

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

5,800

Open access books available

142,000

International authors and editors

180M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Epoxy as Filler or Matrix for Polymer Composites

Xianhui Zhao, Shun Lu, Wei Li, Shuyang Zhang, Kai Li, Kashif Nawaz, Peter Wang, Guang Yang, Arthur Ragauskas, Soydan Ozcan and Erin Webb

Abstract

Epoxy is a widely used polymer because of its ease of processing, high adhesiveness, and high chemical resistance. Epoxy-based composites are commonly used in aerospace, automotive, and marine applications. The epoxy type, function, curing agent, and curing process are discussed in this chapter. Epoxy is used as either a filler or polymer matrix in composite applications. As a filler, the epoxy modification on the fiber is discussed. As a polymer matrix, the epoxy is reinforced by natural and synthetic fibers. The manufacturing process and the fabricated epoxy-based composites' performance (e.g., mechanical and thermal properties) are investigated. The advantages and disadvantages of epoxy's function are discussed and summarized. Epoxy modification is an effective approach to improve the composites' performance.

Keywords: epoxy, filler, fiber, matrix, polymer, composite

1. Introduction

Since the discovery of epoxy in 1909 by Prileschajew [1], epoxy has become an important part of our daily life and integral to numerous industrial sectors. Epoxy is a plastic that has an epoxy ring, which consists of two carbon atoms that are bonded to a common oxygen atom. Epoxy resins are a class of reactive prepolymers and polymers that contain epoxide groups, which are cured using a wide variety of curing agents (i.e., hardener). Epoxy is one of the most important thermosetting polymers and has wide applications in different areas. The products' properties largely depend on the structure of the epoxy resins and curing agents used. The excellent mechanical properties, high adhesiveness to many substrates, low shrinkage after curing, and good heat and chemical resistances make epoxy resins remarkably useful across a wide range of fields, where they act as reinforced materials, adhesives, coatings, etc. [2–5].

Epoxy has been widely used as polymer matrix for composite applications. The properties of composites can be customized by adding functional fibers to endow the functionalities on the composites. For example, the fiber-reinforced epoxy composites have significantly improved mechanical properties. Song et al. [6] developed carbon fiber/epoxy composite laminates with carbon nitride, and their tensile strength and Young's

modulus reached 67 MPa and 58 GPa, respectively. Huang et al. [7] developed continuous bamboo fiber reinforced epoxy composites (i.e., long bamboo fiber as reinforcement rather than chopped fibers through a resin transfer molding process and achieved improved mechanical strain. Epoxy based composites not only have enhanced mechanical properties, they can also feature unique properties, such as electromagnetic interference shielding properties [8], self-healing [9], heat resistance [10], and others [3, 4].

Despite serving as a polymer matrix, epoxy, as a reactive molecule, can be used as fillers (or modifiers) to facilitate reinforce polymer composites. Fillers are typically added to polymers to modify their characteristics and/or reduce their price [11–13]. For instance, Zhao et al. applied epoxy to functionalize pine fibers that were used to reinforce the polylactic acid (PLA) [11]. Their results suggest that the epoxy modification is beneficial to improve the tensile strengths and Young's moduli of the composites compared to that of neat PLA owing to the improved fiber/matrix interfacial adhesion. One reason is that the epoxy exhibits high adhesiveness and compatibilization effect. In another study conducted by Sujaritjun et al. [12], epoxidized polybutadiene treated bamboo fibers were used to reinforce PLA and achieved a 10% increase in the tensile strength. Similarly, Kyutoku et al. [13] utilized cellulose fibers coated with epoxy-based agents to reinforce PLA and found that the epoxy treatment improved the interfacial adhesion between cellulose fibers and PLA. Compared with other non-reactive surface functionalization of the nanofiber [14], the high reactivity of the epoxy group in the epoxy modified fibers is beneficial for improving the interfacial interactions between fibers and matrix, and thus can effectively reinforce polymers.

The cured epoxy resins are brittle due to the high degree of cross-linking, which weakens epoxy's impact strength and other relevant properties [3, 15]. Therefore, chemical modification of epoxy monomers is necessary to improve their flexibility and toughness as well as other properties [16]. Many efforts have been devoted to addressing these challenges through introducing flexible polymers, inorganic solid particles, and elastomers [17–19]. Despite the brittleness, epoxies also have poor thermal and electrical conductivity [20]. To solve these challenges and improve the properties of the epoxy-based materials, different thermal conductive and electrical conductive materials (fibers), such as carbon nanotubes, graphene, carbon fiber, and others, were added [21]. However, the poor interfacial interaction between the fiber and epoxy led to low interfacial strength and impact toughness. Considerable efforts have been made to solve this issue [6, 7]. Additionally, bio-based epoxy [22] and epoxy-based vitrimer [23] also become new hot topics in this field driven by the desire for sustainability and recyclability [24] of composite materials.

Given the importance of the epoxy-based composites, in this chapter, the recent development of epoxies in polymer composites are summarized based on their roles. The basics of epoxy, such as structure, curing agents, and curing process, are discussed. The role of the epoxy compounds in the composites is discussed from the filler and polymer matrix aspects. Finally, the challenges and future opportunities in the epoxy-based composites are summarized.

2. Epoxy

2.1 Epoxy type

Epoxy resin is often regarded as the most valuable polymer. It is widely utilized in numerous modern industries including aerospace [25], electrical encapsulation [26],

chemical engineering [27], civil engineering [28], food industry [29], etc. Epoxy resins are part of the family of monomeric or oligomeric materials with excellent electrical insulation properties and extraordinary resistance to corrosion [30]. Epoxy resin has a group of reactive polymers, which contain epoxy or oxirane groups, as presented in **Figure 1**. According to their structure, characteristic, and functionality, there are three major types of epoxy resins: (i) cycloaliphatic, (ii) epoxidized, and (iii) glycidated epoxy resins [31].

The first two types of resins (cycloaliphatic and epoxidized) are synthesized directly via the corresponding olefin oxidation. Glycidated resins are prepared by glycidation of bisphenol A with epichlorhydrin. Generally, cycloaliphatic epoxy resins provide excellent ultraviolet (UV) stability and electrical properties, as well as good thermal stability due to their fully saturated structure. This feature makes them suitable for structural components under high-temperature situations. Furthermore, these resins are easy to obtain owing to their low viscosities and can be cured at low temperatures. This result is likely because these resins have simple structures, and the low viscosity leads to easy curing. However, they have a short pot life (useable life: the length of time that a system retains a viscosity low enough to be applied), as moisture and other factors easily affect the uncured resins. Bisphenol epoxy resin is a type of commercial resin, commonly composed of a mixture of oligomers. It has a wide variety of viscosities and low molecular weights, resulting in high-performance phenoxy lacquer resins [31].

