1

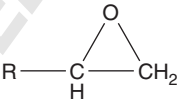
Background and Basic Knowledge of Hyperbranched Epoxy Resins

Junheng Zhang and Daohong Zhang

South-Central Minzu University, Hubei R&D Center of Hyperbranched Polymers Synthesis and Applications, School of Chemistry and Materials Science, No.182, Minzu Ave. Hongshan District, Wuhan Hubei Province, 430074, P.R.China

1.1 Chemistry, Synthesis, Manufacture, and Characterization of Epoxy Resins

1.1.1 Introduction

The term "epoxy resin" (EP) refers to both prepolymers and cured resins. Prepolymers contain reactive epoxy groups,  which give them their name. In cured resins, however, there may be no remaining reactive sites [1, 2]. Despite this, even when no more epoxy groups are present, these materials are still classified as epoxy resins. The market size of epoxy resins indicates their importance as industrial polymers. Due to their higher cost compared to other resins, they are typically used only when specific technological advantages are required. Many of these products offer significant added value [3, 4].

Although materials now known as epoxy resins have been synthesized since 1891, the first commercially available epoxy resin was not introduced until the 1940s and 1950s through the independent work of Swiss chemist Pierre Castan and American chemist Sylvan Greenlee, despite some patents dating back to the 1930s. The earliest commercially available epoxies were created by reacting bisphenol A (BPA) with epichlorohydrin, and this method remains the most common way of producing the majority of epoxies today, though other types of resins are also used [5–7].

Curing of an epoxy resin occurs when it reacts with a hardener, resulting in a rigid three-dimensional (3D) network. Hardeners used for curing typically have more than two reactive functional groups (i.e., $f > 2f > 2f > 2$). For common hardeners used with BPA-based resins, $f = 4f = 4f = 4$ (functionality), though the effective functionality is often $f = 2f = 2f = 2$. This effective functionality can be increased if the curing temperature is high enough to allow secondary hydroxy groups to participate in the curing process [8, 9].

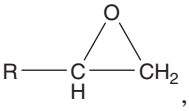
Initially, when the epoxy resin mixes with the hardener, it forms slightly larger molecules [10, 11]. As curing progresses, these molecules grow longer. However, it's important to note that when half of the reactive sites have reacted, the resulting average molecular size is still relatively small. As the molecules continue to grow, highly branched structures begin to form, eventually leading to an extensively branched network. The key event in this process is when branching starts to occur, which marks the gelation point.

Before reaching the gel point, the sample can still dissolve in at least some solvents. Once the gel point is reached, however, the network becomes insoluble and begins to swell as it absorbs the solvent. At the gel point, both small branched molecules and solvable components are still present, meaning the curing sample has both sol and gel phases. The first gel formed is relatively soft and can be easily broken up. To create a stable structural material, curing must continue until most of the sample has transitioned into a stable 3D network.

During the curing process, the glass transition temperature (T_g) of the resin increases [12, 13]. When the cure temperature is well above T_g, the reaction between the epoxy and the hardener is chemically controlled, meaning the rate of the reaction determines its progress. In cases where complete reaction of every epoxy group is desired, the resin can be reheated or "post-cured" at a higher temperature to ensure full curing.

There are several methods for forming epoxy rings. These methods are among the most important processes leading to the development of epoxy compounds. The processes mainly involve the reaction of a halohydrin with a hydroxyl compound and the formation of epoxy products from unsaturated compounds using organic peracids. In industrial applications, epoxy resins require the formation of a 3D network through a reaction with a polyfunctional hardener [14–16].

Curing reactions are heavily influenced by the more reactive nature of the epoxy ring compared to "normal" noncyclic ethers (R–O–R′). Unlike typical ethers, which do not react with bases, ammonia, or amines, epoxy resins can react with some aliphatic amines at room temperature. This increased reactivity is attributed to the strain in the epoxy ring. The reactions most crucial for the formation and curing of epoxy resins involve either electrophilic attack on oxygen or nucleophilic attack on one of the ring carbons. In the case of unsymmetrically substituted epoxies, which



are common in most epoxy resins , the ring opening is influenced by several factors: (i) the nature of the reagent or catalyst, which can be either electrophilic or nucleophilic; (ii) the nature of the substituent and the steric hindrance at the two carbon atoms; and (iii) the specific reagent used, which can lead to two possible outcomes in terms of which carbon undergoes ring opening.

