More prominence is, however, observed in the case of green toughening agents, including agricultural waste powders derived from coconut shell, wood apple shell, rice husk, date seed, etc.; waste tea fiber, and other plant fibers from hemp, jute, pineapple leaf, banana, bamboo, and other plants; particulates like ash, biochar, etc. [90]. Interestingly, the micro sized natural fibers have attained paramount importance in epoxy-based composites. Some fascinating outcomes of natural fiber's inclusion in composites are: reduction of weight and cost, less dependency on fuel-based products, low toxic emissions, enhanced energy recovery, and improved biodegradability [91]. Joshi et al., in their recent work, have demonstrated the use of pinecone and wood apple shell-based fillers integrated with areca sheath fibers in a bio-based epoxy matrix for the preparation of composites. The obtained hybrid composite observed increments in tensile, shear, and impact strengths up to 23.9%, 31.6%, and 16.8%, respectively [92]. Likewise, Kumar et al. infused alkali-treated jute fibers in a vanillin-derived epoxy and obtained better adhesion between the two components compared to DGEBA-based ones [93].

(b) Nanomaterials

Unfortunately, some shortcomings rising from such microfiber-reinforced ecofriendly composites are poor mechanical strength, inefficient interfacial bonding, high water affinity, etc. that limits their wide exploitation [94]. In such circumstances, the inevitable role of nanomaterials can be realized as efficient tougheners for bio-based epoxies. Fundamentally, materials possessing at least one of their dimensions in the

nanometer range (1-100 nm) can be considered as nanostructures [95]. Reducing the size to the nanorange significantly alters the chemical and physical properties of these nanostructures, making them remarkably different form bulk materials [96]. Thus, nanomaterials have the advantage of a very high surface-to-size ratio that offers an extended interaction zone when they are mixed with epoxy systems to fabricate nanocomposites. Essentially, in light of their different sizes or dimensions, nanomaterials can be classified into three broad groups, as illustrated in **Scheme 1.3** and discussed below.
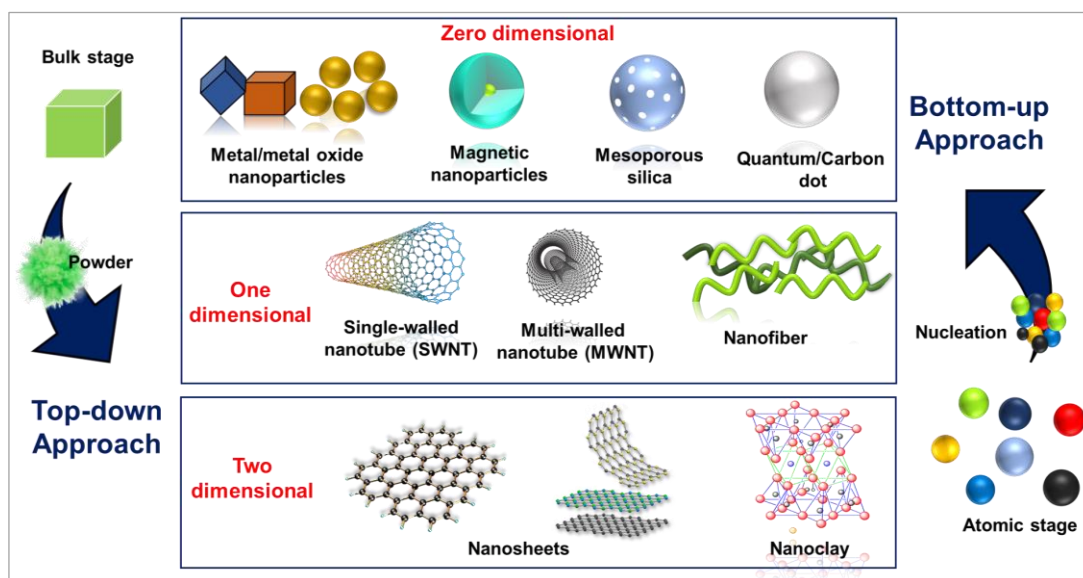
Scheme 1.3: Representation of different nanomaterials produced by top-down and bottom-up approaches

Zero-dimensional (0-D) nanomaterials

Nanoparticles are the most fundamental unit of a nanostructure, having a size that spans the 1 to 100 nm range in all three directions, being tiniest amongst all the Newtonian particles yet bigger than the quantum mechanically governed units (atoms and molecules). Nanostructures such as metal, metal oxide nanoparticles, inorganic quantum dots, carbon dots, and other organic particulates are considered as 0-D nanomaterials [97]. Among them, metal-based nanoparticles are the most exploited ones, the importance of which stems from their unique biological, plasmonic, optoelectronic, magnetic, and physicochemical properties [98]. For instance, Ag, gold (Au), ZnO, iron oxide (FeO). Cu, titanium (Ti), etc. nanoparticles have conquered a decent position in the field of biomedical applications as bactericidal agents, drug carriers, etc. [99-101]. Ganesan et al. demonstrated the antimicrobial properties of fungi-mediated ZnO

nanoparticles against bacteria *Staphylococcus aureus, Escherihcia coli* and *Candida albicans* [102]. The use of green nanoparticles in tissue engineering was attempted by Zulkifli et al. The Ag nanoparticles were prepared by incorporating hydroxyethyl cellulose, which acted as a biocompatible reducing agent for Ag^+ [103]. Several state-of-the-art literature reports have demonstrated the effect of these nanoparticles in bio-based epoxy nanocomposites. In such an attempt by Aung et al., the corrosion-inhibiting effect of ZnO nanoparticles was studied in a jatropha oil-based acrylated epoxy (AEJO) system [104]. Biogenically synthesized FeO nanoparticles using different plant extracts have also acquired profound importance. Das et al. synthesized magnetite (Fe_2O_3) nanoparticles from *Jatropha curcas* and *Cinnamomum tamala* extracts and employed for industrial wastewater remediation [105]. Green tea tannins were exclusively utilized for preparing Fe and FeO nanoparticles for dye removal by Plachtová et al. [106].

One-dimensional (1-D) nanomaterials

This class of nanomaterials has two dimensions in the nanometer range, and the remaining one can vary in the micron range [97]. Nanofibers, single- to multiwalled nanotubes, nanowires, etc. are some active members belonging to the 1-D nanomaterial group. CNTs represents a famous nano-reinforcing agent with an extraordinary tensile strength of 10-200 GPa, making them the best nanostructure for high-performance epoxy nanocomposites. Recently, Wang et al. proved the same by incorporating CNTs into an epoxy system for preparing a fire-safe epoxy with 68 MPa tensile strength, only with a 3 wt% CNT-loading [107]. Inorganic nanofibers exclusively made up of carbon, silicon carbide, and BN are some other important 1-D nanostructures [108]. Similarly, Ag and Cu nanowires are emerging as rising stars with sophisticated attributes that include EMI shielding and joule heating performance [109]. When these nanowires are introduced into an epoxy system, a nanocomposite system with EMI shielding ability is achieved, as exemplified by the recent works of Tran et al. [110] and Rajesh Kumar et al. [111]. However, disadvantages stemming from their laborious synthetic procedures and non-renewable behavior make them less favorable for extensive practices.

In this pretext, sustainably derived nanofibers or cellulosic nanostructures (CNFs, cellulose nanocrystals (CNCs), etc.) are found to be an equitable solution. CNFs, on account of their unique set of properties including high Young's modulus up to 140 GPa, tensile strength (around 2 GPa), optical transparency, and low thermal expansion, have

acquired significant research interest as replacements of the aforementioned inorganic nanofibers [102]. One recent example of CNF-reinforced epoxy nanocomposite was shown by Barari and Pillai, where CNF-based preforms were impregnated with a bio-based epoxy to prepare green composites [112]. Masoodi et al. similarly utilized CNF-based films as reinforcing materials for a bio-based epoxy [94]. Although the intrinsic hydrophilicity and high agglomeration affinity of CNFs raises questions about dispersion stability in an epoxy matrix, but judicious chemical modification can circumvent the internal attraction and enhance their stability [113]. The literature is enriched with numerous reports where surface modification of CNFs using moieties like silanes [114], amine [115], anhydride [116], rosin [117], and others [118] has been accomplished. Frone and coworkers in their latest study have tried functionalizing of nanocellulose with γ-methacryloyloxy propyltrimethoxysilane followed by grafting with methacrylic acid to reinforce an epoxidized linseed oil-itaconic acid-based formulation [119]. Thus, CNFs in their pristine or modified forms have immense projection as sustainable future-generation reinforcing materials for bio-based epoxies.

Two dimensional (2-D) nanomaterials

This class of nanostructures has any one dimension or size parameter in the nanometer range and entails inorganic 2-D structures like nanoflakes, graphene, graphene oxide (GO) or reduced graphene oxide (RGO) nanosheets, graphitic carbon nitride (g-CN) nanosheets, BN nanosheets, transition metal dichalcogenides, layered double hydroxides, montmorillonite, and the most recent example is MXene [120]. It is mandatory to mention that these nanostructures, since their emergence, have experienced systematic evolution and made their entry into almost every single sector of science and engineering. Guo et al., in their intriguing work, prepared a high thermally conductive dielectric nanocomposite by sequentially arranging layers of graphene and microwave-exfoliated BN nanosheets in an alternative manner to a micro-sandwich structure [121]. Similarly, exfoliated BN-tailored exfoliated g-CN nanosheets were used for visible light-mediated photocatalytic degradation of dyes and for the evolution of hydrogen gas [122]. In another study by Wu et al. graphene was functionalized with cardanol-based epoxy and utilized as a reinforcing material in a waterborne epoxy for anticorrosive nanocomposite coating [123].

1.3.2. Preparation methods

The subsequent discussion portrays the experimental methodologies adopted for the synthesis of bio-based epoxies, various reinforcing agents, and the fabrication techniques of nanocomposites.

1.3.2.1. Preparation of epoxy

(a) Taffy process

For the synthesis of commercial epoxy via polycondensation of polyols and epichlorohydrin, the taffy process is generally adopted. The original taffy process involves the reaction of an alkaline (10% NaOH solution) solution of BPA with epichlorohydrin in stoichiometric excess. The reaction proceeds at 95 °C for a period of 80 minutes (min) to obtain the resinous product in the form of a water-resin emulsion. After completion of the reaction, the two phases; the aqueous brine phase and the taffy resin phase, are separated, the resin is washed with water several times, and it is dried under vacuum [124]. The process is, however, suitable only for low to medium molecular weight resins, as with high molecular wight resins, the agitation process becomes hard to complete. However, solvent-assisted workup may sometime lead to easy processibility and a high purity-product. The molecular weight of the product can be tuned as desired by changing the molar ratio of BPA to epichlorohydrin [71].

(b) Fusion or advancement process

The basic principle of this reaction lies in the chain extension reaction. The chain extension of a liquid epoxy resin is performed in the presence of polyols such as BPA and accelerated by basic catalysts to result in a high molecular weight epoxy resin [71]. Interestingly, the DGEBA resin obtained by this process generally has an even numbered degree of polymerization (n) values, as a difunctional BPA reacts with a diglycidyl ether of difunctional phenol through step-growth polymerization [124, 125]. The reaction usually requires a high temperature of 150 °C to 200 °C depending on the desired product. The choice of the catalyst may vary from inorganic bases like NaOH, KOH, $CaCO_3$, etc. to quaternary ammonium salts, phosphonium salts, etc. However, sometimes residual ionic species may interfere with the purity of the product for which special catalysts are utilized [125].

Although both of these processes have their own pros and cons, the fusion process has some additional advantages over the taffy process when it comes to scaled up preparation. The fusion process is preferred for high-scale production because of its low cost, solvent-free nature and simple purification process, which makes product isolation easier [126].

(c) Synthesis of bio-based epoxy

Epoxidation by the polycondensation reaction is a well-practiced method for the preparation of bio-based epoxies where at least one reactant is derived from bioresources. In the simplest procedure, the polyphenolic substance is treated with epichlorohydrin in the presence of NaOH in different stoichiometric ratios to obtain the glycidylated product. However, the diversity in terms of functionality, structural backbone, and number of polyhydric groups present in the raw materials introduces differences in the end products. For example, the eugenol-based epoxy monomer synthesized using this polycondensation method by Wan et al. introduces ultra-stiffness into the thermoset when cured [127]. Genistein was epoxidized using the same procedure by reacting it with an equimolar amount of epichlorohydrin and a catalytic amount of tetrabutylammonium bromide as PTC. The reaction content was agitated at 100 °C for 2 hours (h) after which the addition of NaOH commenced the formation of the diglycidyl ether of genistein [128].

1.3.2.2. Preparation of reinforcing agents

When it comes to the preparation of multidimensional reinforcing agents, different methodologies are applied depending on the type and size of the reinforcing materials selected. Natural fibers need no sophisticated processing conditions, although to improve the interaction with the epoxy matrix, some functionalization can be performed on these microfibers, including alkali treatment, silane grafting, maleic anhydride treatment, enzymatic treatments, etc. [130-132].

However, the synthesis of various nanomaterials requires meticulous preparation techniques. The conventional method of nanomaterial synthesis comprises two elementary approaches referred to as the top-down and bottom-up approaches. In a top-down approach, the nanostructures are derived from bulk material by successively declining their size until the nanoscale range is reached. Typical top-down approaches require physical methods like melt mixing, attrition, quenching, mechanical milling,

laser ablation, arc discharge methods, etc. [133]. The extraction of nanofibers from natural fibers, the preparation of metallic and ceramic nanoparticles, and physical or chemical exfoliation to obtain nanosheets or nanoflakes like graphene nanosheets, BN nanosheets, etc. all fall within this category [134].

Contrarywise, in the bottom-up approach, the sizes of the atoms and molecules of the precursor are raised to the nanorange by nucleation and growth, to obtain the nanomaterials of aspired size and shape. Chemical methods, including sol-gel, solvothermal, electrochemical, pyrolysis, photochemical reduction and biological methods such as biosynthesis assisted by microorganisms or plant extracts, are paradigms of well-practiced bottom-up approaches [133]. The bottom-up approach offers the ability to control the size of the nanomaterial and alter its properties appropriately [134].