2.2 Epoxy functions and advantages

Epoxy resins are utilized in various applications due to their outstanding properties and versatile nature [25, 29, 31]. Epoxy resins can form into thermoset or photosensitive resins, which are determined by reaction conditions and curing agents [32, 33]. Epoxy-based parts are usually manufactured in the desired shape by typical technologies including but not limited to resin infusion [34], injection molding [35], resin transfer molding [36], and autoclave [37]. Nevertheless, the above processed technologies cause several bottlenecks in terms of slow production, difficulties in producing complex geometries, labor-intensiveness, and high cost of the process, particularly considering thermal energy [31].

One significant characteristic of epoxy resins is that the curing process proceeds through a step-growth reaction without the generation of volatile byproducts. Subsequently, the process produces structures free from voids and bubbles. Therefore, the tailoring of cross-linkers and modifiers are critical in the steady growth rate of epoxy resins considering their further functionality. Because of the poor toughness,

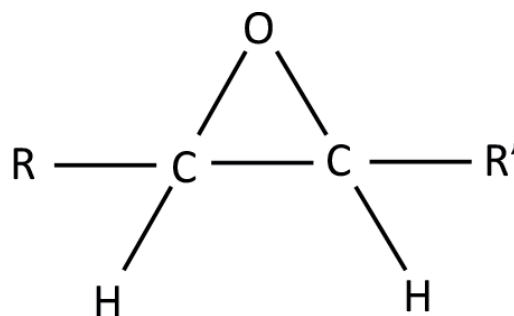


Figure 1.
Epoxy or oxirane group.

researchers explored and developed several strategies to improve the toughness of epoxy resins: (i) change in the chemical structure to make them more flexible [38], (ii) increase in the molecular weight [39], (iii) decrease in the cross-linking density [40], (iv) addition of a tougher phase, and (v) addition of fibers [29].

2.3 Epoxy curing agent

The desired properties of epoxy resins are generally determined by combining an epoxy resin and a curing agent. Curing agents can be catalysts usually drawn from amines, Lewis acids, or hardeners. Hardeners, identified as curing or cross-linking agents, can break the C-O-C ring at the ends of an epoxy molecule and attach themselves to the molecules to convert the resin into a thermoset network structure. Different curing agents can create composites with different properties because the curing agents have different functional sites that lead to different chemical reactions. A specific hardener should be selected based on processing conditions (viscosity, pot life, mixing ratio, and temperature) and the desired properties of the product (strength, chemical and thermal resistance, toughness, and flexibility). The most common hardeners for epoxy resins are amine types: (i) aliphatic, (ii) aromatic, and (iii) cycloaliphatic. The type, amount, functionality of the hardener, as well as the curing conditions (temperature and curing time), affect the properties of hardened epoxy resins. For example, difunctional epoxy resins are prepolymers with an epoxy group at each end of a molecule. The diglycidyl ether of bisphenol F (DGEBF) has similar molecular structures: the two methyl groups attached to the carbon between the benzene groups in the former are replaced with H atoms in the latter. F-type epoxies have lower viscosity than A-type epoxies. For this reason, A and F types are often mixed to lower the viscosity of a mixture, thus preventing the crystallization of the polymers [41].

Ozkul et al. [41] employed three different epoxy resins, diglycidyl ether of bisphenol A, diglycidyl ether of bisphenol F (DGEBF), and a mixture of the two; six amine type hardeners, four of which are aliphatic and the others are cycloaliphatic; and three glycidyl-ether based reactive diluents to study their effects towards the hardened state properties of epoxy mortars. Three epoxy resins and three types of glycidyl ether-based reactive diluents were used together in epoxy mortars. Six different amine-based hardeners, four aliphatic and two cycloaliphatic, were used in the mixtures. A hardener with a higher functionality (reactive point) led to mortars with higher strength.

2.4 Epoxy curing process

Epoxy resins are in liquid form and the curing agent solidifies during the fabrication. During curing, the chemical reaction of the epoxide groups in the epoxy resin is initiated by a curing agent through a step-growth reaction, then form a 3D highly cross-linked network. Curing process conditions impact the properties of the cured resins. For example, the amount of curing agents influences the strength of the cured resin film and the formation time. There are three main methods of curing: (i) room-temperature curing, (ii) thermal curing, and (iii) photocuring [31].

Room temperature curing agents are used to cure epoxy resins at room temperature. These include aliphatic polyamines, low-molecular-weight polyamides, alicyclic polyamines, and modified aromatic amines. This curing system is preferred for higher flexibility, impact resistance, and electrical and thermal shock resistance [31]. The final structure of the cured resin highly depends on the employed temperature.

High temperature curing agents, for example, acid anhydrides, resol resins, aromatic polyamines, dicyandiamides, and hydrazides, are used to cure epoxy resins at elevated temperatures. Generally, high temperature curing is carried out in two stages: (i) precuring stage (gel-status) at a low temperature and (ii) postcuring stage (solid-status) at a high temperature. Epoxy components fabricated at higher temperatures exhibit higher tensile strength, heat resistance, and chemical resistance [31].

Photocuring systems significantly decrease the epoxy curing process time from hours to minutes and save the cost of energy compared to autoclave thermal curing. A wide range of radiation curing wavelengths, such as infrared light, UV light, X-rays, and electron beam irradiations, can be used to cure photosensitive epoxy resins employing photoinitiators. Photocuring is a relatively controllable and consistent process as compared to other curing processes [31].

Two-stage curing systems that combine photocuring and thermal curing enable the use of epoxy resins in additive manufacturing. Traditionally, epoxy resin and its composites are manufactured by curing at high temperatures for several hours. This condition makes epoxy resin impossible to use in additive manufacturing because, curing layer by layer is essential during fabrication. To solve this issue in additive manufacturing the common practice is to use photosensitive epoxy resin. However, this cured resin has poor mechanical properties, low curing rate, and high cost due to photoinitiators. Moreover, it does not meet the need for mechanical parts required in some specified industries. Direct-ink writing is a possible approach to use epoxy or other thermoset resins where the ink can be designed to be viscoelastic with the incorporation of a fiber [31].