1.1.2 The Synthesis of Epoxy Resins

Ethylene oxide can be manufactured by the direct oxidation of ethylene. However, these methods are less effective for higher olefins. The two primary methods for

producing epoxy resins are (i) dehydrohalogenation of halohydrins and (ii) epoxidation of alkenes using peracids or their esters [17]. The formation of an epoxy group begins with the synthesis of a chlorohydrin. In the production of epichlorohydrin, propylene is first chlorinated. Next, allyl chloride undergoes reaction with hypochlorous acid to form dichlorohydrin. The dichlorohydrin is then dehydrochlorinated with a stoichiometric quantity of NaOH to produce epichlorohydrin.

Industrially, epichlorohydrin is typically reacted with sodium hydroxide to produce glycerol or is stripped with steam and purified via distillation. Another method involves the oxidation of propane to produce acrolein. Acrolein is then chlorinated to form 2,3-dichloropropionaldehyde, which is subsequently reduced to yield glycerol β,γ-dichlorohydrin.

Epichlorohydrin can also be synthesized from allyl chloride via epoxidation using a peracid. Epichlorohydrin is used to produce a wide range of epoxy resins, as the epoxy group readily reacts with hydroxyl-containing substances in the presence of an alkali catalyst, MOH. This reaction leads to the formation of a new epoxy ring through dehydrochlorination.

1.1.3 Properties of Epoxy Resins

For uncured resins, infrared (IR) spectroscopy is a simple and effective identification method. While there are compilations of spectra available, it is still useful to have a set of reference spectra recorded under consistent conditions. Spot tests are quick and convenient but should be verified for accuracy. For resin–hardener mixtures and compounded resins, a combination of IR and nuclear magnetic resonance (NMR) spectroscopy, along with chromatography, may be required for more comprehensive analysis [18, 19].

1.1.3.1 Epoxy Content

This is the analysis which is most commonly applied to uncured epoxy resins. This method, which was previously noted, is fairly intuitive for counting epoxy groups per unit mass. Published methods primarily focus on the completeness and quantitativeness of the reaction, but obtaining exact numbers can be challenging. Precision is crucial, and a keen attention to the required procedures and conditions is necessary for accurate results.

1.1.3.2 Determination of Hydroxyl Groups

When using an epoxy resin for which n is greater than or equal to 1, a secondary alcohol group will typically be present, unless the resin has reacted with something like BPA, which would lead to the formation of a branched molecule. Therefore, the resin must contain a secondary hydroxyl group, which needs to be accurately determined. Hydroxyl groups are also reactive toward curing agents, and knowing their quantity is essential for calculating the resin–hardener stoichiometry. These hydroxyl groups also participate in the reaction with the epoxy groups during curing, especially in reactions with amine hardeners.

Other types of hydroxyl groups may also be present, such as α-glycols formed when epoxy groups undergo hydrolysis, or phenolic hydroxyl groups resulting from unreacted phenol used in resin synthesis – particularly when large amounts of BPA are involved. One method to quantify hydroxyl groups is the use of lithium aluminum hydride, which selectively reacts with active hydrogen. This can be measured volumetrically or via gas–liquid chromatography. However, this method is difficult to use quantitatively and requires correction for the presence of water or other hydrogen-containing compounds. A more practical method is acetylation, where both hydroxy and epoxy groups react with acetic anhydride.

1.1.3.3 Chlorine Content

Pure DGEBA (diglycidyl ether of bisphenol A) does not contain chlorine, but commercial resins can have up to about 1% chlorine. Self-extinguishing resins can contain as much as 30% chlorine, serving as organic binders in specific applications. Additionally, bromated and fluorinated resins are also available. However, resins with high chloride content can have reduced stability, particularly when cured with amine hardeners. Flame retardancy is often a specialized feature, but resin manufacturers can develop formulations that meet the specific requirements of various applications.