1.3.2.3. Insights into fabrication of epoxy composites

The manufacturing processes of polymer composites vary depending on the type of reinforcing agent used. In other words, as the size of the reinforcer changes from the micro to the nanorange in composite systems, their fabrication techniques urge significant alternations. The following sections include details of various manufacturing processes for polymer composites, with special emphasis given to biocomposites and nanocomposites.

(a) Fabrication processes of biocomposites

Composites in which at least one component (specifically a discontinuous phase, i.e., a reinforcing agent) emanates from nature are generally termed as biocomposites [135]. Although the term 'biocomposite" has an extended meaning, in the present investigation it is fundamentally used to refer to composite systems encompassing bio-based epoxy and micro sized reinforcing agents. Different techniques are available for the fabrication of epoxy biocomposites, namely open mold processes (hand layup or spray up) and close mold processes (such as extrusion, vacuum infusion, compression molding, injection molding, resin transfer molding, etc.) [136, 137].

In the process of hand layup or spray up, the reinforcing material is manually impregnated with the epoxy by hand mixing or by spraying the epoxy over it to form the semifinished product called prepreg. The prepreg is then cast on molds and cured to

obtain the biocomposite. The compression molding applies heat and pressure to closed molds containing the prepreg, placed between two metal dies [138]. In the resin transfer molding process, a dry preform of the reinforcing material is placed in the mold, and the liquid resin is injected under pressure through various ports to wet the preform. This process is highly efficient for producing three-dimensional complex-structured biocomposites used in transportation, construction, and wind power sectors [138, 139]. A biocomposite was prepared by the hand lay-up technique by mixing a green epoxy with biodegradable bark cloth [140]. Another report utilized the compression molding process to prepare a series of biocomposites from bamboo and hemp fiber incorporated into an AESO matrix [141].

(b) Fabrication processes of nanocomposites

In case of nano dimensioned reinforcing agents, some inevitable changes have to be made in the fabrication strategy as the volume ratios or densities of the nanostructures are considerably low compared to the micro-reinforcing agents. Three primary processes are adopted for compounding epoxy nanocomposites, namely *in-situ* polymerization, solution intercalation, and melt intercalation which are serially discussed in the following sub-sections.

In-situ polymerization

As the name states, the method involves the polymerization of monomers or prepolymers in the presence of nanomaterials. The nanostructure is dispersed in the liquid mixture of monomers or prepolymers by mechanical forces like agitation or sonication, and the polymerization is initiated. The monomer or prepolymer units get intercalated between these nanostructures and after formation of the polymer chain, they get well separated from each other, resulting in a uniformly dispersed nanocomposite formulation [142]. The techniques have several advantages that offered it extraordinary popularity. These include: the use of less or no solvent offers eco-friendliness; the reinforcing material experiences less intra-particle attraction and thus is evenly distributed over the matrix; strong matrix-reinforcing agent bonding and high-filled nanocomposite can be prepared or used as a masterbatch for amalgamating with other polymers [143]. A recent review by Mao et al. offered meaningful insights into polymer/graphene nanocomposites prepared by in-situ intercalation [143]. A hyperbranched epoxy nanocomposite was prepared by this *in-situ* polymerization method by Gogoi et al. The report demonstrated

the *in-situ* growth of Ag nanoparticles over nanofibrillar cellulose (NFCs). These Ag nanoparticles-decorated NFCs were then added to a mixture of BPA and epichlorohydrin followed by epoxidation to produce the nanocomposite [144]. The limitation of this technique, however, the laborious workup process of epoxy by successive washing that may result in separation of nanomaterials from the epoxy network.

Solution intercalation

Solution mixing or intercalation is the most competent technique utilized for fabricating epoxy nanocomposites on account of the magnificent solution-forming ability of epoxy resins in a wide spectrum of solvents. The whole process comprises three phases: first dispersion of the nanomaterial in a suitable solvent or solvent mixture by mechanical forces; amalgamation of these dispersions with the epoxy solution by sufficient agitation; and finally, evaporation/removal of the solvent to create the nanocomposite [142]. The solubility of the epoxy and dispersion stability of the nanomaterial critically determine the final performance of the nanocomposite. Commonly, nanomaterials, due to their inherent surface properties, have an inclination to agglomerate, which can only be conquered by suitably modifying their surface with functional moieties that further result in a homogeneous dispersion in the matrix [145]. The nanocomposite prepared by Frone et al. followed the solution intercalation method by taking the epoxidized linseed oil and itaconic acid in tetrahydrofuran (THF) solvent and then adding the modified NFCs to the mixture. The evaporation of THF in the subsequent stages, followed by curing, resulted in the bio-based epoxy nanocomposite [119]. The very intriguing research by Rajimol et al. illustrated the proficient extraction of oxyresveratrol as a green anticorrosive agent from coconut shell wastes and incorporated inside mesoporous silica nanocontainers. These nanocontainers were then impregnated into an epoxidized castor oil system crosslinked with citric acid to give multifunctional a nanocomposite system [146]. However, the excessive use of solvent raises the sustainability questions and thus facilitates the adaptation of new strategies using green solvents like water, ethanol, ionic liquids, etc.

Melt blending

At this juncture, melt blending is the most practical and versatile nanocomposite-fabrication technique, because the use of toxic solvents can be avoided here. The technique utilizes high shear force to disperse the nanomaterial in the epoxy system, with

or without implementing high temperatures. The mechanical agitation, which requires conventional instruments like an extruder, kneader, injection molding machine, etc., results in intercalation or exfoliation of the nanomaterials [142]. A similar method was adopted for preparing super-crosslinked epoxy nanocomposite by intercalating ionic liquid with montmorillonite clay in an epoxy system. The nano clay was dispersed in the epoxy prepolymer by ultrasonication and then cured with the hardener to get the highly crosslinked nanocomposite [147]. Yue et al. performed surface modification of CNCs by an amino trimethoxy silane The freeze-dried modified CNCs were then added to a bio-based epoxy made from diphenolic acid, ultrasonicated for uniform dispersion, and subsequently mixed with isophorone diamine and cured [148].

The limitation of this process originates from the fact that at high concentrations of nanomaterial, the dispersion becomes inefficient. Moreover, applying high shear force to the highly viscous melt may trigger buckling, shortening, or coiling of the nanomaterials that render their performance [142].

1.4. Characterization and analytical techniques

The following discussion illustrates the various spectroscopic, microscopic, and analytical procedures selected for scrutinization of the chemical structure, composition, morphology, etc. of epoxies, different reinforcing agents, and their composites.

1.4.1. Spectroscopic techniques

1.4.1.1. Fourier transform infrared (FTIR) spectroscope

This renowned spectroscopic technique enables ground-state investigation of the chemical connectivity and infrared active functional moieties present in the materials under observation. In FTIR technique, the sample is measured by blending with potassium bromide (KBr) pallets, while in case of attenuated total reflectance (ATR) FTIR technique, the pristine sample can be used without any prior modification. This technique can be employed as a primary investigation for knowing the formation of epoxy, as the two characteristic stretching vibrations (-C-O- and -C-O-C- bonds) of the oxirane ring always appear near 850-930 cm^{-1}. Interestingly, when the epoxy resin is cured with the hardener, the two distinctive peaks disappear completely. Other conventional stretching vibrations for -OH, -C-H, -C=C-, -C-O-, -C=O, etc. appear in their individual positions near 3300 cm^{-1}, 2950-2800 cm^{-1}, 1600 cm^{-1}, 1200 cm^{-1}, 1700

cm^{-1}, respectively [28, 29]. Shibata et al. prepared bio-based epoxy from a cross-aldol product of vanillin and cyclopentanone, which showed a characteristic epoxy peak at 912 cm^{-1} in the FTIR spectrum that vanished in the cured thermosets [32]. The formation of reinforcing agents such as CNFs, metal nanoparticles, graphene, etc. can also be assured using FTIR spectral analyses. For microfibers or CNFs derived from plant source, distinct peaks appear near 3400 cm^{-1}, 2880 cm^{-1}, 1420 cm^{-1}, 1165 cm^{-1}, and 1600 cm^{-1} which are typical for cellulosic -OH stretching, -C-H stretching, H-C-H bending, glycosidic -C-O-C- stretching, and absorbed water present in cellulose [117, 118]. During modification, some additional peaks may appear, as in the case of ethylene diamine and polyethyleneimine modified CNFs, with a new peak at 1740 cm^{-1} for the ester groups [115]. The characteristic FTIR peak at 588 cm^{-1} corresponding to the Fe-O bond [149] and at 380 cm^{-1}, originating from the Zn-O bond stretching [104] signified the successful formation of FeO and ZnO nanoparticles, respectively.

1.4.1.2. Raman spectroscope

This is a spectroscopic technique used to measure the vibrational modes of molecules based on the renowned Raman effect. The technique has potential utility in the field of polymer composites to probe electrical conductivity, optical nonlinearity, strength, piezoelectric effect, etc. Basically, it evaluates the inelastically scattered monochromatic light of wavelength falling in the near-UV, visible, or near infrared range after interacting with the analyte [150]. Interestingly, different nanomaterials can be distinguished by critically analyzing their Raman spectra. For example, GO nanostructures display two characteristic bands: the G band near 1570 cm^{-1} and the D band near 1350 cm^{-1}, which may undergo shifts post-modification [123]. Other nanomaterials, including CNFs, BN, g-CN nanosheets, and metal nanoparticles, similarly exhibit distinctive Raman spectra. In fact, the intriguing dispersion stability of CNFs has visible credits in their exposure as water-based substrates for surface-enhanced Raman scattering [151].

1.4.1.3. Nuclear magnetic resonance (NMR) spectroscope

For validation of the chemical structures and formation of oxirane rings in the epoxy resins require sophisticated spectroscopic techniques, including NMR. The basic instrumentation principle in NMR revolves around the study of the shift in magnetic frequency of the atoms under consideration due to molecular orbital coupling with

external magnetic field [152]. Both carbon (^{13}C) and proton (^{1}H) NMR can be utilized for confirming the complex structures of epoxy prepolymers, the different chemical environments around them, structure of intermediate species, and reaction dynamics. Presence of other NMR active nuclei inclusive of boron (^{11}B), nitrogen (^{14}N), fluorine (^{19}F), phosphorous (^{31}P) can also be detected by this technique. Conventionally, the appearance of peaks at 2.8-3.5 ppm in the ^{1}H spectra and near 54-60 ppm in the ^{13}C spectra of an epoxy resin validates the presence of epoxy ring, however, shifting may occur depending on the chemical environments [16]. To add more, solid-state NMR is also available for analyzing solid samples, such as epoxy thermosets, CNFs, etc. The solid-state ^{13}C NMR was recorded for neat and modified CNFs by Niu et al. Peaks for all six cellulosic carbons appeared in the range 60-100 ppm, which remained unaltered after modification. Rather, the appearance of some additional peaks in the spectra of modified CNFs authorized surface functionalization [118]. Suzuki et al. implemented an advanced NMR methodology (the saturation transfer difference technique) to comprehend the association of protein receptor molecules with TiO$_2$ nanoparticles [153].

1.4.1.4. UV-visible spectroscope

In this spectroscopic technique, UV or visible light induces electronic excitation among the analyzed samples [150]. Each transition leads to specific absorption bands, from which the presence of functionalities can be detected. Transitions under such irradiation conditions include n to π^{*} or π to π^{*} transitions instigating from the -C=C- or lone pairs present in -C=O, -C-N-, -N-H bonds, etc. UV-visible spectroscopy can be categorically utilized to detect as well as scrutinize the size, shape, and concentration of different nanomaterials like metal, metal oxide nanoparticles, graphene, g-CN, etc. Metal or metal oxide nanoparticles experience the surface plasmon resonance (SPR) phenomenon generated due to the scattering of light by cumulative resonance of conducting electrons. Aziz et al. synthesized biogenic Ag nanoparticles that exhibited a broad absorption peak with a maximum wavelength (λ_{max}) at 440 nm. Changing the pH of the precursor solution to alkaline, however, resulted in a red shift, indicating the formation of larger-sized nanoparticle aggregates, at higher pH [154]. Green ZnO nanoparticles synthesized from plant extract, were similarly conformed by the presence of an absorption peak with λ_{max} 374 nm [155].

Further, the examination of film-transparency; study of reaction kinetics; adsorption of metal ions or degradation of dyes; analysis of biocompatibility, biodegradability, release of drug molecules, etc. are some additional features that further add to its credential.

1.4.1.5. X-Ray photoelectron spectroscope (XPS)

XPS is a surface-sensitive quantitative detection technique capable of furnishing information about the elemental composition, empirical formula, chemical and electronic structure of elements present in the analyzed material. The instrument works under the principle of Einstein's photoelectric effect and measures the number and kinetic energy of electrons ejected from 1-10 nm surface depth of the sample when irradiated with X-ray beams [150, 156]. Literature provides numerous reports on bio-based flame-retardant epoxies that have investigated the presence of foreign elements such as phosphorous (P), sulfur (S), silicon (Si), etc. responsible for fire resistance activity [157, 158]. Howsoever, the mastery of XPS in diagnosing oxidation states of elements is best employed in nanotechnology for inspecting different structures of nanomaterials. The structure of CNFs was established through XPS by Kim and coworkers in their study on CNF/GO-based hybrid filaments [159]. Similarly, S and silane grafting over the surface of pineapple leaf fibers were confirmed by recording their XPS spectrum [160]. In the XPS spectra of metal nanoparticles, the characteristic peak positions and the elemental composition parameters signify the crystal structure of the metal as well as its surrounding environment [103-105].