Kuang et al. [42] demonstrates additive manufacturing of an epoxy resin using digital light processing. The hybrid ink is prepared by blending a thermally curable resin and a photocurable resin and cures in two stages. During manufacturing, the epoxy resin is exposed to UV-LED light with a wavelength of 385 nm (first-stage curing) to create the designed shape and then cured at 100°C for 2 h and another 2 h at 160°C (second-stage curing). The hybrid ink presents low volume shrinkage, desired mechanical properties and high resolution, enabling use in engineering applications. Griffini et al. [43] customizes a hybrid ink of thermal and photocurable epoxy resins to investigate the possibility of the fabrication of carbon fiber-reinforced composite structures. Carbon fibers with a diameter of 7.2 μm and length of 100–150 μm are added into the ink to develop an increased weight concentration. When the hybrid ink is extruded from the syringe, light from two UV-A torches with a wavelength of 405 nm irradiates the hybrid ink to solidify its shape in the first-stage curing. Then, the printed sample is cured at 220°C for 20 min in a ventilated oven for the second-stage curing. The weight ratio between thermal and photocurable components strongly influenced the printing characteristics. Carbon fibers also affected the efficiency of UV-curing.

3. Epoxy-based composites

3.1 Epoxy as filler

Epoxy can be used as a non-matrix component (i.e., filler or minor component) in composites and is usually applied at the fiber and polymer matrix interface. Epoxy can be used to functionalize the surface of fibers with epoxy groups. Thus, the surface of the fibers can be activated to react with other components in the composites.

Cheng et al. [44] uses a two-step method to epoxidize the surface of poly-p-phenylene-benzimidazole-terephthalamide (PBIA) fibers with epoxy groups. The PBIA fibers were first fluorinated and grafted with Si-OH groups. The Si-OH groups were then added with 3-glycidoxypropyltrimethoxysilane (GPTMS) for epoxidation. The modified fibers were then incorporated in an epoxy matrix with respect to surface energy and pull-out strength, where both the two properties were improved. The surface energy increased from 13 to 17 mN/m, while the pull-out strength improved from 0.45 to 0.63 N/(tex·mm). Fei et al. [45] used the epoxy group as an activate site to graft polymer chains for functional composites. The bacterial cellulose was first epoxidized with epoxy chloropropane (ECP) at the hydroxyl groups on cellulose. Aniline was then added and grew from the epoxy group to polyaniline (PANI), providing electrical conductivity in the final cellulose-based flexible paper. The electrical conductivity can reach 1.1 S/cm at proper ECP concentrations and can be further improved up to 1.4 S/cm by introducing polyacrylamide via enhancing the interaction between PANI and the fibers.

Another epoxidation was done by Cao et al. [46] on tunicate cellulose nanocrystals (T-CNC), which exhibit a higher aspect ratio than cotton CNC. GPTMS was used to introduce epoxy groups on the surface of T-CNC first. The modified fibers were then blended with carboxylate styrene-butadiene rubber. The covalent bonding between epoxy and carboxyl groups was improved. The tensile strength, modulus, and toughness were improved with more modified T-CNC added. In addition, the resultant rubber could be reprocessed, attributed to the transesterification of the ester bonding formed by epoxy and carboxyl groups. This modification enabled the composites to maintain their original tensile strength even after reprocessing three times. In these methods, epoxy significantly altered the surface chemistry and the interfacial adhesion. However, one issue was that the epoxidation process usually involved highly activate reagents, like ECP, which may bring an uncontrollable by-reaction that will affect the properties of the final product [45].

Epoxy are utilized to adjust the properties of composites. A single domain or phase with an epoxy group is introduced into composites. The properties of the composites change depending on the inherent properties of the epoxy group. Epoxy can also react with other components to bring new bonding. For example, Immonen et al. [47] used epoxidized linseed oil (ELO) as an epoxy phase in a PLA-based composites with bleached softwood kraft pulp (BSKP) as the fiber. At certain concentrations of ELO, the trinary composites exhibited improved tensile strength, modulus, elongation at break, and impact strength compared with neat PLA and BSKP/PLA composites. This result inferred that ELO could react with both PLA and BSKP, thus enhancing the interfacial adhesion between PLA and BSKP. A similar idea was applied by using tannic acid-crosslinked epoxidized soybean oil (TA-ESO) in bamboo fiber (BF)/PLA composites as reported in Liu et al.'s work [48]. In their composite system, BF was the reinforcing fiber that could improve tensile strength and modulus as more incorporated, while decreasing the elongation at break. TA-ESO was introduced by solution-spray onto the BFs and then dried to modify the surface of BF for better interaction with the PLA matrix. TA-ESO was expected to act as a bridge between the two phases to enhance the interfacial adhesion. At a low concentration (0.5 wt%) of TA-ESO, the epoxy phase mainly acted as a compatibilizer between PLA and BF since hydroxyl groups on both PLA and BF could react with epoxy group on EOS, contributing to the force transfer from PLA to BF to improve the tensile strength. As TA-EOS content increased, excessive TA-EOS could be presented as a single phase, which acted as a toughening domain in PLA composites and a compatibilization effect on the interface.

However, TA-EOS at higher concentration resulted in poor tensile performance and impact strength due to the large domain area. Nevertheless, TA-EOS could be used to balance the tensile strength and toughness by varying the feeding ratio compared to BF and PLA matrix.

Similarly, Zhao et al. [11] impregnated an epoxy solution to pine fibers to fill and penetrate the voids and hollow channels in the pine fibers. By mixing curing agent (Dicyandiamide) and epoxy resin (Poly(bisphenol A-co-epichlorohydrin), glycidyl end-capped), part of the epoxy cured during the drying process, modifying the surface chemistry. This method benefited the tensile strength, where the tensile strength and Young's modulus improved by 20% and 82%, respectively, at 1 wt% loading of the epoxy system. The better interfacial adhesion between PLA and pine fibers came from the compatibilization effect of the epoxy. Epoxy curing during the hot pressing for final composites may bridge PLA and pine fibers by a covalent bond. The epoxy enhanced the interaction between polymer matrix and pine fibers increasing the tensile performance. Through this approach, the preparation of the composites was conducted without complex chemical reactions. However, the property of the final products depended on the inherent property and concentration of the epoxy-included phase which should be carefully selected [48].