For BPA-based epoxy resins, the presence of chlorine-like other polar impurities negatively affects their electrical properties, as well as their color and reactivity. Active chlorine can interfere with weaker base catalysts, such as tert-amine, by blocking the reaction sites. Therefore, the amount of active chlorine is critical. Furthermore, since the chlorine is organically bound, the resin may exhibit lower functionality, resulting in a less cross-linked network. The total chlorine content can be measured using the classical Parr bomb method. Organic chloride in resins exists in two forms: (i) hydrolyzable chlorine and (ii) inactive hydrolyzable chlorine (also known as saponifiable chlorine). The term "inactive hydrolyzable chlorine" refers to chlorine that is partially dehydrochlorinated. In contrast, inactive chloride is formed as a result of reactions between epichlorohydrin and secondary alcohol groups, or it may arise as an unintended side product during the addition of phenolic hydroxyl groups.

1.1.3.4 Molecular Structure

Both IR and NMR spectroscopy can be utilized to identify the type of epoxy resin and determine the structure of its repeat unit. These techniques are also useful for detecting hardeners and other additives in mixed epoxy resin–hardeners. The theory and practical applications of IR and NMR spectroscopy are well-documented in many texts, with Rabek offering a thorough discussion of their use in polymer chemistry.

1.1.3.5 Physical Properties

DGEBA, in its pure form, tends to crystallize; however, when mixed with higher molecular weight compounds, it loses its tendency to crystallize. In general, most epoxy resins are amorphous and do not crystallize. Upon cooling, they form a glassy, amorphous solid with a glass transition temperature (T_g), which has been measured

using broad-line NMR spectroscopy. The most common method for characterizing resin softening is by measuring its softening point. Since resins soften gradually with temperature and do not exhibit a sharp melting point, the softening temperature is not precisely defined and can vary depending on the testing method. Ball-and-ring method: In this method, a resin sample is placed in a ring with a steel ball positioned on top. The temperature is gradually increased, and the softening point is reached when the ball sinks 2.5 cm (1 in.) under its own weight due to gravity. Durran's Mercury method: A fixed mass of resin is heated in a standard test tube, then cooled and hardened. Clean mercury is poured on top, and the temperature is increased. The softening point is recorded when the first drop of mercury falls through the resin to the bottom of the tube.

Good control over epoxy resins is essential, which requires comprehensive knowledge of their properties. Schoff provides a detailed discussion of various rheological measures. High-viscosity liquid resins can be challenging to mix with hardeners, making it difficult to achieve uniform molecular blending. Some hardeners may begin reacting at room temperature, causing the resin to thicken prematurely before it is fully mixed. This can lead to micro-gelation, where parts of the epoxy–hardener mixture behave differently than intended.

Even though hardeners may require high temperatures, preheating the resin is often necessary to reduce its viscosity and facilitate proper molecular-level blending. Inadequate mixing between the hardener and the epoxy prepolymer can lead to morphological irregularities in the cured epoxy. This is particularly important for applications such as casting, nondiluted adhesives, and lamination resins, where maintaining a low viscosity is crucial during fabrication. If viscosity increases before all the entrapped air has escaped, large air bubbles can remain in the final product.

Epoxy resin viscosity is influenced by factors such as molecular weight, molecular weight distribution, molecular structure, and temperature. For "compounded" resins, which are liquid at room temperature, viscosities can be measured directly without difficulty. However, for solid resins, a 40 wt% solution in diethylene glycol monobutyl ether is typically prepared, and its viscosity is measured using various methods. The most common methods include a bubble viscometer, such as the Gardner–Holdt tube, a capillary, or an instrument with a spindle. When measuring viscosity, it is essential to control both the solution concentration and the temperature.