1.4.2. Diffraction and scattering techniques

1.4.2.1. X-ray diffraction technique

XRD is a ubiquitous technique used to garner information including crystallinity, crystal size and shape, phase identification, purity, and morphology of different polymers, reinforcing agents or composites within a very short period of time [150, 161]. X-rays have wavelengths in atomic ranges, and on interaction with atoms or molecules, the rays get diffracted which are further used for harnessing information about the particle sizes, crystal structure, position of atoms in unit cells, spacing between atomic planes, etc. of the analyte [162]. Epoxy generally contains amorphous moieties rising to broad amorphous peaks in its pristine XRD diffractograms. On incorporating different micro- or nanostructures into epoxy, characteristic peaks owned by these foreign agents can be

observed in the modified system. As an illustration, the ZnO/AEJO nanocomposite possessed the characteristic ZnO peaks in its XRD spectrum, along with a broad amorphous peak originating from the pristine matrix [104]. Furthermore, the use of Bragg's equation ($2d\sin\theta = n\lambda$; where d, θ, n, and λ represents the interplanar distance, diffraction angle, order of diffraction, and wavelength of X-ray used, respectively) offers an evaluation of the interplanar distance. Correlating these distances and peak intensities with Joint Committee on Powder Diffraction Standards, JCPDS files, the phase structure can be correctly predicted. For example, Aung et al. predicted the structure of synthesized ZnO nanoparticles to be hexagonal wurtzite type from their XRD spectra [104].

1.4.2.2. Dynamic light scattering (DLS) technique

This technique assesses the particle size, distribution, and stability (in terms of Zeta potential (ζ)) of aerosols, colloids, suspensions, and solid samples by measuring the scattering of laser beam and Brownian motion of particles. In the field of nanotechnology, DLS measurements are crucial for determining the particle size of different nanostructures, while the ζ value demonstrates interparticle affinities and their dispersion stability. Traditionally, a ζ value above ±30 mV signifies good dispersion stability and minimum interaction among the particles [163]. The Fe nanoparticles prepared by Plachtová et al. appeared to be 300 nm of diameter with a ζ value of -35 mV as obtained from the DLS study, indicating their outstanding stability in aqueous medium [106]. Similarly, biogenic Ag nanoparticles possessed a ζ value of -22 mV with a zeta particle size of 183 nm [164].

1.4.3. Microscopic techniques

1.4.3.1. Scanning electron microscope (SEM)

This technique involves the use of a focused electron beam to probe the topography of the observed specimen. As the high-speed electrons reach the sample surface, several surface interactions occur, leading to the ejection of electrons from or near the surface, which collectively construct the images of the surface [150]. In the realm of epoxy composites, SEM imaging is generally implemented to assess the topography of thermosets, nanomaterials, and composites. For instance, pine microfibers modified with an epoxy resin were observed under SEM to obtain picturesque inferences. The fractured surfaces of these fiber-incorporated composites provided a visible improvement in the

fiber-matrix interaction [165]. Likewise, morphologies of neat and modified nanosheets as well as their amalgamated products as epoxy composites were also observed in SEM [123]. The extended version of SEM, the field emission SEM (FESEM) further expands the observation dimensions of surface morphology with magnification ranging from 10× to 300,000×.

1.4.3.2. Transmission electron microscope (TEM)

Like SEM, TEM is another eminent microscopic technique that employs highly focused electron beams to construct images of samples, but unlike SEM, which is limited only to surfaces, the beam in TEM is transmitted through the whole sample. The electrons either get scattered or transmitted through the thin samples, and from the images constructed, crucial aspects of morphology, crystal structure, and composition can be attained [150]. The technique is incredibly good for assessing the size and shape of nanoparticles, evenly dispersed networks of CNFs, layered nanosheets, and their integration even with epoxy matrices. The TEM images recorded for CNFs and modified CNFs for epoxy nanocomposite fabrication unveiled finely dispersed web-like nanofibers, and the diameter measured from the images appeared to be 10-60 nm for CNFs that decreased to less than 10 nm during modification [117]. When the biogenically synthesized Ag and Au nanoparticle dispersions were observed under TEM, spherically shaped Ag nanoparticles of 15 nm average diameter were marked. Alternatively, Au nanoparticles possessed significant irregularity, even though they seemingly appeared spherical [99].

1.4.3.3. Atomic force microscopy (AFM)

AFM is a sophisticated analytical tool to image and evaluate the surface properties of all kinds of samples, from hard to soft, natural to synthetic, insulating to conducting surfaces, and much more. It employs a highly sensitive probe (tip) for tracking the surface, which is in turn connected to a flexible beam. The force between the tip and the surface deflects the beam elastically, monitoring which, the surface morphology can be mapped [150]. This technique is extensively used for mapping as well as evaluating the size and thickness parameters of nanosheets and nanofibers. As observed by Guo et al., in their graphene-BN based nanocomposites, the exfoliated BN nanosheets appeared to be 4-14 nm thick with a lateral size of 2 μm [121]. Frone et al. similarly investigated the morphology of CNFs to establish the changes occurred during the extraction process [166].

1.4.3.4. Energy dispersive X-ray spectroscope (EDX)

This technique is essential for the detection and estimation of different elements on the investigated sample surfaces. The process utilizes the high-speed electron beam, as in the case of SEM and TEM, and maps the distribution of different elements in the corresponding imaged area of the sample. This technique was used to measure the purity of CNFs by Krishnan and Ramesh [167]. The EDX spectrum of biogenic Ag nanoparticles synthesized from plant extracts explicitly unveiled the presence of 61% Ag with 26% oxygen content [164].

1.4.4. Testing methods

1.4.4.1. Physical testing methods

The synthesis of epoxy resin is accompanied by the evaluation of their numerous physical characteristics, inclusive of molecular weight, epoxy equivalent weight (EEW), hydroxyl value, etc. following some established protocols.

The molecular weight determination of epoxy prepolymer is important to establish its structural attributes. Generally, like other polymers, the molecular weight of epoxy can be evaluated using gel permeation chromatography (GPC), vapor pressure osmometry, light scattering, NMR, mass spectrometry, etc. GPC is the most commonly used technique that provides valuable information such as the number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index of epoxy prepolymers [168]. The EEW or epoxide content of an epoxy resin is the mass in grams of the resin containing one mole equivalent of epoxide. The EEW value is needed to know the accurate amount of hardener required for curing of the epoxy resin [9]. Industrially, a variety of methods are utilized for calculating EEW, including the hydrochloric acid (HCl)-acetone method, the HCl-pyridine method, the hydrogen bromide (HBr)-glacial acetic acid (standard American Society for Testing and Methods (ASTM) D1652-73) method, etc. [169]. The hydroxyl value, likewise, measures the number of free hydroxyl groups available in the epoxy prepolymer and is measured by acetylation of the free hydroxyls with acetic anhydride in pyridine medium. It is expressed in milligrams of KOH or NaOH consumed by one gram of epoxy during the analysis. Another important feature of epoxy resins is their inherent viscosity that can be measured using standard techniques. The changes in viscosity with time, temperature, and stress offer useful insights into the rheological behavior of epoxy. Rheological

measurements can also provide information about the crosslinking density of epoxy thermosets, required to assess the extent of curing occurred in the thermosets.

1.4.4.2. Mechanical and thermal tests

The current status of epoxy thermosets is all because of their extraordinary mechanical and thermal properties. The mechanical properties of epoxy and its composites, such as tensile strength or stress, tensile modulus, strain or elongation at break percentage, flexural strength and modulus, etc., can be measured in a universal testing machine (UTM). Following standard ASTM methods (ASTM D 638), rectangular or dog-bone-shaped thermosets are stretched by applying loads of 0.5-10 kN, when the stress-strain profiles are obtained, yielding the ultimate tensile strength and elongation at break of the specimen [170]. Other important aspects of epoxy thermosets are impact strengths and scratch resistance. Impact strength is evaluated by the standard falling ball method (ASTM d5628-16), where a metal ball of a certain weight is allowed to fall on the specimen coated metal plates from known heights, and the maximum height recorded before sample failure is noted for evaluating the impact strength. The scratch resistance measurement is performed in a scratch tester by an indenter loaded with standard weights to scratch the thermoset surface coated in plates (ASTM D7027-13) [171].

Thermal analysis of epoxy thermosets, different reinforcing agents, and their composites is performed using Thermogravimetric analyzer (TGA) that reveals the degradation profiles of the specimens when heated continuously to a high temperature. As the temperature increases, the variations in the weight of the specimen are observed. By monitoring these weight changes, the decomposition patterns can be understood, which in turn unveils details of thermal stability, onset degradation temperature, weight residue after degradation, etc. [172]. Furthermore, Differential scanning calorimetry (DSC) discloses facts about the melting (T_m) and glass transition (T_g) temperatures, crystallinity, kinetic parameters, etc. during the curing process of the epoxy thermosets and nanocomposites that help in understanding the structure-property relationship of the specimens [172]. More critical aspects of the thermo-mechanical behavior of bio-based epoxy and composites can be understood from the Dynamic mechanical analyzer (DMA).

1.4.4.3. Chemical resistance and aging tests

The chemical resistance behavior of epoxy thermosets and their composites can be

evaluated by monitoring the weight loss profiles during prolonged exposure to different harsh chemical media (ASTM D 543-67). Similarly, to understand the weathering resisting of epoxy composites against UV irradiation, extreme temperature exposure, solvent treatment, etc. the aging tests can be performed using the established protocols.

1.4.4.4. Biological tests

(a) Biocompatibility

Bio-based epoxy and its derivatives like biocomposites and nanocomposites can be utilized in different biomedical applications, for which assessing their biocompatible (i.e., cell-loving) behavior becomes crucial. The biocompatibility can be evaluated by performing a series of *in vitro* or *in vivo* analyses, including hemocompatibility tests, cytotoxicity tests, cell viability and proliferation tests, etc. [150]. The hemocompatibility test simply tracks the possible adverse effects (hemolysis, thrombosis, activation of platelets, etc.) of the prepared material when it comes in contact with mammalian blood [150]. The extent of red blood cell (RBC) lysis initiated by the polymer materials is evaluated from the hemoglobin concentration obtained using a UV-visible spectrophotometer (λ_{max} = 560 nm). Similarly, in the cytotoxicity test, the material is either implanted inside a living body or cells are allowed to grow over it in outdoor conditions. If the material leaches any toxic chemicals, the cells seeded over the material start dying, and cell propagation are no longer be observed [173]. However, the observation of normal cell growth signifies good cell compatibility of the material.

(b) Biodegradability

For examining the biodegradability of epoxy thermosets and their composites, several established protocols are adopted. Degradation by soil burial is a standard method for quantitative estimation of the extent of biodegradability of a material. The test involves burying the analyte sample of a definite dimension in soil. The experimental conditions can be varied according to the requirements; tests can be performed in outdoor soil as well as by incubating the materials in collected soil samples in laboratory conditions [174]. However, in the case of indoor soil burying, the soil parameters like humidity, moisture content, etc. need to be controlled precisely. The degradation of the epoxy is initiated with the help of the microorganisms present in soil, by breaking the polymer linkages through their enzymatic action. The percentage of biodegradation that occurred is evaluated by recording the weight loss or observing the samples under SEM or

FESEM. The McFarland turbidity method is another crucial technique of biodegradation where test specimens are subject to different bacterial solutions and the change in turbidity of the solution is monitored by recording their absorbance periodically [171]. The increasing turbidity of the solution confirms the growth of the bacterial colony, which in turn suggests the degradation of polymer chains producing nutrients for the bacteria. The weight loss measurements during the test further confirm the degradation process [174].

(c) Antibacterial test

To test the bactericidal activity of the prepared epoxy thermosets and their composites, the antibacterial test is performed by the agar well and disk diffusion methods. In the disk diffusion method, the bacterial strains are allowed to grow in the disk of agar medium containing the specimens and incubated to obtain the inhibition zone diameters. In the well diffusion method, the colony formation unit is measured to imitate the antibacterial activity of the materials.

1.4.4.5. Electrical tests

Different electrical properties present in the epoxy thermosetting materials, such as conductivity, oxidation-reduction potential, impedance, potentiodynamic polarization (PDP), etc., can be measured using sophisticated instruments. Specifically, the PDP and impedance study is crucial for analyzing corrosion resistance parameters for epoxy coatings. These studies measure the impedance created by the coating in the passage of electrons that in turn determine the anticorrosion activity of the coating. In the PDP study, the epoxy-coated metal acts as the test electrode to which a range of potential is applied, and the redox reaction happening on the metal generates the current. From the plot of potential versus current density, different corrosion parameters are reckoned [175].

1.5. Properties

All the fame and credibility currently achieved by bio-based epoxy resins undoubtedly originates from their inherent mechanical and thermal properties. The amalgamation of these resins with prudently designed reinforcing materials produces composite systems with extravagant performances along with some add-in features. The subsequent segments exemplify some recent advancements on the intriguing features of bio-based

epoxy thermosets and their composites.

1.5.1. Physical properties

As stated in **Section 1.4.4.1,** the various physical properties of bio-based epoxy are important for the processing and fabrication of thermosets and composites. EEW precisely determines the hardener amount for obtaining an ideal crosslinked system. For instance, eugenol was glycidylated to give an epoxy with an EEW of 195 g/eq [29]. A series of biobased epoxies were fabricated by Patil et al. from gallic acid and epichlorohydrin that encompassed variable epoxy content depending on changing reacting times. The epoxy content of the resins increased with reaction time and critically affected coating properties [176]. Similarly, the high molecular weight of the epoxy resin prepared from lignin positively affected the thermal stability of the cured thermoset [177].