3.2 Epoxy as polymer matrix

Epoxyes are extensively used as the polymer matrix of composites for their salient features of high specific strength, good dimensional stability, and excellent dielectric properties [1, 30, 49]. Due to the high cross-link density formed during curing, neat epoxy resins are intrinsically brittle and have low fracture toughness, which can limit their application in some specified fields. Moreover, epoxy resins are relatively expensive in comparison with other commonly used thermosetting resins, such as unsaturated polyester and vinyl ester resins. Adding fibers into epoxyes could enhance the thermal and durability properties [50]. However, the addition of fibers can impart adverse influence on composites' physical and mechanical properties alongside the reinforcement on other properties. Therefore, attention needs to be paid to optimizing and balancing different properties and costs when designing composites for specific applications. **Table 1** summarizes the general types and fabrication techniques of epoxy-based composites. Some applications and recent developments of high-performance and cost-effective epoxy composites are briefly reviewed herein.

Fiber reinforcement is a common strategy for preparing epoxy composites and is widely adopted in the industry [50, 54]. Synthetic fibers, such as glass, carbon, and aramid, offer load bearing capability and enhancement of mechanical properties, while the epoxy functions as a binder that forms an overall solid shape and transfers the stress uniformly onto the fibers inside the matrix. Particularly, epoxyes exhibit a low viscosity before curing that helps with fiber wetting and minimizing air voids, aiding in the composite strength. Meanwhile, the low viscosity provides a unique processing versatility such that various options of fabrication techniques can be applied for the industrial manufacture of epoxy composites (see **Table 1**). These characteristics, alongside outstanding chemical and mechanical properties after being cured, let fiber-reinforced epoxyes find a broad range of commercial applications in structural materials, commercial and sporting goods, and civil infrastructures, as well as diverse lightweight engineering applications in automotive, marine, aerospace, and wind turbine construction, for which the high strength-to-weight ratio allows for substantial fuel and energy savings [50].

Type	Fiber	Fabrication techniques
Conventional composites	• silica	• extrusion
	• metal	• pultrusion
	• rubber	• lamination
	• basalt	• solvent casting
	• fly ash	• filament winding
	• aramid	• vacuum bag molding
	• ceramic	• compression molding
	• natural fiber	• prepreg/autoclave process
	• carbon black	• vacuum-assisted resin transfer molding
	• synthetic fiber	
	• flame retardant fiber	
	• thermoplastic polymer	
Nanocomposites	• clay	• melt mixing
	• nanofiber	• shear mixing
	• metallic oxide	• electrospinning
	• carbon nanotube	• solution mixing
	• silica nanoparticle	• ultrasonic mixing
	• graphene nanoplatelet	• surface modification
	• boron nitride nanosheet	

Table 1.
Types and fabrication techniques of epoxy-based composites [8, 16, 17, 21, 36, 50–53].

Glass fibers are readily available and relatively cheap on the commodity market, making them the most used fibers in the composite industry. Glass fibers have high tensile strength and excellent insulating properties [54, 55]. Glass fiber-reinforced epoxy composites are often fabricated by distributing discontinuous or continuous glass fibers, randomly oriented, inside the epoxy matrices. By combining the complementary features of glass fiber and epoxy, the ensuing composite provides a superior material for the replacement of heavier metal and ceramic parts in structural and insulation applications. Being another commonly used reinforcement fiber, carbon fiber is stronger, lighter, and more expensive than glass fiber (see **Table 2**). Epoxy adheres well to carbon fiber. The manufacturing of carbon fiber composites usually involves the epoxy impregnation of carbon fabric [34, 36]. The strength of laminated composites depends on the weave pattern, orientation, and weight fraction of the carbon fabric, which is generally stronger than that of the glass fiber reinforcement, leading to more advanced applications.

In addition to synthetic fibers, natural fibers received considerable attention in past decades in view of environmental concerns [56–59]. Natural fibers are mostly sourced from plants or animals and are biodegradable and renewable [60, 61]. Their replacement of synthetic fibers in composite applications can reduce carbon footprint, improve recyclability, and enhance environmental sustainability. Studies have examined epoxy composites reinforced by natural fibers, such as kenaf, coir, sisal, banana, jute, bamboo, cotton, bagasse, flax, ramie, and luffa. These studies suggest these natural fibers reinforce epoxy’s physical and mechanical properties and

Material	Bulk density (g/cm ³)	Tensile strength (MPa)	Young's modulus (GPa)	Toughness (mJ/mm ³)
Glass	2.5	1048	62	21
Carbon	1.8	2302	168	46
Aramid	1.4	2273	47	92

Table 2.
Typical properties of commonly used reinforcement fibers [54].

are suitable for low-load applications [62, 63]. Despite growing interest, bio-based materials have seen relatively slow market growth in the consumption of natural fibers [64]. This result provides an opportunity for fostering applications of natural fiber reinforced epoxy composites. However, the development of fiber processing and chemical treatment technologies is needed to improve the performance of epoxy composites with natural fibers.

Given the increasing demand of high-performance materials in lightweight construction and renewable energy generation, significant research efforts are devoted to improving the mechanical properties of fiber-reinforced epoxies and extending their functional applications. Poor damage tolerance and fire resistance are significant obstacles that limit the applications of conventional epoxy-based composites [53]. Notably, their anisotropic nature and weak out-of-plane mechanical properties induce low impact resistance for composites with aligned reinforcement fibers. Meanwhile, the debonding between fiber and matrix under transverse and compression loading can cause delamination that significantly deteriorates the mechanical performances and hence, reduces the service life of composite materials. In addition, the cured epoxy matrix decomposes when exposed to high temperatures (300–400 °C), releasing heat, smoke, and toxic volatiles and byproducts [65]. Managing the fire risk and subsequent environmental hazard is thus crucial for broadening the application range of epoxy composites.

Strategies for composite property improvement focus on developing the matrix, fiber, and the interface of composite materials [66]. Toughening of the epoxy matrix is the most effective way to improve the composite impact strength for structural applications [17, 67]. Standard methodologies for the epoxy toughening include the chemical modification of the epoxy and the integration of toughening agents. In the former scenario, reducing the cross-link density (by increasing the segment length between crosslinks), increasing the molecular weight of epoxy monomers, or modifying the rigid backbone structure to be flexible increases the impact toughness. However, these changes impose significant reductions in other properties, e.g., modulus, tensile and flexural strength, as well as decrease the glass transition temperature that affects the thermal stability. Considering this synergistic effect, the industrial formulations of epoxies often reflect the tradeoff of balancing different properties for end applications. In this regard, blending toughening agents (typically, 5–20 wt%) becomes a more facile approach [16, 17].