For liquid resins, the viscosity may also be measured using a Hoeppler viscometer. This technique records the descent time of a ball in a resin-filled tube set at a specific tilt. The ball size, tube diameter, and tilt angle must meet the standardized specifications. Even with these measures in place, the viscosity results obtained using the Hoeppler viscometer may differ by around 15% when compared to those obtained through other methods like capillary flow or rotational viscosity tests.

The molecular structure of epoxy resin significantly influences its viscosity. Aromatic bisphenol-based epoxy resins, for example, have higher viscosities than cyclic aliphatics, which, in turn, have higher viscosities than linear types, as mentioned earlier [20, 21]. Other properties that can be determined for uncured resins include density and refractive index, the latter being particularly important as it depends

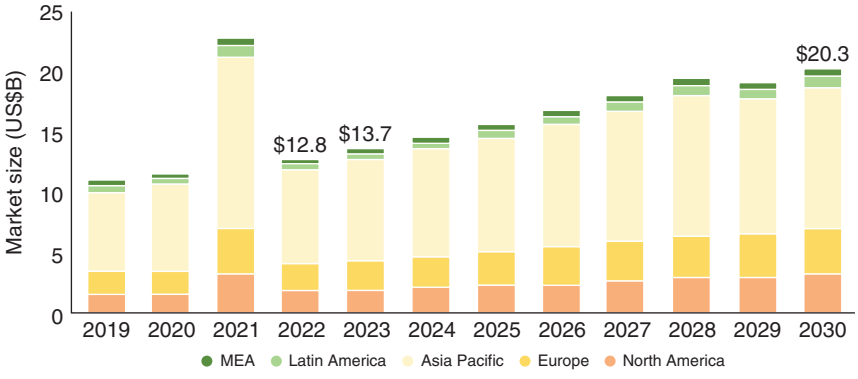


Figure 1.1 Epoxy resin market from 2019 to 2030.

critically on the resin's molecular structure and purity. Color is typically evaluated against established color standards. Additionally, the vapor pressure, especially for resins, is an important property, as is the flash point, which is crucial for safety considerations.

1.1.3.6 Epoxy Resin Market

The global epoxy resin market size was estimated at US$11.25 billion in 2023 and is anticipated to reach US$16.87 billion by 2030, growing at a compound annual growth rate (CAGR) of 6.3% from 2024 to 2030. The following are the leading companies in the epoxy resin market. These companies collectively hold the largest market share and dictate industry trends: 3M, Aditya Birla Management Corporation Pvt. Ltd., Atul Ltd., BASF SE, Solvay, Huntsman International LLC, KUKDO CHEMICAL CO., LTD., Olin Corporation, Sika AG, NAN YA PLASTICS CORPORATION, Jiangsu Sanmu Group Co., Ltd., Jubail Chemical Industries LLC, China Petrochemical & Chemical Corporation (SINOPEC), Hexion, Kolon Industries, Inc., Techstorm, and NAGASE & CO., LTD (Figure 1.1).

1.2 Chemistry, Synthesis, Manufacture, and Characterization of Hyperbranched Epoxy Resins

Hyperbranched polymers (HBPs) are the class of highly branched macromolecules. Compared with common linear polymers and other types of branched polymers, HBPs have the following advantages: nonentanglement or low entanglement, low viscosity, high solubility, compact molecular size, and the presence of numerous functional end groups [22–24]. In recent years, significant progress has been made in the synthesis and characterization of HBPs, leading to the development of many novel structures and functions. Owing to the convenience of nontoxic one-pot reaction and the potential of large-scale production, HBPs have already attracted much attention and have begun to be widely used in biomedical materials, analytical and

detection chemistry, polymer coatings and processing aids, optoelectronic materials and devices, and polymer-derived ceramics [25–27].