1.5.2 Mechanical properties

The mechanical properties of bio-based epoxies play a decisive role in their end applications. The undervalued mechanical strength of bio-based epoxy can be improvised by incorporating exciting reinforcing agents into the epoxy. Different micro-reinforcing agents with high loading percentages are added to bio-based epoxies in order to significantly enhance their performance. Contrary to this, due to the large surface area, only a minute amount of nanomaterial (even less than 5 wt% of the epoxy) is needed to increase the strength of pristine epoxy by many folds. A dose-dependent strength gradient is the typical case for both micro- and nano-sized additives; however, after a maximum loading limit, agglomeration occurs that tends to lower the mechanical properties. The biocomposite of jute fiber and vanillin-based epoxy exhibited a maximum tensile strength of 83 MPa and a Young's modulus of 2.8 GPa, which was way better than the pristine epoxy and DGEBA-jute fiber composite, although strain decreased to 4% (while 12% in the pristine thermoset) [93]. Most of the time, the matrix-reinforcing agent interface also determines the final performance of the composite, as poor interfaces serve as crack generation points, deteriorating the overall properties. To conveniently modulate the interfacial connectivity, micro- or nanomaterials are often functionalized with suitable chemical moieties [145]. In the fully bio-based composite system prepared from bacterial cellulose and bio-based epoxy, the cellulose was modified with silane groups that showcased 30% and 35% increase in Young's modulus

and stress values in the final composite, respectively [178]. The nanocomposite prepared from lignin-containing CNFs and vanillin-based epoxy similarly exhibited improvement in tensile strength up to 59.5 MPa (81% higher than the pristine) with 1 wt% nanomaterial content. Further increasing the CNF content lowered the strength, while strain at break values were independent of the nanofiber loading [61].

Other mechanical performances, including pull-off or adhesive strength, impact strength, etc. can be determined accordingly, as obtained for DGEBA-competing bio-epoxy prepared by Nikafshar et al. [179]. The bio-epoxy possessed 30.5 MPa tensile strength, 1.72% elongation at break, 3.71 MPa pull-off strength, and 29.6 kJm^{-2} impact strength which were better than DGEBA (with respective values of 29.6 MPa, 1.79%, 4.41 MPa, and 27.3 kJm^{-2}) [179]. Here also, the incorporation of reinforcing agents significantly increases these properties in the composite.

1.5.3. Thermal properties

Measurement of different thermal properties of bio-based epoxies and their composites by TGA or DSC techniques unveils thermal stabilities and enables their exploitation in high-temperature-based applications. Normally, as high temperatures are gradually applied, epoxy thermosets and their composites show two typical degradation stages: the first one above 200 °C and the second one above 400 °C. The thermal stability of these thermosets changes according to the crosslinking density and the amount of aromatic moiety present; more crosslinking or aromatic content triggers a higher T_g and better thermal stability. Dense crosslinking and higher aromatic content evidently restrict the motion of polymer chains and increase rigidity in the system, resulting in higher T_g values. This type of conventional correlation was observed in the gallic acid-based epoxy prepared by Patil et al. [176]. Moreover, adding suitable reinforcing agents to the pristine epoxy has been proven to be an efficient way to attain high thermal stability. The modified CNC-incorporated bio-based epoxy system illustrated a remarkable increase in T_g (136 °C with 10% CNC loading) compared to the virgin epoxy (126 °C) because of the restriction effect [148]. The DMA study further provides some important aspects of the thermo-mechanical properties of epoxy, like crosslinking density, storage modulus, loss modulus, dimensional stability, etc.

1.5.4. Weathering resistance

Weathering is basically the deterioration of a material after prolonged exposure to harsh

environmental conditions. The bio-based epoxy derived composite materials are expected to have good weathering resistance for outdoor-based applications. They are subject to acidic, alkaline, or corrosive electrolytes to test their chemical resistance [176]. Similarly, solvent spot tests, water absorption tests, exposure to UV and high temperatures, etc. are some typical experiments performed to understand the weathering resistivity of epoxy-based materials [93]. The biocomposite of sisal fiber, hemp fiber, and their hybrid mixture with bio-based epoxy has been studied for UV exposure and water spray tests for a one-year period. Studying the different mechanical and thermal properties of the weathered samples and characterizing them with FTIR suggested the acceptability of the biocomposite for outdoor-based structural applications [180].

1.5.5. Biological properties

1.5.5.1. Antibacterial properties

Bio-based epoxies with antibacterial properties have attracted admirable consideration from the research community. The biocidal activity is either inherently present in the native epoxy or adventitiously introduced by different additives, and possible modes to achieve the bactericidal effect include contact killing, anti-adhesion or bacteria repelling, antibacterial agent release, etc. [157]. The degradable, betaine ester group-abundant epoxy prepared by Han et al. owned intrinsic bactericidal activity against *Escherichia coli* and *Staphylococcus aureus*, credited by the cetyl chloroacetate groups present in the epoxy [20]. The epoxy derived from the syringaldehyde-furan system also demonstrated bacteria-repelling activity [157]. Such benignly degradable epoxy delivers an interesting platform as an antibacterial coating for biomedical applications. A variety of metal nanoparticles own in-built antibacterial activity that can be infused into bio-based epoxy systems with an intention to prepare antibacterial nanocomposites. The nanocomposite of a TiO_2-infused lignin-epoxy system exemplified the same by exhibiting antibacterial activity along with good mechanical strength and UV absorptivity [101]. These proficient nanoparticles can deform the cell walls of the microorganisms and disrupt their metabolic cycles, which in turn slows down their growth [100].

1.5.5.2. Biocompatibility

The fact that bio-based epoxies are derived from non-toxic plant-based compounds leads one to hypothesize the presence of an inherent biocompatible nature in them, which may not always be the case. Biocompatibility is a vital feature for epoxy systems to have

employability in the field of biomedical engineering, where they are subject to direct contact with the living cells. A number of tests are performed to establish the cell-loving nature of the epoxy systems, including cell adhesin, cell proliferation, tissue response, hemocompatibility, etc. Epoxy-derived medical devices such as coatings, dental sealants, bone scaffolds, soft tissues, etc. are either implanted inside a living system (*in vivo*) or in cultured cell media (*in vitro*) to monitor their interference in normal cell functions [181]. An interesting study by Jiang et al. established the lower estrogenic activity (and hence low toxicity) of a dihydric phenol (lower than BPA) derived from eugenol that was used as an epoxy precursor [182]. The elastomeric epoxies prepared from plant oils as flexible sensors demonstrated excellent cell viability against colorectal adenocarcinoma cells (Caco-2) cells at a considerably high concentration of 20 mg/mL [25].

1.5.5.3. Biodegradability

With the imposed ecological legislation and green technology principles, degradability has become the primary required criterion for polymers. Bio-based epoxy systems possess biodegradable feedstocks that trigger their degradation under environmental conditions. Recently, several bio-based epoxy systems have been prepared in the light of vitrimer chemistry that can be degraded using suitable stimuli (for example solvent). The seawater-degradable betaine ester-modified epoxy is the best example of such a system, which can undergo auto-degradation in a weakly alkaline buffer solution within a short period of time (13.8 days) [20]. Although epoxy possesses degradable linkages such as hydrolysable esters, glycosidic linkages, etc. that can facilitate its degradation in atmospheric conditions, rapid biodegradation of epoxy is sometimes rendered impossible by its high crosslinking density [3]. In such situations, different biodegradable, natural reinforcing agents serve the cause and promote the degradation of the epoxy or composite systems by excessing the ingress of microorganisms (present in the environment like soil or aquatic bacteria, fungi, algae, etc.) into the polymer network [183]. These species first cause fragmentation of the polymer chains, hydrolysis of ester and amide linkages, and then finally depolymerization and mineralization to carbon dioxide and water [183]. Kadam et al. has studied the biodegradation of karanja-oil epoxy cured with citric acid and tartaric acid by using bacterial granules. A maximum degradation of 82% (69 days) and 95% (259 days) was recoded for citric and tartaric acid cured films, respectively. The SEM images revealed the presence of cracks and large holes in the film's surface as an outcome of initial biodegradation [183]. The

degradability using soil burial test was studied in the biocomposites prepared from epoxy and palm kernel shell derived $CaCO_3$ [184].

1.5.6. Barrier properties

The presence of an extended crosslinking structure and the introduction of a protective reinforcing agent enable the epoxy-based systems to prevent the ingress or passage of ions, solvents or gas molecules through them. Thus, these systems exhibit excellent barrier properties. Anticorrosion activity has been recorded in a number of bio-derived epoxies, such as the cashew nutshell liquid-derived one-component epoxy that on curing with 1-methylimidazol displayed excellent anticorrosion performance [185], and ESO cured with hempseed oil-derived anhydride curing agent possessed strong corrosion resistance [186]. Nanomaterials such as GO, BN nanosheets, ZnO, SiO_2, TiO_2, etc. are proficiently utilized in bio-based epoxy systems to introduce anticorrosive activity in the latter [104, 123, 187].

1.5.7. Fire resistance

The fire-resistance or flame retardancy is a salient feature of bio-based epoxy systems originating from their inherent structural attributes: presence of aromatic rings, fire-safe elements like fluorine, Si, P, N, etc. Additionally, different fire-resistant reinforcing materials can be incorporated to fabricate flame-retardant composites [158]. For instance, the biocomposite prepared by Kumar et al. demonstrated good flame retardancy [93]. Lou et al. functionalized microcrystalline cellulose with chitosan and sodium phytate and incorporated them (in 15 wt%) to an epoxy system. The material passed the UL-94 test and disclosed a limiting oxygen index of 26.2% that demonstrated its excellent fire-resisting behavior [188].

1.6. Applications

All the intriguing features of pristine epoxy and its composites designed with efficient reinforcing materials amplify their prospective applications to a wide range of technical sectors. Some advanced applications of bio-based epoxy and its composites are highlighted in the succeeding sections.

1.6.1. Coatings and adhesives

Epoxy, as an esteem thermosetting polymer, has managed to enter in a plenty of

industrial coating formulations. The excellent chemical and weathering resistance of bio based epoxies and the high-performance anticorrosive behavior of multifarious nanocomposite systems attained with the aid of nanotechnology won these achievements [189]. Recently, a waterborne hydrophobic coating was prepared by Zheng et al. by incorporating SiO_2 nanoparticles into a bio-based epoxy. The nanocomposite system demonstrated anticorrosion performance with 93.75% inhibition efficiency against metallic substrates [190]. Again, on account of the toughening effect inherently present or induced by reinforcing agents, bio-based epoxies have been highly desired in the field of adhesive and structural applications [191]. Now, pressure-sensitive adhesives have started gaining attention, which can adhere to substrates with light external pressure and can be cleaned easily from the substrate because of the cohesive force present. Paul et al. utilized acrylated epoxidized linseed oil, along with other formulations, to fabricate such pressure sensitive adhesives [192].

1.6.2. Aviation and industrial tooling

The unprecedented toughness, mechanical strength, and thermal stability of bio-based epoxy composites have made them to debut in the aviation industry as light-weight, durable composites. Such composites are being employed for compounding body parts of aircraft, cars, boats, wind turbines, and for producing industrial tools like molds, fixtures, master models, castings, laminates, etc. [63]. The bio-based epoxy thermosets derived from vanillin and phloroglucinol with high mechanical strength and a T_g of 100 °C enabled their usage in high-end applications, including space, aircraft, and automobiles [12]. A recent well-defined review has ingeniously discussed the possibilities of bio-based epoxies and their composites in the field of engineering applications, obviously not excluding the aviation industry [193]. A miraculously high thermal stability was achieved in an epoxy derived from magnolol, showing a T_g as high as 326 °C and a weight residue of 52% with good flame retardancy, making it the best choice for the aerospace industry [194]. Additionally, in view of the rising energy costs, light-weight natural fiber-derived hybrid epoxy biocomposites are gaining remarkable attention for energy-efficient applications. The soy fiber-reinforced bio-based epoxy biocomposite is one such example of a light-weight composite [195].

1.6.3. Biomedical and health care

Bio-based epoxy thermosetting resins are steadily emerging as the dominant polymer of

the bioscience and engineering sectors on account of their innocuous nature and inbuilt features. They are slowly replacing the conventional toxic contenders used in dental sealants, prosthetics, antibacterial coatings, tissue scaffolds, etc. The inborn biocompatibility of these epoxies and the competent performances induced by different reinforcing materials combine to provide efficient medical devices. To prove the same, Hadi et al. fabricated a biocomposite from a bio-based epoxy, flex fiber, and seashell nanoparticles. The biocomposite with strength up to 84 MPa has potential antibacterial activity and the lowest value of total deformation that is essential for its application as prosthetic sockets [196]. A ZnO and ESO-based nanocomposite was similarly prepared for soft tissue application. The optimized mechanical properties, inherent antibacterial activity, reduced water absorption, and porous structure with low gas permeability of the nanocomposite highlighted its prospects in the tissue engineering field [197]. In a very recent study, a hyperbranched epoxy was loaded with curcumin and MXene to prepare bactericidal patches. The study focused on self-healing and shape memory attributes as well as curcumin-induced antibacterial activity of the patches [198].

1.6.4. Electronics and electrical circuits

Epoxy resins have quite good insulating properties, because of which they have been widely employed in electronics and circuits as insulating sealants for protecting them from short circuits, dust, and moisture [63]. Their characteristic fire-resistance behavior is a bonus for such applications. Moreover, by incorporating suitable nanostructures, epoxy nanocomposites can be tuned as thermally conductive systems for heat dissipation in electronic devices [191]. Examples of such potential nanostructures include SiO_2, alumina, MXene, BN nanosheets, Ag or Cu nanowires, etc. Such nanostructures, when inserted in bio-based epoxies, attain additional advanced features such as EMI shielding, electrical conductivity, etc. Ag nanowire-decorated cellulose was incorporated in a bio-based epoxy that demonstrated good thermal conductivity and EMI shielding for thermal management applications [110]. ESO was cured with bio-derived benzoxazine that resulted in a high-performance eco-friendly material with a quite low dielectric constant suitable for printed circuit board applications [199].

1.7. Scopes and objectives of the present study

The aforesaid facts lead to the inference that bio-derived epoxies are crucial for the derivation of sustainable and innocuous materials. Such bio-based epoxies can

potentially replace toxic commercial counterparts when utilized as pristine or in amalgamated forms with micro- and nano-reinforcing agents. These environment-friendly biocomposites and nanocomposites with intriguing structural attributes find pertinency in the field of adhesives, structural architectures, corrosion-resistant coatings, in biomedical sciences as drug delivery systems, antibacterial coatings, etc.