Typical toughening agents include liquid rubbers, thermoplastics, hyperbranched polymers, block copolymers, and inorganic nanoparticles, among which the liquid rubber is a more common choice for industrial applications as it is more economical and easier to process [68]. Several types of reactive liquid rubbers, namely, carboxyl-terminated poly (butadiene-co-acrylonitrile), amine-terminated poly (butadiene-co-acrylonitrile), and hydroxyl terminated polybutadiene, have been developed to

increase the epoxy toughness [27, 69]. However, these polybutadiene derivatives have unsaturated sites along the backbone that are susceptible to degradation in a high-temperature and oxidative environment. To overcome this deficiency, saturated liquid rubbers, such as polyacrylates, polysiloxane, and polyurethane, are introduced as alternatives that offer better oxidative stability [70]. The liquid rubber toughening is found to be effective for difunctional epoxy resins but ineffective for tri and tetra-functional epoxy resins that have a higher degree of cross-linking, suggesting that the toughening of the matrix increases with increasing the inherent ductility of the epoxy [53, 69].

Thermoplastics constitute another significant type of toughening agents, which enhance the toughness for both difunctional and multifunctional epoxy resins without sacrificing other desirable mechanical properties (as is the case for the rubber toughening). Since the early 1980s, several thermoplastics have been applied, including polysulfone, poly (ether imide), poly (ether sulfone), and poly (phenylene oxide) [70, 71]. It is well recognized that the toughening effect of thermoplastic depends on its phase structure inside the matrix. Notably, a co-continuous morphology at a high thermoplastic concentration, in contrast to the discrete morphology, can induce a sharper increase in the fracture toughness with increasing the thermoplastic content [71]. Nevertheless, the manipulation of phase structures (through varying the composition and curing condition) and the optimization of formulations for different applications require additional engineering.

Alongside the development in conventional toughening strategies, block copolymers and nanoparticles emerge as promising additives for epoxy toughening, which gain increasing interest in recent years [17, 19, 72]. Specifically, block copolymers can undergo microphase separation under the thermodynamic driving force. This result imparts a fine-tuning of phase structures at the nanoscale that affects the properties of nanodomains inside the matrix, resulting in stronger enhancement effects compared to conventional agents of larger sizes. Similarly, nanoparticles significantly enlarge the interface between fiber and matrix upon good dispersion inside epoxy. A small amount of nanoparticles can dramatically improve the matrix properties. Moreover, the incorporation of different types of nanoparticles (**Table 1**), and surface modifications [4], lead to epoxy nanocomposites with enhanced electrical conductivity, thermal conductivity, magnetic, flame retardant, and radiation resistant properties [51, 73], expanding their utility in functional applications.

Overall, considering that different types of agents are associated with different toughening mechanisms (functioning at different length scales), a hybridization strategy can be adopted to prepare fiber-reinforced hybrid epoxy composites that enable synergistic toughening [67, 72, 74, 75]. Given the large degree of freedom of the components, the development of multiscale computer simulations [76, 77], machine learning, and experimental studies are needed to expedite the rational design of advanced epoxy composites.

4. Conclusion

Epoxy has high adhesiveness and is widely used in industry. However, no systematic study has been performed on using epoxy as a filler or polymer matrix for composite applications. This chapter has systematically reviewed recent research and advances on epoxy-based composites. Discussion includes analysis of the epoxy type, epoxy function, curing agent, curing process, and performance of epoxy-based composites.

Epoxy resin has a group of reactive polymers that contain epoxy or oxirane groups. There are three major types of epoxy resins: cycloaliphatic, epoxidized, and glycidated epoxy resins. Epoxy-based materials are manufactured into the desired shape by injection molding, resin transfer molding, or resin infusion. The desired properties of epoxy resins are generally determined by the combination of an epoxy resin and a curing agent. Three main methods of curing are room-temperature curing, thermal curing, and photocuring. During curing, the chemical reaction of the epoxide groups in the epoxy resin is initiated by a curing agent to form a highly cross-linked network.

As a filler, there are two common approaches to utilize epoxy. One is to functionalize the fiber's surface with epoxy groups so that the fiber's surface can be activated to react with other components in the composites. The other one is to incorporate epoxy as a single domain or phase in the composites with epoxy groups. However, the composites' performance will be influenced by the inherent property of the epoxy and the concentration of the epoxy-included phase.

Epoxy is used as a polymer matrix because of its high specific strength, excellent adhesion, and good dimensional stability. Adding fibers into epoxies improves the thermal and durability properties while reducing the cost for composite applications. However, the addition of fibers can adversely influence the mechanical and physical properties of composites. Toughening the epoxy is an effective way to improve the composite's impact strength for structural applications. Typical toughening agents include thermoplastics, liquid rubbers, block copolymers, and nanoparticles. Liquid rubbers are a more common choice for industrial applications as they are more economical and easier to process.

Challenges and future directions:

1. As a filler, the epoxy's inherent property affects the composites' performance. In addition, the epoxidation process typically involves highly active reagents that can cause uncontrollable side effects that influence the properties of the composites. The selection of appropriate epoxies with a high functionality is a challenge. The epoxy solution concentration, drying process, and advanced epoxy with outstanding mechanical properties can be investigated in the future.
2. As a polymer matrix, the poor interfacial interaction between the epoxy matrix and fibers is a key challenge. Toughening of the epoxy is an effective pathway to address this challenge. The manipulation of phase structures and the optimization of formulations for different applications require additional engineering.
3. Bio-based epoxy can be developed towards the sustainability and recyclability of the composites. Environmentally friendly and economically viable bio-based epoxies are needed.

Acknowledgements

The authors acknowledge the support from the US Department of Energy (DOE) FY 2021 BETO Project under Contract 1.2.1.9 with UT-Battelle LLC, and the US DOE, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under CPS Agreement 35714. This book chapter was authored in part by UT-Battelle LLC under contract DE-AC05-00OR22725 with DOE. The US government retains and the publisher, by accepting the article for publication, acknowledges that the US

government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this book chapter, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

Conflict of interest

The authors declare no conflict of interest.