HBPs are considered promising candidates for future bioimaging probes because of their tree-like architectures and the ease of their synthesis. They can be covalently or noncovalently coupled with, or encapsulated by, predesigned targeting sequences on their outer surface. Unlike other HBPs being less, epoxy-functionalized hyperbranched polymers (EHPs) have been used more widely than other ones as they would provide both reinforcement and toughening to conventional EPs due to their thermosetting property [28–31]. Table 1.1 shows properties of some typical liquid epoxy resins. The viscosities of some commercially available liquid epoxies containing linear chains exceed 2000 mPa·s, such as diglycidyl ether of bisphenol-A (DGEBA), diglycidyl ether of bisphenol-F (DGEBF), and *N,N,N′,N′*-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM). In contrast, resins such as hyperbranched poly(trimellitic anhydride-diethylene glycol) ester epoxy resin (HTDE) with a polyester chain, hyperbranched poly (trimellitic anhydride ethylene glycol) epoxy (HTME) with a polyester chain, and hyperbranched epoxy resins with a silicone skeleton (HERSS) with a silicone skeleton chain—representing EHPs with relatively low epoxy equivalent weights—exhibit much lower viscosities than DGEBA or DGEBF. However, Boltorn E, 1, which is hyperbranched, has high viscosity. The main reason for the high viscosity of Boltorn

Table 1.1 The history of epoxy resin.

Years	Processes
1934	Schlack of I.G. Farbenindustrie AG in Germany filed a patent application for the preparation of reaction products of amines with epoxies, including one epoxy based on bisphenol A and epichlorohydrin.
1936	Pierre Castan of DeTrey Freres Co. produced a low-melting epoxy resin from bisphenol A and epichlorohydrin that gave a thermoset composition with phthalic anhydride.
1946	Ciba AG of Basel, Switzerland, first reported epoxy adhesive, and samples of casting resin were offered to the electrical industry.
1950s	The peracetic acid epoxidation of olefins was developed by Union Carbide in the United States and by Ciba AG in Europe for cycloaliphatic structures.
1960s	A number of multifunctional epoxy resins were developed for higher temperature applications. Ciba Products Co. manufactured and marketed o-cresol epoxy novolac resins, which had been developed by Koppers Co. Ciba Products marketed cycloaliphatic epoxy resins in 1963 and licensed several multifunctional resins from Union Carbide in 1965.
1970s	Epoxy resins became known for excellent chemical resistance properties, which led to the development and commercialization of epoxy vinyl ester resins.
1980s	Dow Chemical introduced a number of new, high-performance products such as hydrocarbon epoxy novolacs based on dicyclopentadiene.
1990s	Dow Chemical introduced a new epoxy-based thermoplastic resin, BLOX*, for gas barrier, adhesives, and coatings applications.

Table 1.2 Properties of liquid epoxy resins.

Type	Epoxy equivalent weight (g/eq)	Viscosity (25 °C, mPa·s)	Molecular weight
DGEBA (E44)	217–238	91,000	420–475
DGEBA (E54)	180–190	8000–11,000	360–380
DGEBA (E51)	184–194	12,000–15,000	370–390
DGEBF	160–180	2000–5000	330–360
TGDDM	110–120	3000–6000	440–480
EHPs (Boltorn E1)	875	Solid	10,500
EHPs (HTDE)	313–526	350–700	1700–3900
EHPs (HTME)	350–467	1000–1250	1300–2000
EHPs (HERSS)	417–588	104–697	1800–6600

E, 1 is its high epoxy equivalent weight of about 875 g/eq and the hydrogen bond interactions of a large number of hydroxyl groups [32–35] (Table 1.2).

Another major shortcoming of epoxy resins (EPs) is their low toughness and inherent brittleness, which limits their applications in low-shrinkage and high-toughness materials [36, 37]. Therefore, toughening modification of EPs is essential in practical applications. Compared with many other modifiers such as rubbers, epoxidized oleic esters, thermoplastic polyetherimide (PEI), core–shell particles, and graphene oxide, functional HBPs are considered the most effective additives for improving the performance of EPs [38–40]. Hydroxyl-functionalized HBPs (Boltorn H30, H50) and epoxide-functionalized HBPs (Boltorn E1, Boltorn E2), hydroxyl/epoxy-functionalized hyperbranched block copolycarbonate and polyethers with core/shell structure, and amine ended ones can increase the fracture toughness of DGEBA at least tens of times by only adding 5–20 wt% HBPs. However, their T_g and flexural strength and tensile strength are usually reduced to some degrees because of the low reactivity and low cross-linking density [41–43]. EHPs, carrying numerous reactive epoxy groups, can cross-link with hardeners and thus improve the tensile and flexural strength of DGEBA. For this reason, extensive research efforts have been devoted to synthesizing EHPs and modifying EPs.