Considering the above discussion, the following objectives have been constructed for the current investigation:

- ☑ To synthesize a bio-derived epoxy, employing TA as the primary precursor.
- ☑ To characterize the prepared TA-based epoxy with different analytical and spectroscopic techniques.
- ☑ To study the thermal, mechanical, and chemical properties of the bio-based epoxy thermosets.
- ☑ To prepare multifunctional reinforcing agents such as natural microfibers, CNFs, metal oxide nanoparticles decorated CNFs, etc. with their structural scrutinization using various analytical and instrumental techniques.
- ☑ To incorporate these micro- and nanostructures into the bio-based epoxy resin to obtain the desired epoxy bio/nanocomposites.
- ☑ To characterize the epoxy biocomposites and nanocomposites and to explore their thermomechanical performances.
- ☑ To apply the prepared epoxy biocomposites and nanocomposites as advanced functional materials in the field of biomedical engineering, anticorrosive coatings, structural composites, etc.

1.8. Plan of research

To accomplish the above-stated objectives for the investigation, the following plan of action has been adopted.

- ❖ A comprehensive literature survey on state-of-the-art technologies in the field of bio-based epoxy, their biocomposites and nanocomposites has been carried out primarily.
- ❖ Following conventional routes, a bio-based epoxy resin has been prepared from TA as the primary raw material.
- ❖ Optimization of the reaction conditions has been performed that has been accompanied by synthesis of the resin.

❖ Interpretation of the structural characteristics of the bio-based epoxy resin have been performed by spectroscopic and analytical techniques such as FTIR, NMR, UV, TGA-DSC, GPC, etc.

❖ The physical, chemical, mechanical, thermal, biodegradation, as well as antioxidant properties of the epoxy have been evaluated using different standard techniques.

❖ Different sustainable micro- or nano-sized reinforcing agents have been intended to design and synthesize using potential bio-resources.

❖ The bio-based epoxy resin has been imbedded with these micro- or nano-reinforcing agents to get biocomposites and nanocomposites for anticipated attributes.

❖ Detail characterization of the biocomposites and nanocomposites has been performed using instrumentation techniques such as TEM, SEM, XRD, XPS, etc.

❖ The thermal and mechanical properties along with the biodegradability of the biocomposites and nanocomposites have been evaluated.

❖ The biocomposites and nanocomposites exhibiting preeminent performance has been further employed for possible applications in the field of adhesives, structural architectures, corrosion-resistant coatings, drug delivery systems in biomedicine, etc.

References

[1] Negoita, C., Cristache, N., and Bodor, M. The epoxy resin-History and perspectives. *Materiale Plastice*, 53(3):564-571. 2016.

[2] Rahman, M. R., Taib, N. A. A. B., Bakri, M. K. B., and Taib, S. N. L. Importance of sustainable polymers for modern society and development. In *Advances in Sustainable Polymer Composites*, pages 185-207, ISBN:978-0-12-820338-5. Woodhead Publishing, 2021.

[3] Aggarwal, J., Sharma, S., Kamyab, H., and Kumar, A. The realm of biopolymers and their usage: An overview. *Journal of Environmental Treatment Techniques*, 8(2):1005-1016, 2020.

[4] Rosenboom, J. G., Langer, R., and Traverso, G. Bioplastics for a circular economy. *Nature Reviews Materials*, 7(2):117-137, 2022.

[5] Thompson, R. C., Moore, C. J., Vom Saal, F. S., and Swan, S. H. Plastics, the environment and human health: Current consensus and future trends. *Philosophical Transformation of the Royal Society*, 364:2153–2166, 2009.

[6] Tuladhar, R. and Yin, S. Sustainability of using recycled plastic fiber in concrete. In *Use of Recycled Plastics in Eco-efficient Concrete*, pages 441-460, ISBN:978-0-08-102676-2. Woodhead Publishing, 2019.

[7] Sidek, I. S., Draman, S. F. S., Abdullah, S. R. S., and Anuar, N. Current development on bioplastics and its future prospects: An introductory review. *INWASCON Technology Magazine* 1:3-8, 2019.

[8] Karak, N. Biodegradable polymers. In *Vegetable Oil-based Polymers: Properties, Processing, and Applications*, pages 31-53, ISBN:978-0-85709-710-1. Woodhead Publishing, 2012.

[9] Auvergne, R., Caillol, S., David, G., Boutevin, B., and Pascault, J. P. Biobased thermosetting epoxy: Present and future. *Chemical Reviews*, 114(2):1082-1115, 2014.

[10] Dahiya, S., Katakojwala, R., Ramakrishna, S., and Mohan, S. V. Biobased products and life cycle assessment in the context of circular economy and sustainability. *Materials Circular Economy*, 2:1-28, 2020.

[11] Mashouf Roudsari, G., Mohanty, A. K., and Misra, M. Green approaches to engineer tough biobased epoxies: A review. *ACS Sustainable Chemistry & Engineering*, 5(11):9528-9541, 2017.

[12] Dinu, R., Lafont, U., Damiano, O., and Mija, A. High glass transition materials from sustainable epoxy resins with potential applications in the aerospace and space sectors. *ACS Applied Polymer Materials*, 4(5):3636-3646, 2022.

[13] Yang, X., Wang, C., Li, S., Huang, K., Li, M., Mao, W., Cao, S., and Xia, J. Study on the synthesis of bio-based epoxy curing agent derived from myrcene and castor oil and the properties of the cured products. *RSC Advances*, 7(1):238-247, 2017.

[14] Jin, Y., Hu, C., Wang, Z., Xia, Z., Li, R., Shi, S., Xu, S., and Yuan, L., Bio-based reprocessable and degradable epoxy resins via inverse vulcanization. *ACS Sustainable Chemistry & Engineering*, 11(30):11259-11268, 2023.

[15] Ménard, R., Negrell, C., Fache, M., Ferry, L., Sonnier, R., and David, G. From a bio-based phosphorus-containing epoxy monomer to fully bio-based flame-retardant thermosets. *RSC Advances*, 5(87):70856-70867, 2015.

[16] Liu, R., Zhang, X., Gao, S., Liu, X., Wang, Z., and Yan, J. Bio-based epoxy-anhydride thermosets from six-armed linoleic acid-derived epoxy resin. *RSC Advances*, 6(58):52549-52555, 2016.

[17] Maffini, M. V., Rubin, B. S., Sonnenschein, C., and Soto, A. M. Endocrine disruptors and reproductive health: The case of bisphenol-A. *Molecular and Cellular Endocrinology*, 254–255:179–186, 2006.

[18] Vandenberg, L. N., Chahoud, I., Heindel, J. J., Padmanabhan, V., Paumgartten, F. J. R., and Schoenfelder, G. Urinary, circulating, and tissue biomonitoring studies indicate widespread exposure to bisphenol A. *Environmental and Health Perspectives*, 118 (8):1055–1070, 2010.

[19] Maiorana, A., Spinella, S., and Gross, R. A. Bio-based epoxy resins from diphenolate esters—Replacing the diglycidyl ether of bisphenol A. In *Green Polymer Chemistry: Biobased Materials and Biocatalysis*, pages 371-386, ISBN:9780841230651. American Chemical Society, 2015.

[20] Han, J., Chen, Q., Feng, Y., Shen, Y., Wu, D., Zhong, M., Zhang, Q., Zhao, Z., Zhai, Y., and Bockstaller, M. R. Seawater-degradable and antibacterial epoxy thermosets employing betaine ester linkages. *ACS Applied Polymer Materials*, 5(5):3298-3305, 2023.

[21] Rad, E. R., Vahabi, H., de Anda, A. R., Saeb, M. R., and Thomas, S. Bio-epoxy resins with inherent flame retardancy. *Progress in Organic Coatings*, 135:608-612, 2019.

[22] Chrysanthos, M., Galy, J., and Pascault, J. P. Preparation and properties of bio-based epoxy networks derived from isosorbide diglycidyl ether. *Polymer*, 52(16):3611–3620, 2011.

[23] Feng, X., East, A., Hammond, W., and Jaffe, M. Sugar-based chemicals for environmentally sustainable applications. *ACS Symposium Series*, 1061:3–27, 2010.

[24] Masutani, K. and Kimura, Y. Biobased polymers. In *Encyclopedia of Polymeric Nanomaterials*, pages 118-124, ISBN: 978-3-642-29648-2. Springer, 2021.

[25] Yang, X., Li, J., Wang, Y., Tan, L., Han, L., Lu, J., Li, M., Fang, D., Huang, X., Xu, Y. H., and Zhang, C. Synthesis and characterization of fully biobased epoxy elastomers prepared from different plant oils. *ACS Sustainable Chemistry & Engineering*, 2023.

[26] Mu, S., Zhang, Y., Zhou, J., Wang, B., and Wang, Z. Recyclable and mechanically robust palm oil-derived epoxy resins with reconfigurable shape-memory properties. *ACS Sustainable Chemistry & Engineering*, 8(13):5296-5304, 2020.

[27] Qi, M., Xu, Y. J., Rao, W. H., Luo, X., Chen, L., and Wang, Y. Z. Epoxidized soybean oil cured with tannic acid for fully bio-based epoxy resin. *RSC Advances*, 8(47):26948-26958, 2018.

[28] Thiele, K., Eversmann, N., Krombholz, A., and Pufky-Heinrich, D. Bio-based epoxy resins based on linseed oil cured with naturally occurring acids. *Polymers*, 11(9):1409, 2019.

[29] Faye, I., Decostanzi, M., Ecochard, Y., and Caillol, S. Eugenol bio-based epoxy thermosets: From cloves to applied materials. *Green Chemistry*, 19(21):5236-5242, 2017.

[30] Jahanshahi, S., Pizzi, A., Abdulkhani, A., and Shakeri, A. Analysis and testing of bisphenol A-free bio-based tannin epoxy-acrylic adhesives. *Polymers*, 8(4):143-56, 2016.

[31] Nicastro, K. H., Kloxin, C. J., and Epps III, T. H. Potential lignin-derived alternatives to bisphenol A in diamine-hardened epoxy resins. *ACS Sustainable Chemistry & Engineering*, 6(11):14812-14819, 2018.

[32] Shibata, M. and Ohkita, T. Fully biobased epoxy resin systems composed of a vanillin-derived epoxy resin and renewable phenolic hardeners. *European Polymer Journal*, 92:165-173, 2017.

[33] Liu, T., Hao, C., Zhang, S., Yang, X., Wang, L., Han, J., Li, Y., Xin, J., and Zhang, J. A self-healable high glass transition temperature bioepoxy material based on vitrimer chemistry. *Macromolecules*, 51(15):5577-5585, 2018.

[34] Meng, J., Zeng, Y., Zhu, G., Zhang, J., Chen, P., Cheng, Y., Fang, Z., and Guo, K. Sustainable bio-based furan epoxy resin with flame retardancy. *Polymer Chemistry*, 10(19):2370-2375, 2019.

[35] Marotta, A., Ambrogi, V., Cerruti, P., and Mija, A. Green approaches in the synthesis of furan-based diepoxy monomers. *RSC Advances*, 8(29):16330-16335, 2018.

[36] Karlsson, I., Ponting, D. J., Ortega, M. A., Niklasson, I. B., Ndreu, L., Stéen, E. J. L., Seifert, T., Luthman, K., and Karlberg, A. T. Nature-derived epoxy resin

monomers with reduced sensitizing capacity-isosorbide-based bis-epoxides. *Chemical Research in Toxicology*, 36(2):281-290, 2023.

[37] Xia, Z., Kiratitanavit, W., Facendola, P., Thota, S., Yu, S., Kumar, J., Mosurkal, R., and Nagarajan, R. Fire resistant polyphenols based on chemical modification of bioderived tannic acid. *Polymer Degradation and Stability*, 153:227-243, 2018.

[38] Kuo, P. Y., Sain, M., and Yan, N. Synthesis and characterization of an extractive-based bio-epoxy resin from beetle infested *Pinus contorta* bark. *Green Chemistry*, 16(7):3483-3493, 2014.

[39] Anwer, M. A., Wang, J., Guan, A. Q., and Naguib, H. E. Chitin nano-whiskers (CNWs) as a bio-based bio-degradable reinforcement for epoxy: Evaluation of the impact of CNWs on the morphological, fracture, mechanical, dynamic mechanical, and thermal characteristics of DGEBA epoxy resin. *RSC Advances*, 9(20):11063-11076, 2019.

[40] Joy, J., George, E., Thomas, S., and Anas, S. Effect of filler loading on polymer chain confinement and thermomechanical properties of epoxy/boron nitride (h-BN) nanocomposites. *New Journal of Chemistry*, 44(11):4494-4503, 2020.

[41] Fu, S., Sun, Z., Huang, P., Li, Y., and Hu, N. Some basic aspects of polymer nanocomposites: A critical review. *Nano Materials Science*, 1(1):2-30, 2019.

[42] Pulikkalparambil, H., Rangappa, S. M., Siengchin, S., and Parameswaranpillai, J. Introduction to epoxy composites. In *Epoxy Composites: Fabrication, Characterization and Applications*, pages 1-21, ISBN:9783527346783. Wiley, 2021.

[43] Arshad, M., Kaur, M., and Ullah, A. Green biocomposites from nanoengineered hybrid natural fiber and biopolymer. *ACS Sustainable Chemistry & Engineering*, 4(3):1785-1793, 2016.

[44] Podzimek, S., Polymers Synthetic. In *Encyclopaedia of Analytical Science (Third Edition)*, pages 360-370, ISBN:978-0-08-101984-9. Academic Press: Oxford, 2019.

[45] Jia, P., Ma, Y., Kong, Q., Xu, L., Li, Q., and Zhou, Y. Progress in development of epoxy resin systems based on biomass resources. *Green Materials*, 8(1):6-23, 2019.

[46] Mohan, T, P. and Kanny, K. Synthesis and manufacturing of epoxy composites. In *Epoxy Composites: Fabrication, Characterization and Applications*, pages 23-60, ISBN:9783527346783. Wiley, 2021.

[47] Hamerton, I. *Recent developments in epoxy resins*. ISSN:08893144, iSmithers Rapra Publishing, Akron, Ohio, 1996.