Appendices and nomenclature

BF	Bamboo fiber
BSKP	Bleached softwood kraft pulp
DGEBF	Diglycidyl ether of bisphenol F
ECP	Epoxy chloropropane
ELO	Epoxidized linseed oil
GPTMS	3-glycidoxypropyltrimethoxysilane
PANI	Polyaniline
PBIA	Poly-p-phenylene-benzimidazole-terephthalamide
PLA	Polylactic acid
T-CNC	Tunicate cellulose nanocrystals
TA-ESO	Tannic acid-crosslinked epoxidized soybean oil
UV	Ultraviolet



Author details

Xianhui Zhao^{1*}, Shun Lu², Wei Li³, Shuyang Zhang³, Kai Li⁴, Kashif Nawaz⁴, Peter Wang⁵, Guang Yang⁶, Arthur Ragauskas^{3,7,8}, Soydan Ozcan^{5*} and Erin Webb^{1*}

1 Environmental Sciences Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee, United States

2 Agricultural and Biosystems Engineering Department, South Dakota State
University, Brookings, South Dakota, United States

3 Department of Chemical and Biomolecular Engineering, University of Tennessee,
Knoxville, Tennessee, United States

4 Buildings and Transportation Science Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee, United States

5 Manufacturing Science Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee, United States


6 Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee,
United States

7 Department of Forestry, Wildlife, and Fisheries, Center for Renewable Carbon, The
University of Tennessee Institute of Agriculture, Knoxville, Tennessee, United States

8 Joint Institute for Biological Sciences, Biosciences Division, Oak Ridge National
Laboratory, Oak Ridge, Tennessee, United States

*Address all correspondence to: zhaox@ornl.gov, ozcans@ornl.gov
and webbeg@ornl.gov

IntechOpen

© 2022 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] May C. *Epoxy Resins: Chemistry and Technology*. Boca Raton, Florida, USA: Routledge; 2018
- [2] Wang Y, Chen S, Chen X, Lu Y, Miao M, Zhang D. Controllability of epoxy equivalent weight and performance of hyperbranched epoxy resins. *Composites Part B: Engineering*. 2019;**160**:615-625
- [3] Jin F-L, Li X, Park S-J. Synthesis and application of epoxy resins: A review. *Journal of Industrial and Engineering Chemistry*. 2015;**29**:1-11
- [4] Gu H, Ma C, Gu J, Guo J, Yan X, Huang J, et al. An overview of multifunctional epoxy nanocomposites. *Journal of Materials Chemistry C*. 2016;**4**:5890-5906
- [5] Ahmadi Z. Epoxy in nanotechnology: A short review. *Progress in Organic Coatings*. 2019;**132**:445-448
- [6] Song B, Wang T, Wang L, Liu H, Mai X, Wang X, et al. Interfacially reinforced carbon fiber/epoxy composite laminates via in-situ synthesized graphitic carbon nitride (g-C₃N₄). *Composites Part B: Engineering*. 2019;**158**:259-268
- [7] Huang J-K, Young W-B. The mechanical, hygral, and interfacial strength of continuous bamboo fiber reinforced epoxy composites. *Composites Part B: Engineering*. 2019;**166**:272-283
- [8] Chen Y, Zhang H-B, Yang Y, Wang M, Cao A, Yu Z-Z. High-performance epoxy nanocomposites reinforced with three-dimensional carbon nanotube sponge for electromagnetic interference shielding. *Advanced Functional Materials*. 2016;**26**:447-455
- [9] Hu Z, Zhang D, Lu F, Yuan W, Xu X, Zhang Q, et al. Multistimuli-responsive intrinsic self-healing epoxy resin constructed by host-guest interactions. *Macromolecules*. 2018;**51**:5294-5303
- [10] Miao J-T, Yuan L, Guan Q, Liang G, Gu A. Biobased heat resistant epoxy resin with extremely high biomass content from 2, 5-furandicarboxylic acid and eugenol. *ACS Sustainable Chemistry & Engineering*. 2017;**5**:7003-7011
- [11] Zhao X, Li K, Wang Y, Tekinalp H, Larsen G, Rasmussen D, et al. High-strength polylactic acid (PLA) biocomposites reinforced by epoxy-modified pine fibers. *ACS Sustainable Chemistry & Engineering*. 2020;**8**:13236-13247
- [12] Sujaritjun W, Uawongsuwan P, Pivsa-Art W, Hamada H. Mechanical property of surface modified natural fiber reinforced PLA biocomposites. *Energy Procedia*. 2013;**34**:664-672
- [13] Kyutoku H, Maeda N, Sakamoto H, Nishimura H, Yamada K. Effect of surface treatment of cellulose fiber (CF) on durability of PLA/CF bio-composites. *Carbohydrate Polymers*. 2019;**203**:95-102
- [14] Li K, McGrady D, Zhao X, Ker D, Tekinalp H, He X, et al. Surface-modified and oven-dried microfibrillated cellulose reinforced biocomposites: Cellulose network enabled high performance. *Carbohydrate Polymers*. 2021;**256**:117525
- [15] Vidil T, Tournilhac F, Musso S, Robisson A, Leibler L. Control of reactions and network structures of epoxy thermosets. *Progress in Polymer Science*. 2016;**62**:126-179
- [16] Paluvai NR, Mohanty S, Nayak S. Synthesis and modifications of epoxy

resins and their composites: A review. *Polymer-Plastics Technology and Engineering*. 2014;**53**:1723-1758

[17] Domun N, Hadavinia H, Zhang T, Sainsbury T, Liaghat G, Vahid S. Improving the fracture toughness and the strength of epoxy using nanomaterials—a review of the current status. *Nanoscale*. 2015;**7**:10294-10329

[18] Kim BC, Park SW. Fracture toughness of the nano-particle reinforced epoxy composite. *Composite Structures*. 2008;**86**:69-77

[19] Huang F, Liu Y, Zhang X, Wei G, Gao J, Song Z, et al. Effect of elastomeric nanoparticles on toughness and heat resistance of epoxy resins. *Macromolecular Rapid Communications*. 2002;**23**:786-790

[20] Garg AC, Mai Y-W. Failure mechanisms in toughened epoxy resins—A review. *Composites Science and Technology*. 1988;**31**:179-223

[21] Nouri-Borujerdi A, Kazemi-Ranjbar S. Thermal and electrical conductivity of a graphene-based hybrid filler epoxy composite. *Journal of Materials Science*. 2021;**56**:15151-15161

[22] Baroncini EA, Kumar Yadav S, Palmese GR, J.F. Stanzione III, Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *Journal of Applied Polymer Science*. 2016;**133**(45):44103

[23] Shi Q, Yu K, Kuang X, Mu X, Dunn CK, Dunn ML, et al. Recyclable 3D printing of vitrimer epoxy. *Materials Horizons*. 2017;**4**:598-607