There are then quite common types of strategy regarding the spacers used in the synthesis of EHPs, depending on the different mechanisms employed for the precursor or the epoxy monomer. One approach involves grafting epoxy groups onto precursors through etherification, esterification, hydrosilylation, or thiol-ene reactions (including Michael addition and coupling) [44, 45]. Another method is that the epoxy monomers are polymerized by proton/group transfer polymerization [46]. The third method involves the oxidation of double bonds of precursors.

This book wants to summarize the current situation concerning EHPs. This book will describe how EHPs were prepared, how EHPs are used, and what are the

advantages and disadvantages. Finally, it will provide perspectives on the use of EHPs for reinforcing and toughening epoxy resins.

Acknowledgments

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (U23A20691), Natural Science Foundation of Hubei Province (2024AFB800), and Innovation Group of National Ethnic Affairs Commission of China (MZR20006).

References

1 Jin, F.L., Li, X., and Park, S.J. (2015). Synthesis and application of epoxy resins: a review. *J. Ind. Eng. Chem.* 29: 1–11.
2 Rakotomalala, M., Wagner, S., and Döring, M. (2010). Recent developments in halogen free flame retardants for epoxy resins for electrical and electronic applications. *Materials* 3: 4300–4327.
3 Liu, S., Chevali, V.S., Xu, Z.G. et al. (2018). A review of extending performance of epoxy resins using carbon nanomaterials. *Compos. Part B Eng.* 136: 197–214.
4 Chruściel, J.J. and Leśniak, E. (2015). Modification of epoxy resins with functional silanes, polysiloxanes, silsesquioxanes, silica and silicates. *Prog. Polym. Sci.* 41: 67–121.
5 Mohan, P. (2013). A critical review: the modification, properties, and applications of epoxy resins. *Polym. Plast. Technol. Eng.* 52: 107–125.
6 Saba, N., Jawaid, M., Alothman, O.Y. et al. (2016). Recent advances in epoxy resin, natural fiber-reinforced epoxy composites and their applications. *J. Reinf. Plast. Compos.* 35: 447–470.
7 Baroncini, E.A., Kumar Yadav, S., Palmese, G.R., and Stanzione, J.F. III (2016). Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *J. Appl. Polym. Sci.* 133: 44103.
8 Paluvai, N.R., Mohanty, S., and Nayak, S.K. (2014). Synthesis and modifications of epoxy resins and their composites: a review. *Polym. Plast. Technol. Eng.* 53: 1723–1758.
9 Kumar, S., Krishnan, S., Samal, S.K. et al. (2018). Toughening of petroleum based (DGEBA) epoxy resins with various renewable resources based flexible chains for high performance applications: a review. *Ind. Eng. Chem. Res.* 57: 2711–2726.
10 Chen, J., Chu, N., Zhao, M. et al. (2020). Synthesis and application of thermal latent initiators of epoxy resins: a review. *J. Appl. Polym. Sci.* 137: 49592.
11 Peerzada, M., Abbasi, S., Lau, K.T., and Hameed, N. (2020). Additive manufacturing of epoxy resins: materials, methods, and latest trends. *Ind. Eng. Chem. Res.* 59: 6375–6390.

12 Müller-Pabel, M., Rodríguez Agudo, J.A., and Gude, M. (2022). Measuring and understanding cure-dependent viscoelastic properties of epoxy resin: a review. *Polym. Test.* 114: 107701.