[48] Gandini, A. Epoxy polymers based on renewable resources. In *Epoxy Polymers: New Materials and Innovations*, pages 55-78, ISBN:9783527324804. John Wiley & Sons, 2009.

[49] Meier, M. A., Metzger, J. O., and Schubert, U. S. Plant oil renewable resources as green alternatives in polymer science. *Chemical Society Reviews*, 36(11):1788-1802, 2007.

[50] Crivello, J. V. and Narayan, R. Epoxidized triglycerides as renewable monomers in photoinitiated cationic polymerization. *Chemistry of Materials*, 4(3):692-699, 1992.

[51] Frischinger, I. and Dirlikov, S. Toughening of epoxy resins by epoxidized vegetable oils. *Polymer Communications (Guildford)*, 32(17):536-537, 1991.

[52] Wan, J., Zhao, J., Zhang, X., Fan, H., Zhang, J., Hu, D., Jin, P., and Wang, D. Y. Epoxy thermosets and materials derived from bio-based monomeric phenols: Transformations and performances. *Progress in Polymer Science*, 108:101287-101333, 2020.

[53] Tomita, H. and Yonezawa, K. U. S. *Epoxy resin and process for preparing the same*. **U.S. Patent no.** 4540802, 1985.

[54] Esmaeili, N., Vafayan, M., Salimi, A., and Zohuriaan-Mehr, M. J. Kinetics of curing and thermo-degradation, antioxidizing activity, and cell viability of a tannic acid based epoxy resin: From natural waste to value-added biomaterial. *Thermochimica Acta*, 655:21-33, 2017.

[55] Bhatt, A. T., Gohil, P. P., and Chaudhary, V. Primary manufacturing processes for fiber reinforced composites: History, development & future research trends. In *IOP Conference Series: Materials Science and Engineering*, volume 330, pages 012107-012128, Hyderabad, India, IOP Publishing, 2018.

[56] Khot, S. N., Lascala, J. J., Can, E., Morye, S. S., Williams, G. I., Palmese, G. R., Kusefoglu, S.H., and Wool, R. P. Development and application of triglyceride-based polymers and composites. *Journal of Applied Polymer Science*, 82(3):703-723, 2001.

[57] O'donnell, A., Dweib, M. A., and Wool, R. P. Natural fiber composites with plant oil-based resin. *Composites Science and Technology*, 64(9):1135-1145, 2004.

[58] Gupta, R. K., Kennel, E. B., and Kim, K. J. Overview of challenges and opportunities. In *Polymer Nanocomposite Handbook*, pages 1-6, ISBN:9781420009804. CRC press, 2009.

[59] Ghaffarkhah, A., Hashemi, S. A., Rostami, S., Amini, M., Ahmadijokani, F., Pournaghshband Isfahani, A., Mhatre, S. E., Rojas, O. J., Kamkar, M., Wuttke, S., and Soroush, M. Ultra-flyweight cryogels of MXene/graphene oxide for electromagnetic interference shielding. *Advanced Functional Materials*, 2304748, 2023.

[60] Zaghloul, M. M. Y., Zaghloul, M. M. Y., and Fuseini, M. Recent progress in Epoxy Nanocomposites: Corrosion, structural, flame retardancy and applications— A comprehensive review. *Polymers for Advanced Technologies*, 2023.

[61] Wang, Z., Gnanasekar, P., Sudhakaran Nair, S., Farnood, R., Yi, S., and Yan, N. Biobased epoxy synthesized from a vanillin derivative and its reinforcement using lignin-containing cellulose nanofibrils. *ACS Sustainable Chemistry & Engineering*, 8(30):11215-11223, 2020.

[62] Necolau, M. I., Bălănucă, B., Frone, A. N., and Damian, C. M. Tailoring an effective interface between nanocellulose and the epoxidized linseed oil network through functionalization. *ACS Omega*, 8(18):15896-15908, 2023.

[63] Jin, F. L., Li, X., and Park, S. J. Synthesis and application of epoxy resins: A review. *Journal of Industrial and Engineering Chemistry*, 29:1-11, 2015.

[64] Marotta, A., Faggio, N., Ambrogi, V., Mija, A., Gentile, G., and Cerruti, P. Biobased furan-based epoxy/TiO$_2$ nanocomposites for the preparation of coatings with improved chemical resistance. *Chemical Engineering Journal*, 406:127107-127117, 2021.

[65] Miao, Z., Peng, C., Xia, L., Xu, H., He, S., Chi, C., Zhong, J., Wang, S., Luo, W., Chen, G., and Zeng, B. Fire-safe fully bio-based Schiff base epoxy thermosets with excellent mechanical properties and adjustable degradability. *ACS Applied Polymer Materials*, 5(8):6325-6337, 2023.

[66] Faggio, N., Marotta, A., Ambrogi, V., Cerruti, P., and Gentile, G. Fully bio-based furan/maleic anhydride epoxy resin with enhanced adhesive properties. *Journal of Materials Science*, 58:7195-7208, 2023.

[67] Sienel, G., Rieth, R., and Rowbottom, K. T. Epoxides. In *Ullmann's Encyclopedia of Industrial Chemistry*. 2000, Wiley-VCH.

[68] Bell, B. M., Briggs, J. R., Campbell, R. M., Chambers, S. M., Gaarenstroom, P. D., Hippler, J. G., Hook, B. D., Kearns, K., Kenney, J. M., Kruper, W. J., and Schreck, D. J., Glycerin as a renewable feedstock for epichlorohydrin production. The GTE process. *CLEAN–Soil, Air, Water*, 36(8):657-661, 2008.

[69] Haveren, J. V., Scott, E. L., and Sanders, J. Bulk chemicals from biomass. *Biofuels, Bioproducts and Biorefining: Innovation for a sustainable economy*, 2(1):41-57, 2008.

[70] Philippe, K., Patrick, G., Benoit, G., and Sara, C. *Process for producing dichloropropanol from glycerol, the glycerol coming eventually from the conversion of animal fats in the manufacture of biodiesel*. **U.S. Patent no.** 8415509 B2, 2004.

[71] Karak, N. Overview of epoxies and their thermosets, In *Sustainable Epoxy Thermosets and Their Nanocomposites*, pages 1-36, ISBN:9780841298309. American Chemical Society, 2021.

[72] Aouf, C., Le Guernevé, C., Caillol, S., and Fulcrand, H. Study of the O-glycidylation of natural phenolic compounds. The relationship between the phenolic structure and the reaction mechanism. *Tetrahedron*, 69(4):1345-1353, 2013.

[73] Kuo, P. Y., de Assis Barros, L., Sain, M., Tjong, J. S., and Yan, N. Effects of reaction parameters on the glycidyl etherification of bark extractives during bioepoxy resin synthesis. *ACS Sustainable Chemistry & Engineering*, 4(3):1016-1024, 2016.

[74] Kurańska, M., Beneš, H., Prociak, A., Trhlíková, O., Walterova, Z., and Stochlińska, W. Investigation of epoxidation of used cooking oils with homogeneous and heterogeneous catalysts. *Journal of Cleaner Production*, 236:117615-117624, 2019.

[75] Gerbase, A. E., Gregório, J. R., Martinelli, M., Brasil, M. C., and Mendes, A. N. Epoxidation of soybean oil by the methyltrioxorhenium-CH_2Cl_2/H_2O_2 catalytic biphasic system. *Journal of the American Oil Chemists' Society*, 79:179-181, 2002.

[76] Farias, M., Martinelli, M., and Bottega, D. P. Epoxidation of soybean oil using a homogeneous catalytic system based on a molybdenum (VI) complex. *Applied Catalysis A: General*, 384(1-2):213-219, 2010.

[77] Janković, M., Sinadinović-Fišer, S., Govedarica, O., Pavličević, J., and Budinski-Simendić, J. Kinetics of soybean oil epoxidation with peracetic acid formed in situ

in the presence of an ion exchange resin: pseudo-homogeneous model. *Chemical Industry and Chemical Engineering Quarterly*, 23(1):97-111, 2017.

[78] Wu, J., Jiang, P., Qin, X., Ye, Y., and Leng, Y. Peroxopolyoxotungsten-based ionic hybrid as a highly efficient recyclable catalyst for epoxidation of vegetable oil with H_2O_2. *Bulletin of the Korean Chemical Society*, 35(6):1675-1680, 2014.

[79] Turco, R., Pischetola, C., Di Serio, M., Vitiello, R., Tesser, R., and Santacesaria, E. Selective epoxidation of soybean oil in the presence of h–y zeolite. *Industrial & Engineering Chemistry Research*, 56(28):7930-7936, 2017.

[80] Turco, R., Pischetola, C., Tesser, R., Andini, S., and Di Serio, M. New findings on soybean and methylester epoxidation with alumina as the catalyst. *RSC Advances*, 6(38):31647-31652, 2016.

[81] Campanella, A., Baltanas, M. A., Capel-Sanchez, M. C., Campos-Martin, J. M., and Fierro, J. L. G. Soybean oil epoxidation with hydrogen peroxide using an amorphous Ti/SiO_2 catalyst. *Green Chemistry*, 6(7):330-334, 2004.

[82] Kalkandelen, M. and Yılmaz, S. Epoxidation of soybean oil over titanium or niobium incorporated SBA-15 and sulfated lanthanum titania silicate catalysts. *Industrial Crops and Products*, 188(A):115656, 2022.

[83] Ng, F., Couture, G., Philippe, C., Boutevin, B., and Caillol, S. Bio-based aromatic epoxy monomers for thermoset materials. *Molecules*, 22(1):149-197, 2017.

[84] Wang, J., Huo, S., Wang, J., Yang, S., Chen, K., Li, C., Fang, D., Fang, Z., Song, P., and Wang, H. Green and facile synthesis of bio-based, flame-retardant, latent imidazole curing agent for single-component epoxy resin. *ACS Applied Polymer Materials*, 4(5):3564-3574, 2022.

[85] Ding, C. and Matharu, A. S. Recent developments on biobased curing agents: A review of their preparation and use. *ACS Sustainable Chemistry & Engineering*, 2(10):2217-2236, 2014.

[86] Baroncini, E. A., Kumar Yadav, S., Palmese, G. R., and Stanzione III, J. F. Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *Journal of Applied Polymer Science*, 133(45):44103-44124, 2016.

[87] Altuna, F. I., Hoppe, C. E., and Williams, R. J. J. Shape memory epoxy vitrimers based on DGEBA crosslinked with dicarboxylic acids and their blends with citric acid. *RSC Advances*, 6(91):88647-88655, 2016.

[88] Huang, Y., Ma, T., Wang, Q., and Guo, C. Synthesis of biobased flame-retardant carboxylic acid curing agent and application in wood surface coating. *ACS Sustainable Chemistry & Engineering*, *7*(17):14727-14738, 2019.

[89] Fusteş-Dămoc, I., Măluţan, T., and Mija, A. Chitosan as a polyfunctional crosslinker for a renewable-based resorcinol diglycidyl ether. *ACS Sustainable Chemistry & Engineering*, 11(19):7605-7616, 2023.

[90] Sienkiewicz, N., Dominic, M., and Parameswaranpillai, J. Natural fillers as potential modifying agents for epoxy composition: A review. *Polymers*, 14(2):265-282, 2022.

[91] Bledzki, A. K., Urbaniak, M., Boettcher, A., Berger, C., and Pilawka, R. Bio-based epoxies and composites for technical applications. *Key Engineering Materials*, 559:1-6, 2013.

[92] Joshi, R., Bajpai, P. K., and Mukhopadhyay, S. Processing and performance evaluation of agro wastes reinforced bio-based epoxy hybrid composites. *Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications*, 237(2):482-499, 2023.

[93] Kumar, B., Adil, S., and Kim, J. Adhesion improvement of bio-based epoxy in environmentally friendly and high-performance natural fiber-reinforced composites. *Macromolecular Materials and Engineering*, 308:2300003-2300015, 2023.

[94] Masoodi, R., El-Hajjar, R. F., Pillai, K. M., and Sabo, R. Mechanical characterization of cellulose nanofiber and bio-based epoxy composite. *Materials & Design (1980-2015)*, 36:570-576, 2012.

[95] Baig, N., Kammakakam, I., and Falath, W. Nanomaterials: A review of synthesis methods, properties, recent progress, and challenges. *Materials Advances*, 2(6):1821-1871, 2021.

[96] Khan, A. A. P., Khan, A., and Asiri, A. M. Chemistry of nanoscience and technology. In *Nanomaterials and Nanocomposites: Zero-to Three-dimensional Materials and Their Composites*, pages 21-106, ISBN:9783527683741. John Wiley & Sons, 2016.

[97] Kolahalam, L. A., Viswanath, I. K., Diwakar, B. S., Govindh, B., Reddy, V., and Murthy, Y. L. N. Review on nanomaterials: Synthesis and applications. *Materials Today: Proceedings*, 18:2182-2190, 2019.

[98]   Purohit, J., Chattopadhyay, A., and Singh, N. K. Green synthesis of microbial nanoparticle: Approaches to application. *Microbial Nanobionics: Volume 2, Basic Research and Applications*, 2:35-60, 2019.

[99]   Velmurugan, P., Anbalagan, K., Manosathyadevan, M., Lee, K. J., Cho, M., Lee, S. M., Park, J. H., Oh, S. G., Bang, K. S., and Oh, B. T. Green synthesis of silver and gold nanoparticles using *Zingiber officinale* root extract and antibacterial activity of silver nanoparticles against food pathogens. *Bioprocess and Biosystems Engineering*, 37:1935-1943, 2014.

[100] Slavin, Y. N., Asnis, J., Hńfeli, U. O., and Bach, H. Metal nanoparticles: Understanding the mechanisms behind antibacterial activity. *Journal of Nanobiotechnology*, 15:65-85, 2017.

[101] Yang, J., Dai, J., Liu, X., Fu, S., Zong, E., and Song, P. A lignin-based epoxy/TiO$_2$ hybrid nanoparticle for multifunctional bio-based epoxy with improved mechanical, UV absorption and antibacterial properties. *International Journal of Biological Macromolecules*, 210:85-93,2022.