[24] Zhao X, Korey M, Li K, Copenhaver K, Tekinalp H, Celik S, et al. Plastic waste upcycling toward a circular economy. *Chemical Engineering Journal*. 2022;**428**:131928

[25] Kumar A, Anant R, Kumar K, Chauhan SS, Kumar S, Kumar R. Anticorrosive and electromagnetic shielding response of a graphene/TiO₂-epoxy nanocomposite with enhanced mechanical properties. *RSC Advances*. 2016;**6**:113405-113414

[26] Pulikkalparambil H, Siengchin S, Parameswaranpillai J. Corrosion protective self-healing epoxy resin coatings based on inhibitor and polymeric healing agents encapsulated in organic and inorganic micro and nanocontainers. *Nano-Structures & Nano-Objects*. 2018;**16**:381-395

[27] Chikhi N, Fellahi S, Bakar M. Modification of epoxy resin using reactive liquid (ATBN) rubber. *European Polymer Journal*. 2002;**38**:251-264

[28] Griffin S, Askarinejad H, Farrant B. Evaluation of epoxy injection method for concrete crack repair. *International Journal of Structural and Civil Engineering Research*. 2017;**6**:177-181

[29] Yousef S, Eimontas J, Subadra SP, Striūgas N. Functionalization of char derived from pyrolysis of metallised food packaging plastics waste and its application as a filler in fiberglass/epoxy composites. *Process Safety and Environmental Protection*. 2021;**147**:723-733

[30] Lee H, Neville K. *Handbook of Epoxy Resins*. New York, New York, USA: McGraw-Hill; 1967

[31] Peerzada M, Abbasi S, Lau KT, Hameed N. Additive manufacturing of epoxy resins: Materials, methods, and latest trends. *Industrial & Engineering Chemistry Research*. 2020;**59**:6375-6390

[32] Dagdag O, El Harfi A, Essamri A, El Gouri M, Chraibi S, Assouag M, et al. Phosphorous-based epoxy resin

composition as an effective anticorrosive coating for steel. *International Journal of Industrial Chemistry*. 2018;**9**:231-240

[33] Calza P, Rigo L, Sangermano M. Investigations of photocatalytic activities of photosensitive semiconductors dispersed into epoxy matrix. *Applied Catalysis B: Environmental*. 2011;**106**:657-663

[34] Zhang K, Gu Y, Zhang Z. Effect of rapid curing process on the properties of carbon fiber/epoxy composite fabricated using vacuum assisted resin infusion molding. *Materials & Design (1980-2015)*. 2014;**54**:624-631

[35] Zhan J, Li J, Wang G, Guan Y, Zhao G, Lin J, et al. Review on the performances, foaming and injection molding simulation of natural fiber composites. *Polymer Composites*. 2021;**42**:1305-1324

[36] Cheng QF, Wang JP, Wen JJ, Liu CH, Jiang KL, Li QQ, et al. Carbon nanotube/epoxy composites fabricated by resin transfer molding. *Carbon*. 2010;**48**:260-266

[37] Mezeix L, Seman A, Nasir MNM, Aminanda Y, Rivai A, Castanié B, et al. Spring-back simulation of unidirectional carbon/epoxy flat laminate composite manufactured through autoclave process. *Composite Structures*. 2015;**124**:196-205

[38] Ma S, Liu X, Fan L, Jiang Y, Cao L, Tang Z, et al. Synthesis and properties of a bio-based epoxy resin with high epoxy value and low viscosity. *ChemSusChem*. 2014;**7**:555-562

[39] Fang Q, Yao J, Niu K, Tang J, Wei Y, Guo Q, et al. Effect of molecular weight of self-emulsifying amphiphilic epoxy sizing emulsions on the carbon fibres and interfacial properties of their composites. *Polymers*. 2020;**12**:2439

[40] Iijima T, Yoshioka N, Tomoi M. Effect of cross-link density on modification

of epoxy resins with reactive acrylic elastomers. *European Polymer Journal*. 1992;**28**:573-581

[41] Ozeren Ozgul E, Ozkul MH. Effects of epoxy, hardener, and diluent types on the hardened state properties of epoxy mortars. *Construction and Building Materials*. 2018;**187**:360-370

[42] Kuang X, Zhao Z, Chen K, Fang D, Kang G, Qi HJ. High-speed 3D printing of high-performance thermosetting polymers via two-stage curing. *Macromolecular Rapid Communications*. 2018;**39**:1700809

[43] Griffini G, Invernizzi M, Levi M, Natale G, Postiglione G, Turri S. 3D-printable CFR polymer composites with dual-cure sequential IPNs. *Polymer*. 2016;**91**:174-179

[44] Cheng Z, Li B, Huang J, Chen T, Liu Y, Wang X, et al. Covalent modification of aramid fibers' surface via direct fluorination to enhance composite interfacial properties. *Materials & Design*. 2016;**106**:216-225

[45] Fei G, Wang Y, Wang H, Ma Y, Guo Q, Huang W, et al. Fabrication of bacterial cellulose/polyaniline nanocomposite paper with excellent conductivity, strength, and flexibility. *ACS Sustainable Chemistry & Engineering*. 2019;**7**:8215-8225

[46] Cao L, Gong Z, Xu C, Chen Y. Mechanical strong and recyclable rubber nanocomposites with sustainable cellulose nanocrystals and interfacial exchangeable bonds. *ACS Sustainable Chemistry & Engineering*. 2021;**9**:9409-9417

[47] Immonen K, Anttila U, Wikström L. Coupling of PLA and bleached softwood Kraft pulp (BSKP) for enhanced properties of biocomposites. *Journal of*

Thermoplastic Composite Materials. 2019;**32**:328-341

[48] Liu W, Qiu J, Chen T, Fei M, Qiu R, Sakai E. Regulating tannic acid-crosslinked epoxidized soybean oil oligomers for strengthening and toughening bamboo fibers-reinforced poly (lactic acid) biocomposites. *Composites Science and Technology*. 2019;**181**:107709

[49] Karak N. Overview of Epoxies and their Thermosets, Sustainable Epoxy Thermosets and Nanocomposites. Washington, D.C., USA: American Chemical Society; 2021. pp. 1-36

[50] Rajak DK, Pagar DD, Menezes PL, Linul E. Fiber-reinforced polymer composites: Manufacturing, properties, and applications. *Polymers*. 2019;**11**: 1667