13 Rafique, I., Kausar, A., Anwar, Z., and Muhammad, B. (2016). Exploration of epoxy resins, hardening systems, and epoxy/carbon nanotube composite designed for high performance materials: a review. *Polym. Plast. Technol. Eng.* 55: 312–333.

14 Mi, X.Q., Liang, N., Xu, H.F. et al. (2022). Toughness and its mechanisms in epoxy resins. *Prog. Mater. Sci.* 130: 100977.

15 Ou, B.L., Wang, Y.W., and Lu, Y. (2021). A review on fundamentals and strategy of epoxy-resin-based anticorrosive coating materials. *Polym. Plast. Technol. Mater.* 60: 601–625.

16 Gonçalves, F.A.M.M., Santos, M., Cernadas, T. et al. (2022). Advances in the development of biobased epoxy resins: insight into more sustainable materials and future applications. *Int. Mater. Rev.* 67: 119–149.

17 Jia, P.Y., Ma, Y.F., Kong, Q.Y. et al. (2020). Progress in development of epoxy resin systems based on biomass resources. *Green Mater.* 8: 6–23.

18 Capricho, J.C., Fox, B., and Hameed, N. (2020). Multifunctionality in epoxy resins. *Polym. Rev.* 60: 1–41.

19 Verma, C., Olasunkanmi, L.O., Akpan, E.D. et al. (2020). Epoxy resins as anticorrosive polymeric materials: a review. *React. Funct. Polym.* 156: 104741.

20 Kumar, S., Krishnan, S., Mohanty, S., and Nayak, S.K. (2018). Synthesis and characterization of petroleum and biobased epoxy resins: a review. *Polym. Int.* 67: 815–839.

21 Kumar, S., Samal, S.K., Mohanty, S., and Nayak, S.K. (2018). Recent development of biobased epoxy resins: a review. *Polym. Plast. Technol. Eng.* 57: 133–155.

22 Tang, Y., Zhang, X.Y., Liu, X.Y. et al. (2024). Facile synthesis of hyperbranched epoxy resin for combined flame retarding and toughening modification of epoxy thermosets. *Chem. Eng. J.* 482: 148992.

23 Zhang, J.H., Jiang, C., Deng, G.Y. et al. (2024). Closed-loop recycling of tough epoxy supramolecular thermosets constructed with hyperbranched topological structure. *Nat. Commun.* 15: 4869.

24 Fan, H.Y., Sun, T., Zhang, S.J., and Wu, Z.J. (2025). High strength and toughness epoxy nanocomposites reinforced with epoxy-terminated hyperbranched polymer. *J. Appl. Polym. Sci.* 142: e57071.

25 Liu, H.N., Wang, C.J., Liu, S.Y. et al. (2025). Enhancing interfacial properties of epoxy coatings via hyperbranched modification of SiC fillers: experimental and simulation insights. *Chem. Eng. J.* 511: 161841.

26 Zhang, Y.B., Yan, H.X., Yu, R.Z. et al. (2024). Hyperbranched dynamic crosslinking networks enable degradable, reconfigurable, and multifunctional epoxy vitrimer. *Adv. Sci.* 11: 2306350.

27 Qiao, H.W., Chen, M.F., Chen, B. et al. (2023). Understanding the curing kinetics of boron-based hyperbranched polysiloxane reinforced and toughened epoxy resin by rheology. *Chem. Eng. J.* 467: 143542.

28 Zhang, Y.B., Yuan, J.S., Hu, J.Z. et al. (2024). Toward understanding the cross-linking from molecular chains to aggregates by engineering terminals of supramolecular hyperbranched polysiloxane. *Aggregate* 5: e404.

29 Miao, C.F., Zhou, X., Huang, X.Y. et al. (2023). Effectively synthesized functional Si-doped carbon dots with the applications in tyrosinase detection and lysosomal imaging. *Anal. Chim. Acta* 1279: 341789.

30 Wang, R.Z., Cao, L., Wang, W. et al. (2024). Construction of smart coatings containing core-shell nanofibers with self-healing and active corrosion protection. *ACS Appl. Mater. Interfaces* 16: 42748–42761.