[102] Ganesan, V., Hariram, M., Vivekanandhan, S., and Muthuramkumar, S. *Periconium sp.* (endophytic fungi) extract mediated sol-gel synthesis of ZnO nanoparticles for antimicrobial and antioxidant applications. *Materials Science in Semiconductor Processing*, 105:104739-104751, 2020.

[103] Zulkifli, F. H., Hussain, F. S. J., Zeyohannes, S. S., Rasad, M. S. B. A., and Yusuff, M. M. A facile synthesis method of hydroxyethyl cellulose-silver nanoparticle scaffolds for skin tissue engineering applications. *Materials Science and Engineering: C*, 79:151-160, 2017.

[104] Aung, M. M., Li, W. J., and Lim, H. N. Improvement of anticorrosion coating properties in bio-based polymer epoxy acrylate incorporated with nano zinc oxide particles. *Industrial & Engineering Chemistry Research*, 59(5):1753-1763, 2020.

[105] Das, C., Sen, S., Singh, T., Ghosh, T., Paul, S. S., Kim, T. W., Jeon, S., Maiti, D. K., Im, J., and Biswas, G. Green synthesis, characterization and application of natural product coated magnetite nanoparticles for wastewater treatment. *Nanomaterials*, 10(8):1615-1634, 2020.

[106] Plachtová, P., Medrikova, Z., Zboril, R., Tucek, J., Varma, R. S., and Maršálek, B. Iron and iron oxide nanoparticles synthesized with green tea extract: Differences in ecotoxicological profile and ability to degrade malachite green. *ACS Sustainable Chemistry & Engineering*, 6(7):8679-8687, 2018.

[107] Wang, Q., Su, D. S., and Wang, D. Y. Carbon nanotube/epoxy composites for improved fire safety. *ACS Applied Nano Materials*, 3(5):4253-4264, 2020.

[108] Nersisyan, H. H., Lee, J. H., Ding, J. R., Kim, K. S., Manukyan, K. V., and Mukasyan, A. S. Combustion synthesis of zero-, one-, two- and three-dimensional nanostructures: Current trends and future perspectives. *Progress in Energy and Combustion Science*, 63:79-118, 2017.

[109] Zhu, M., Yan, X., Li, X., Dai, L., Guo, J., Lei, Y., Xu, Y., and Xu, H. Flexible, transparent, and hazy composite cellulosic film with interconnected silver nanowire networks for EMI shielding and Joule heating. *ACS Applied Materials & Interfaces*, 14(40):45697-45706, 2022.

[110] Tran, T. T. V., Vo, D. V. N., Nguyen, S. T., and Vu, C. M. Silver nanowires decorated recycled cigarette filters-based epoxy composites with high through-plane thermal conductivity and efficient electromagnetic interference shielding. *Composites Part A: Applied Science and Manufacturing*, 149:106485, 2021.

[111] Rajesh Kumar, B. and Etika, K. C. Facile one-pot hydrothermal synthesis of copper nanowires and their impact on the EMI shielding capability of epoxy composites. *Chemical Engineering & Technology*, 45(3):410-416, 2022.

[112] Barari, B. and Pillai, K. M. Green composites made from cellulose nanofibers and bio-based epoxy: Processing, performance, and applications. In *Natural Fiber-reinforced Biodegradable and Bioresorbable Polymer Composites*, pages 31-49, ISBN:978-0-08-100656-6. Woodhead Publishing, 2017.

[113] Sakakibara, K., Moriki, Y., Yano, H., and Tsujii, Y. Strategy for the improvement of the mechanical properties of cellulose nanofiber-reinforced high-density polyethylene nanocomposites using diblock copolymer dispersants. *ACS Applied Materials & Interfaces*, 9(50):44079-44087, 2017.

[114] Tan, Y., Liu, Y., Chen, W., Liu, Y., Wang, Q., Li, J., and Yu, H. Homogeneous dispersion of cellulose nanofibers in waterborne acrylic coatings with improved properties and unreduced transparency. *ACS Sustainable Chemistry & Engineering*, 4(7):3766-3772, 2016.

[115] Zhao, J., Li, Q., Zhang, X., Xiao, M., Zhang, W., and Lu, C. Grafting of polyethylenimine onto cellulose nanofibers for interfacial enhancement in their epoxy nanocomposites. *Carbohydrate Polymers*, 157:1419-1425, 2017.

[116] Ma, J., Wang, X., Fu, Q., Si, Y., Yu, J., and Ding, B. Highly carbonylated cellulose nanofibrous membranes utilizing maleic anhydride grafting for efficient lysozyme adsorption. *ACS Applied Materials & Interfaces*, 7(28):15658-15666, 2015.

[117] Niu, X., Liu, Y., Song, Y., Han, J., and Pan, H. Rosin modified cellulose nanofiber as a reinforcing and co-antimicrobial agent in polylactic acid/chitosan composite film for food packaging. *Carbohydrate Polymers*, 183:102-109, 2018.

[118] Niu, X., Liu, Y., Fang, G., Huang, C., Rojas, O. J., and Pan, H. Highly transparent, strong, and flexible films with modified cellulose nanofiber bearing UV shielding property. *Biomacromolecules*, 19:4565–4575, 2018.

[119] Frone, A. N., Uşurelu, C. D., Oprică, G. M., Panaitescu, D. M., Gabor, A. R., Nicolae, C. A., Ciuprina, F., Damian, C. M., and Raduly, F. M. Contribution of the surface treatment of nanofibrillated cellulose on the properties of bio-based epoxy nanocomposites intended for flexible electronics. *International Journal of Molecular Sciences*, 24(7):6544-6564, 2023.

[120] Parvez, K. Two-dimensional nanomaterials: Crystal structure and synthesis. In *Biomedical Applications of Graphene and 2D Nanomaterials*, pages 1-25, ISBN: 978-0-12-815889-0. Elsevier, 2019.

[121] Guo, F., Shen, X., Zhou, J., Liu, D., Zheng, Q., Yang, J., Jia, B., Lau, A. K., and Kim, J. K. Highly thermally conductive dielectric nanocomposites with synergistic alignments of graphene and boron nitride nanosheets. *Advanced Functional Materials*, 30(19):1910826-1910839, 2020.

[122] Acharya, L., Pattnaik, S. P., Behera, A., Acharya, R., and Parida, K. Exfoliated boron nitride (e-BN) tailored exfoliated graphitic carbon nitride (e-CN): An improved visible light mediated photocatalytic approach towards TCH degradation and H_2 evolution. *Inorganic Chemistry*, 60(7):5021-5033, 2021.

[123] Wu, H., Cheng, L., Liu, C., Lan, X., and Zhao, H. Engineering the interface in graphene oxide/epoxy composites using bio-based epoxy-graphene oxide nanomaterial to achieve superior anticorrosion performance. *Journal of Colloid and Interface Science*, 587:755-766, 2021.

[124] Sudha, G. S. Synthesis of biobased epoxy resins: Effect of modification of castor oil and incorporation of carbon fiber on mechanical, thermal, viscoelastic properties and morphological behaviour of the composites. Master's thesis, Department of Plastic Technology, CIPET, Chennai, 2018.

[125] Barua, S. Hyperbranched epoxy nanocomposites for biomedical applications. Master's thesis, Department of Chemical Sciences, Tezpur University, Assam, 2015.

[126] Kumar, B., Agumba, D. O., Pham, D. H., Latif, M., Dinesh, Kim, H. C., Alrobei, H., and Kim, J. Recent research progress on lignin-derived resins for natural fiber composite applications. *Polymers*, 13(7):116, 2021.

[127] Wan, J., Zhao, J., Gan, B., Li, C., Molina-Aldareguia, J., Zhao, Y., Pan, Y. T., and Wang, D. Y. Ultrastiff biobased epoxy resin with high T_g and low permittivity: From synthesis to properties. *ACS Sustainable Chemistry & Engineering*, 4(5):2869-2880, 2016.

[128] Dai, J., Teng, N., Liu, J., Feng, J., Zhu, J., and Liu, X. Synthesis of bio-based fire-resistant epoxy without addition of flame retardant elements. *Composites Part B: Engineering*, 179:107523, 2019.

[129] Hassan, M. F., Sabri, M. A., Fazal, H., Hafeez, A., Shezad, N., and Hussain, M. Recent trends in activated carbon fibers production from various precursors and applications—A comparative review. *Journal of Analytical and Applied Pyrolysis*, 145:104715-104805, 2020.

[130] Khoathane, M. C., Sadiku, E. R., and Agwuncha, C. S. Surface modification of natural fiber composites and their potential applications. In *Surface Modification of Biopolymers*, pages 370-400, ISBN:9781119044901, John Wiley & Sons, 2015.

[131] Fathi, B., Foruzanmehr, M., Elkoun, S., and Robert, M. Novel approach for silane treatment of flax fiber to improve the interfacial adhesion in flax/bio epoxy composites. *Journal of Composite Materials*, 53(16):2229-2238, 2019.

[132] Kumar, S. and Bhowmik, S. Extraction of bio-fillers from natural solid wastes (*Citrus limetta* peel) and characterization of the physical, mechanical, and tribological performance of sustainable biocomposites. *Journal of Material Cycles and Waste Management*, 84:1-14, 2023.

[133] Nagajyothi, P. C., Prabhakar Vattikuti, S. V., Devarayapalli, K. C., Yoo, K., Shim, J., and Sreekanth, T. V. M. Green synthesis: Photocatalytic degradation of textile dyes using metal and metal oxide nanoparticles-latest trends and advancements. *Critical Reviews in Environmental Science and Technology*, 50(24):.2617-2723, 2020.

[134] Benelmekki, M. Introduction. In *Nanomaterial: The Original Product of Nanotechnology*, pages 1-14, ISBN:9781643276441. Morgan and Claypool Publishers, 2019.

[135] Abhilash, M. and Thomas, D. Biopolymers for biocomposites and chemical sensor applications. In *Biopolymer Composites in Electronics*, pages 405-435, ISBN:978-0-12-809261-3. Elsevier, 2017.

[136] Chohan, J. S., Boparai, K. S., Singh, R., and Hashmi, M. S. J. Manufacturing techniques and applications of polymer matrix composites: A brief review. *Advances in Materials and Processing Technologies*, 8(1):884-894, 2022.

[137] Nagalakshmaiah, M., Afrin, S., Malladi, R. P., Elkoun, S., Robert, M., Ansari, M. A., Svedberg, A., and Karim, Z. Biocomposites: Present trends and challenges for the future. In *Green Composites for Automotive Applications*, pages 197-215, ISBN:978-0-08-102177-4. Woodhead Publishing, 2019.

[138] Campbell Jr, F. C. Introduction to composite materials and processes. In *Manufacturing Processes for Advanced Composites*. Pages 2-39, ISBN: 978-1-85617-415-2. Elsevier Science, 2003.

[139] Erden, S. and Ho, K. Fiber reinforced composites. In *Fiber Technology for Fiber Reinforced Composites*, pages 51-79, ISBN:978-0-08-101871-2. Woodhead Publishing, 2017.

[140] Rwawiire, S., Tomkova, B., Militky, J., Jabbar, A., and Kale, B. M. Development of a biocomposite based on green epoxy polymer and natural cellulose fabric (bark cloth) for automotive instrument panel applications. *Composites Part B: Engineering*, 81:149-157, 2015.

[141] Liu, W., Chen, T., Fei, M. E., Qiu, R., Yu, D., Fu, T., and Qiu, J. Properties of natural fiber-reinforced biobased thermoset biocomposites: Effects of fiber type and resin composition. *Composites Part B: Engineering*, 171:87-95, 2019.

[142] Galpayage Dona, D. G., Wang, M., Liu, M., Motta, N., Waclawik, E., and Yan, C. Recent advances in fabrication and characterization of graphene-polymer nanocomposites. *Graphene*, 1(2):30-49, 2012.

[143] Mao, H. N. and Wang, X. G. Use of in-situ polymerization in the preparation of graphene/polymer nanocomposites. *New Carbon Materials*, 35(4):336-343, 2020.

[144] Gogoi, B., Barua, S., Sarmah, J. K., and Karak, N. In situ synthesis of a microbial fouling resistant, nanofibrillar cellulose-hyperbranched epoxy composite for advanced coating applications. *Progress in Organic Coatings*, 124:224-231, 2018.

[145] Gu, H., Ma, C., Gu, J., Guo, J., Yan, X., Huang, J., Zhang, Q., and Guo, Z. An overview of multifunctional epoxy nanocomposites. *Journal of Materials Chemistry C*, 4(25):5890-5906, 2016.

[146] Rajimol, P. R., Ulaeto, S. B., Puthiyamadam, A., Sahoo, S. K., Rajan, T. P. D., Radhakrishnan, K. V., and Sukumaran, R. K. Development of an oxyresveratrol incorporated bio-based smart nanocomposite coating with anti-corrosive, self-healing, and anti-microbial properties. *Green Chemistry*, 2023.

[147] Seidi, F., Jouyandeh, M., Akbari, V., Paran, S. M. R., Livi, S., Ducos, F., Vahabi, H., Ganjali, M. R., and Saeb, M. R. Super-crosslinked ionic liquid-intercalated montmorillonite/epoxy nanocomposites: Cure kinetics, viscoelastic behavior and thermal degradation mechanism. *Polymer Engineering & Science*, 60(8):1940-1957, 2020.

[148] Yue, L., Maiorana, A., Khelifa, F., Patel, A., Raquez, J. M., Bonnaud, L., Gross, R., Dubois, P., and Manas-Zloczower, I. Surface-modified cellulose nanocrystals for biobased epoxy nanocomposites. *Polymer*, 134:155-162, 2018.

[149] Singh, N., Riyajuddin, S., Ghosh, K., Mehta, S. K., and Dan, A. Chitosan-graphene oxide hydrogels with embedded magnetic iron oxide nanoparticles for dye removal. *ACS Applied Nano Materials*, 2(11):7379-7392, 2019.