[51] Li R, Gu Y, Zhang G, Yang Z, Li M, Zhang Z. Radiation shielding property of structural polymer composite: Continuous basalt fiber reinforced epoxy matrix composite containing erbium oxide. *Composites Science and Technology*. 2017;**143**:67-74

[52] Kausar A, Anwar Z, Muhammad B. Recent developments in epoxy/graphite, epoxy/graphene, and epoxy/graphene nanoplatelet composites: A comparative review. *Polymer-Plastics Technology and Engineering*. 2016;**55**:1192-1210

[53] Ratna D. *Epoxy Composites: Impact Resistance and Flame Retardancy*. Shawbury, Shrewsbury, Shropshire, UK: iSmithers Rapra Publishing; 2007

[54] Yao Y, Zhu D, Zhang H, Li G, Mobasher B. Tensile behaviors of basalt, carbon, glass, and aramid fabrics under various strain rates. *Journal of Materials in Civil Engineering*. 2016;**28**:04016081

[55] Ogbonna VE, Popoola API, Popoola OM, Adeosun SO. A review on

corrosion, mechanical, and electrical properties of glass fiber-reinforced epoxy composites for high-voltage insulator core rod applications: Challenges and recommendations. *Polymer Bulletin*. 2021;1-28. DOI: 10.1007/s00289-021-03846-z

[56] Wang L, Gardner DJ, Wang J, Yang Y, Tekinalp HL, Tajvidi M, et al. Towards industrial-scale production of cellulose nanocomposites using melt processing: A critical review on structure-processing-property relationships. *Composites Part B: Engineering*. 2020;**201**:108297

[57] Bhagia S, Bornani K, Agrawal R, Satlewal A, Đurković J, Lagaña R, et al. Critical review of FDM 3D printing of PLA biocomposites filled with biomass resources, characterization, biodegradability, upcycling and opportunities for biorefineries. *Applied Materials Today*. 2021;**24**:101078

[58] Zhao X, Copenhaver K, Wang L, Korey M, Gardner DJ, Li K, et al. Recycling of natural fiber composites: Challenges and opportunities. *Resources, Conservation and Recycling*. 2022;**177**:105962

[59] Zhao X, Li K, Wang Y, Tekinalp H, Richard A, Webb E, et al. Bio-treatment of poplar via amino acid for interface control in biocomposites. *Composites Part B: Engineering*. 2020;**199**:108276

[60] Meng X, Scheidemantle B, Li M, Wang YY, Zhao X, Toro-Gonzalez M, et al. Synthesis, characterization, and utilization of a lignin-based adsorbent for effective removal of azo dye from aqueous solution. *ACS Omega*. 2020;**5**:2865-2877

[61] Zhao X, Tekinalp H, Meng X, Ker D, Benson B, Pu Y, et al. Poplar as biofiber reinforcement in composites for large-scale 3D printing. *ACS Applied Bio Materials*. 2019;**2**:4557-4570

- [62] Mohammed L, Ansari MNM, Pua G, Jawaaid M, Islam MS. A review on natural Fiber reinforced polymer composite and its applications. *International Journal of Polymer Science*. 2015;**2015**:243947
- [63] Jeyapragash R, Srinivasan V, Sathiyamurthy S. Mechanical properties of natural fiber/particulate reinforced epoxy composites – A review of the literature. *Materials Today: Proceedings*. 2020;**22**:1223-1227
- [64] Wang L, Li K, Copenhaver K, Mackay S, Lamm ME, Zhao X, et al. Review on nonconventional fibrillation methods of producing cellulose Nanofibrils and their applications. *Biomacromolecules*. 2021;**22**:4037-4059
- [65] Mouritz AP, Gibson AG. *Fire Properties of Polymer Composite Materials*. Dordrecht, The Netherlands: Springer Science and Business Media; 2007
- [66] Copenhaver K, Li K, Lamm ME, Walker C, Johnson D, Han Y, et al. Recycled cardboard containers as a low energy source for cellulose Nanofibrils and their use in poly(l-lactide) nanocomposites. *ACS Sustainable Chemistry & Engineering*. 2021;**9**:13460-13470
- [67] Carolan D, Ivankovic A, Kinloch A, Sprenger S, Taylor A. Toughening of epoxy-based hybrid nanocomposites. *Polymer*. 2016;**97**:179-190
- [68] Wang Y, Li K, Zhao X, Tekinalp H, Li T, Ozcan S. Toughening by nanodroplets: Polymer–droplet biocomposite with anomalous toughness. *Macromolecules*. 2020;**53**:4568-4576
- [69] Ratna D, Banthia AK. Rubber toughened epoxy. *Macromolecular Research*. 2004;**12**:11-21
- [70] Cho J, Hwang J, Cho K, An J, Park C. Effects of morphology on toughening of tetrafunctional epoxy resins with poly (ether imide). *Polymer*. 1993;**34**:4832-4836
- [71] Ma H, Aravand MA, Falzon BG. Phase morphology and mechanical properties of polyetherimide modified epoxy resins: A comparative study. *Polymer*. 2019;**179**:121640
- [72] Klingler A, Bajpai A, Wetzel B. The effect of block copolymer and core-shell rubber hybrid toughening on morphology and fracture of epoxy-based fibre reinforced composites. *Engineering Fracture Mechanics*. 2018;**203**:81-101
- [73] Zhang J, Kong Q, Wang D-Y. Simultaneously improving the fire safety and mechanical properties of epoxy resin with Fe-CNTs via large-scale preparation. *Journal of Materials Chemistry A*. 2018;**6**:6376-6386
- [74] Wang J, Xue Z, Li Y, Li G, Wang Y, Zhong W-H, et al. Synergistically effects of copolymer and core-shell particles for toughening epoxy. *Polymer*. 2018;**140**:39-46
- [75] Li K, Wang Y, Rowe M, Zhao X, Li T, Tekinalp H, et al. Poly(lactic acid) toughening through chain end engineering. *ACS Applied Polymer Materials*. 2020;**2**:411-417
- [76] Li W, Jana PK, Behbahani AF, Kritikos G, Schneider L, Polińska P, et al. Dynamics of long entangled Polyisoprene melts via multiscale modeling. *Macromolecules*. 2021;**54**:8693-8713
- [77] Wu X, Aramoon A, El-Awady JA. Hierarchical multiscale approach for modeling the deformation and failure of epoxy-based polymer matrix composites. *The Journal of Physical Chemistry B*. 2020;**124**:11928-11938