31 Jiang, Y.Q., Yuan, X.Y., Wang, P.R. et al. (2025). Dihydroxy functionalized binuclear carbonate based poly(ionic liquid)s for highly efficient conversion of low-concentration CO_2 into cyclic carbonate. *J. Environ. Chem. Eng.* 13: 116247.

32 Xu, W.M., Zhou, X.Z., Fang, Y.L. et al. (2024). Water-assisted reprocessing and shape programming of epoxy vitrimer. *Adv. Funct. Mater.* 34: 2403681.

33 Wang, C., Huo, S.Q., Ye, G.F. et al. (2024). Strong self-healing close-loop recyclable vitrimers via complementary dynamic covalent/non-covalent bonding. *Chem. Eng. J.* 500: 157418.

34 Zeng, X.Q., Wang, L.G., Cao, Y. et al. (2024). Solvent-free and recyclable polyether/polyphenol supramolecular adhesives with robust, water- and low-temperature-resistant properties. *ACS Appl. Polym. Mater.* 6: 1336–1347.

35 Cai, L., Li, Y., Zhang, X. et al. (2025). A mussel protein-inspired biomimetic soy protein adhesive with strong moisturizing properties. *Chem. Eng. J.* 515: 163875.

36 Wang, M.L., Liu, Z.Y., Wang, T.C. et al. (2025). The UV aging resistance of strong and ductile epoxy resin achieved by UV-induced self-compensated crosslinking points. *Chem. Eng. J.* 510: 161661.

37 Shen, Q.B., Yu, B.B., Chen, D. et al. (2025). Novel furfuryl-based phosphaphenanthrene containing N/P flame retardant: towards epoxy resin with excellent flame retardancy, enhanced toughness and low dielectric constant. *Chem. Eng. J.* 519: 165034.

38 Wang, C.J., Xin, M.H., Gao, M. et al. (2025). A rigid and flexible combination 3D network with hyperbranched materials as bridge and the enhancement of mass transfer resistance in coatings. *Compos. Part B Eng.* 304: 112688.

39 Zhou, Y.X., Huang, Q.B., Wang, L., and Wang, X.H. (2024). Enhancing cross-linking network for superior wet strength of paper by sustainable hyperbranched polyimines. *ACS Appl. Mater. Interfaces* 16: 15383–15393.

40 Son, W., Saha, S., Tran, D.T. et al. (2024). Rational design of semi-interpenetrating network based on hyperbranched polyglycerol grafted MXene/polyurethane-epoxy for compressed hydrogen storage. *Carbon* 228: 119427.

41 Shao, J.W., Li, X.Y., Liu, T. et al. (2024). Multiple function hyperbranched polysiloxane nanoclusters for controlling a cross-linking structure to convert soy meal into a strong, tough, and multifunctional adhesive. *ACS Sustain. Chem. Eng.* 12: 3966–3976.

42 You, T.L., Guo, G.X., and Li, W.B. (2024). Waterborne liquid-like coatings with high transparency, superior scratch resistance, and antismudge properties. *ACS Appl. Mater. Interfaces* 16: 43907–43917.

43 Tang, Y., Zhang, X.Y., Ge, A.X. et al. (2024). Novel hyperbranched phosphaphenanthrene-terminaled silicon-nitrogen cocuring agent towards high-performance epoxy thermosets. *Prog. Org. Coat.* 197: 108828.

44 Cai, J.J., Zhang, X.R., Wang, Z.M. et al. (2024). A bio-based antibacterial epoxy resin coating with outstanding flame retardant and mechanical properties. *Prog. Org. Coat.* 190: 108369.

45 Khan, A. (2025). Thiol-epoxy 'click' reaction in polymer synthesis. *Prog. Polym. Sci.* 169: 102022.

46 Lv, X., Zhang, H.P., Zhang, H. et al. (2025). Exploring the properties and performance of Lewis base organocatalysts in epoxy/polyester hybrid low-cure powder coatings. *Prog. Org. Coat.* 200: 109053.