[150] Omidi, M., Fatehinya, A., Farahani, M., Akbari, Z., Shahmoradi, S., Yazdian, F., Tahriri, M., Moharamzadeh, K., Tayebi, L., and Vashaee, D. Characterization of biomaterials. In *Biomaterials for Oral and Dental Tissue Engineering*, pages 97-115, ISBN:978-0-08-100961-1. Woodhead Publishing, 2017.

[151] Rusin, C. J., El Bakkari, M., Du, R., Boluk, Y., and McDermott, M. T. Plasmonic cellulose nanofibers as water-dispersible surface-enhanced Raman scattering substrates. *ACS Applied Nano Materials*, 3(7):6584-6597, 2020.

[152] Saalwächter, K. Applications of NMR in polymer characterization– An introduction. In *NMR Methods for Characterization of Synthetic and Natural Polymers*, pages 1-22, ISBN:978-1-78801-863-0. Royal Society of Chemistry, 2019.

[153] Suzuki, Y., Shindo, H., and Asakura, T. Structure and dynamic properties of a Ti-binding peptide bound to TiO_2 nanoparticles as accessed by ^1H NMR spectroscopy. *The Journal of Physical Chemistry B*, 120(20):4600-4607, 2016.

[154] Aziz, N., Faraz, M., Pandey, R., Shakir, M., Fatma, T., Varma, A., Barman, I., and Prasad, R. Facile algae-derived route to biogenic silver nanoparticles: Synthesis, antibacterial, and photocatalytic properties. *Langmuir*, 31(42):11605-11612, 2015.

[155] Selim, Y. A., Azb, M. A., Ragab, I., and HM Abd El-Azim, M. Green synthesis of zinc oxide nanoparticles using aqueous extract of *Deverra tortuosa* and their cytotoxic activities. *Scientific Reports*, 10(1):3445-3454, 2020.

[156] Lefebvre, J., Galli, F., Bianchi, C. L., Patience, G. S., and Boffito, D. C. Experimental methods in chemical engineering: X-ray photoelectron spectroscopy-XPS. *The Canadian Journal of Chemical Engineering*, 97(10):2588-2593, 2019.

[157] Nabipour, H., Wang, X., Song, L., and Hu, Y. A high performance fully bio-based epoxy thermoset from a syringaldehyde-derived epoxy monomer cured by furan-derived amine. *Green Chemistry*, 23(1):501-510, 2021.

[158] Wang, X., Huang, J., Song, L., and Hu, Y. Synthesis of phosphorus-containing cardanol-derived phenalkamine: A sustainable curing agent to access high-performance bio-based epoxy thermosets. *Green Chemistry*, 24(23):9269-9281, 2022.

[159] Kim, H. C., Panicker, P. S., Kim, D., Adil, S., and Kim, J. High-strength cellulose nanofiber/graphene oxide hybrid filament made by continuous processing and its humidity monitoring. *Scientific Reports*, 11(1):13611, 2021.

[160] Surajarusarn, B., Hajjar-Garreau, S., Schrodj, G., Mougin, K., and Amornsakchai, T. Comparative study of pineapple leaf microfiber and aramid fiber reinforced natural rubbers using dynamic mechanical analysis. *Polymer Testing*, 82:106289, 2020.

[161] Holder, C. F. and Schaak, R. E. Tutorial on powder X-ray diffraction for characterizing nanoscale materials. *ACS Nano*, 13(7):7359-7365, 2019.

[162] Ali, A., Chiang, Y. W. and Santos, R. M. X-ray diffraction techniques for mineral characterization: A review for engineers of the fundamentals, applications, and research directions. *Minerals*, 12(2):205-230, 2022.

[163] Samimi, S., Maghsoudnia, N., Eftekhari, R. B., and Dorkoosh, F. Lipid-based nanoparticles for drug delivery systems. *Characterization and Biology of Nanomaterials for Drug Delivery*, pages 47-76, ISBN:978-0-12-814031-4. Elsevier, 2019.

[164] Chandraker, S. K., Lal, M., Khanam, F., Dhruve, P., Singh, R. P., and Shukla, R. Therapeutic potential of biogenic and optimized silver nanoparticles using *Rubia cordifolia* L. leaf extract. *Scientific Reports*, 12(1):8831-8846, 2022.

[165] Zhao, X., Li, K., Wang, Y., Tekinalp, H., Larsen, G., Rasmussen, D., Ginder, R. S., Wang, L., Gardner, D. J., Tajvidi, M., and Webb, E. High-strength polylactic acid (PLA) biocomposites reinforced by epoxy-modified pine fibers. *ACS Sustainable Chemistry & Engineering*, 8(35):13236-13247, 2020.

[166] Frone, A. N., Berlioz, S., Chailan, J. F., and Panaitescu, D. M. Morphology and thermal properties of PLA–cellulose nanofibers composites. *Carbohydrate Polymers*, 91(1):377-384, 2013.

[167] Krishnan, V. N. and Ramesh, A. Synthesis and characterization of cellulose nanofibers from coconut coir fibers. *IOSR Journal of Applied Chemistry*, 6(3):18-23, 2013.

[168] Hou, Q. Q., Liu, X., Gong, W., Xu, F., Zhang, W. S., Dong, Y. Z., Xun, Q. N., and Ji, K. J. Development of methods for determining molecular weights of epoxy resin. In *Journal of Physics: Conference Series* Vol. 2460(1) pages 012115-012122, IOP Publishing, 2023.

[169] He, Z., Wang, Y., Zhao, T., Ye, Z., and Huang, H. Ultrasonication-assisted rapid determination of epoxide values in polymer mixtures containing epoxy resin. *Analytical Methods*, 6(12):4257-4261, 2014.

[170] Duarah, R. and Karak, N. Hyperbranched polyurethane/reduced carbon dot-zinc oxide nanocomposite-mediated solar-assisted photocatalytic degradation of organic contaminant: An approach towards environmental remediation. *Chemical Engineering Journal*, 370:716-728, 2019.

[171] Dutta, G. K. and Karak, N. Waste brewed tea leaf derived cellulose nanofiber reinforced fully bio-based waterborne polyester nanocomposite as an environmentally benign material. *RSC Advances*, 9(36):20829-20840, 2019.

[172] Duarah, R. and Karak, N. Hyperbranched polyurethane/palladium-reduced carbon dot nanocomposite: An efficient and reusable mesoporous catalyst for visible-light-driven C–C coupling reactions. *Industrial & Engineering Chemistry Research*, 58(36):16307-16319, 2019.

[173] Ramakrishna, S., Tian, L., Wang, C., Liao, S., and Teo, W. E. Safety testing of a new medical device. In *Medical Devices Regulations, Standards, and Practices*, pages 137-153, ISBN:978-0-08-100289-6. Woodhouse Publishing, 2015.

[174] Nissa, R. C., Fikriyyah, A. K., Abdullah, A. H. D., and Pudjiraharti, S. Preliminary study of biodegradability of starch-based bioplastics using ASTM G21-70, dip-hanging, and soil burial test methods. In *IOP Conference Series: Earth and Environmental Science,* volume 277(1), pages 012007-012014, IOP Publishing, 2019.

[175] Telegdi, J., Shaban, A., and Vastag, G. Biocorrosion-Steel. In *Encyclopedia of Surface Chemistry Surface Science and Electrochemistry*, pages 28-42, ISBN:978-0-12-809894-3. Elsevier, 2018.

[176] Patil, D. M., Phalak, G. A., and Mhaske, S. T. Synthesis of bio-based epoxy resin from gallic acid with various epoxy equivalent weights and its effects on coating properties. *Journal of Coatings Technology and Research*, 14:355-365, 2017.

[177] Van Aelst, K., Van Sinay, E., Vangeel, T., Zhang, Y., Renders, T., Van den Bosch, S., Van Aelst, J., and Sels, B. F. Low molecular weight and highly functional RCF lignin products as a full bisphenol a replacer in bio-based epoxy resins. *Chemical Communications*, 57(46):5642-5645, 2021.

[178] Yue, L., Liu, F., Mekala, S., Patel, A., Gross, R. A., and Manas-Zloczower, I. High performance biobased epoxy nanocomposite reinforced with a bacterial cellulose nanofiber network. *ACS Sustainable Chemistry & Engineering*, 7(6):5986-5992, 2019.

[179] Nikafshar, S., Zabihi, O., Hamidi, S., Moradi, Y., Barzegar, S., Ahmadi, M., and Naebe, M. A renewable bio-based epoxy resin with improved mechanical performance that can compete with DGEBA. *RSC Advances*, 7(14):8694-8701, 2017.

[180] Senthilkumar, K., Ungtrakul, T., Chandrasekar, M., Senthil Muthu Kumar, T., Rajini, N., Siengchin, S., Pulikkalparambil, H., Parameswaranpillai, J., and Ayrilmis, N. Performance of sisal/hemp bio-based epoxy composites under accelerated weathering. *Journal of Polymers and the Environment*, 29:624-636, 2021.

[181] Cintra, L. T. A., Benetti, F., de Azevedo Queiroz, Í. O., Ferreira, L. L., Massunari, L., Bueno, C. R. E., de Oliveira, S. H. P., and Gomes-Filho, J. E. Evaluation of the cytotoxicity and biocompatibility of new resin epoxy–based endodontic sealer containing calcium hydroxide. *Journal of Endodontics*, 43(12):2088-2092, 2017.

[182] Jiang, H., Sun, L., Zhang, Y., Liu, Q., Ru, C., Zhang, W., and Zhao, C. Novel biobased epoxy resin thermosets derived from eugenol and vanillin. *Polymer Degradation and Stability*, 160:45-52, 2019.

[183] Kadam, A., Pawar, M., Yemul, O., Thamke, V., and Kodam, K. Biodegradable biobased epoxy resin from Karanja oil. *Polymer*, 72:82-92, 2015.

[184] Oladele, I. O., Akinwekomi, A. D., Agbabiaka, O. G., and Oladejo, M. O. Influence of biodegradation on the tensile and wear resistance properties of bio-derived $CaCO_3$/epoxy composites. *Journal of Polymer Research*, 26:1-9, 2019.

[185] da Silva, L. R., Carvalho, B. A., Pereira, R. C., Diogenes, O. B., Pereira, U. C., da Silva, K. T., Araujo, W. S., Mazzetto, S. E., and Lomonaco, D. Bio-based one-component epoxy resin: Novel high-performance anticorrosive coating from agro-industrial byproduct. *Progress in Organic Coatings*, 167:106861, 2022.

[186] Oktay, B., Türkcan, J. H., Özdemir, O. K., and Kayaman-Apohan, N. Vegetable oil-based epoxy coating materials for self-healing and anticorrosive applications. *Macromolecular Research*, 1-10, 2023.

[187] Wu, Y., He, Y., Chen, C., Zhong, F., Li, H., Chen, J., and Zhou, T. Non-covalently functionalized boron nitride by graphene oxide for anticorrosive reinforcement of water-borne epoxy coating. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 587:124337, 2020.

[188] Lou, G., Ma, Z., Dai, J., Bai, Z., Fu, S., Huo, S., Qian, L., and Song, P. Fully biobased surface-functionalized microcrystalline cellulose via green self-assembly toward fire-retardant, strong, and tough epoxy biocomposites. *ACS Sustainable Chemistry & Engineering*, 9(40):13595-13605, 2021.

[189] Ahmadi, Z. Epoxy in nanotechnology: A short review. *Progress in Organic Coatings*, 132:445-448, 2019.

[190] Zheng, S., Bellido-Aguilar, D. A., Hu, J., Huang, Y., Zhao, X., Wang, Z., Zeng, X., Zhang, Q., and Chen, Z. Waterborne bio-based epoxy coatings for the corrosion protection of metallic substrates. *Progress in Organic Coatings*, 136:105265-105265, 2019.

[191] Shundo, A., Yamamoto, S., and Tanaka, K. Network formation and physical properties of epoxy resins for future practical applications. *Journal of American Chemical Society Au*, 2(7):1522-1542, 2022.

[192] Paul, R., John, B., and Sahoo, S. K. UV-curable bio-based pressure-sensitive adhesives: Tuning the properties by incorporating liquid-phase alkali lignin-acrylates. *Biomacromolecules*, 23(3):816-828, 2022.

[193] Ramon, E., Sguazzo, C., and Moreira, P. M. A review of recent research on bio-based epoxy systems for engineering applications and potentialities in the aviation sector. *Aerospace*, 5(4):110-145, 2018.

[194] Qi, Y., Weng, Z., Kou, Y., Li, J., Cao, Q., Wang, J., Zhang, S., and Jian, X. Facile synthesis of bio-based tetra-functional epoxy resin and its potential application as high-performance composite resin matrix. *Composites Part B: Engineering*, 214:108749-108759, 2021.

[195] Vinod, A., Sanjay, M. R., Siengchin, S., and Fischer, S. Fully bio-based agro-waste soy stem fiber reinforced bio-epoxy composites for lightweight structural applications: Influence of surface modification techniques. *Construction and Building Materials*, 303:124509-124526, 2021.

[196] Hadi, A. N., Mohammed, M. R., and Al-Bakri, A. F. Numerical and experimental assessment of mechanical properties of biobased epoxy reinforced by flax fibres and seashell nanoparticles for prosthetic socket. *Advances in Materials Science and Engineering*, 2022:1-11, 2022.

[197] Díez-Pascual, A. M. and Diez-Vicente, A. L. Epoxidized soybean oil/ZnO biocomposites for soft tissue applications: preparation and characterization. *ACS Applied Materials & Interfaces*, 6(19):17277-17288, 2014.

[198] Zou, Y., Jin, X., Zhang, X., Kong, X., Zhang, Q., Xie, X., Liu, C., Ke, L., Liu, W., and Wang, W. A multifunctional biomedical patch based on hyperbranched epoxy polymer and MXene. *Science China Technological Sciences*, 64(12):2744-2754, 2021.

[199] Fu, F., Shen, M., Wang, D., Liu, H., Xu, X., Shang, S., Song, Z., and Song, J. Green preparation of robust hydrophobic bio-based epoxy resin with low dielectric constant. *Industrial Crops and Products*, 188:115615, 2022.