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Recent Advances in Epoxy Resin Applications

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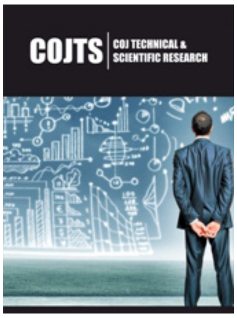

Jong-Hyun Joo[1], Ju-Ra Jeong[1], Yoon-Ji Yim[3], Seong-Hwang Kim[1]* and Jin-Seok Bae[2]*

[1]Korea Institute of Convergence Textile, Republic of Korea

[2]Department of Textile System Engineering, Kyungpook National University, Korea

[3]Busan Textile Materials Research Center, Korea Dyeing and Finishing Technology Institute, Republic of Korea

***Corresponding authors:** Jin-Seok Bae and Seong-Hwang Kim, Department of Textile System Engineering, Kyungpook National University, Daegu 41566, Korea and Korea Institute of Convergence Textile, Iksan 54588, Republic of Korea

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Abstract

Epoxy resins (EPs) have attracted significant attention across industries owing to their exceptional mechanical properties, high strength-to-weight ratios, and resistance to corrosion and chemicals. Due to their unique chemical structure, EPs play a pivotal role in transportation, construction, electronics, insulation, aerospace, and other industries. As materials science and technology continue to advance, novel epoxy composites are emerging, pushing the boundaries of high-performance materials. However, it remains challenging to strike a balance among strength, toughness, and flexibility, which is crucial for achieving optimal performance across diverse applications. Additionally, growing environmental concerns and emphasis on sustainability have made it imperative to explore bio-based and degradable epoxy composites for addressing these issues effectively. This review comprehensively examines diverse epoxy resin systems, encompassing mono-functional, di-functional, cycloaliphatic, and multifunctional epoxy resins. Emphasis is placed on recent advancements in epoxy resin synthesis, including the development of biodegradable variants and flame-retardant formulations.

Keywords: Epoxy resin; Biodegradable epoxy resin; Chemically degradable epoxy resin; Flame retardant

Abbreviations: EPs: Epoxy Resins; DGEBA: Diglycidylether of Bisphenol A; BPA: Bisphenol-A; DGEBF: Diglycidylether of Bisphenol F; CAE: 3,4-Epoxycyclohexylmethyl-3',4'-Epoxycyclohexane Carboxylate; TGDDM: N,N,N',N'-Tetraglycidyl-4,4′-Diaminodipehnylmethane; LEPs: Lignin-Based Epoxy Resins; ECGE: Epoxidized Cardanol Glycidyl Ether

Introduction

Epoxy resins, which are reactive pre-polymers characterized by the presence of epoxy groups cyclic structures composed of two carbon atoms and one oxygen atom undergo cross-linking reactions to form macromolecular networks via self-homo-polymerization or curing reactions with co-reactants such as amines, anhydrides, acids, alcohols, or esters [1-3]. Epoxy resins have been recognized as the most widely used thermosetting materials with strategic significance, which are generally applied in anti-corrosive coatings, adhesives, semiconductor packaging materials, electrical insulation substances, and high-performance composites because of their intrinsic mechanical and chemical stability, heat and corrosion resistance, electrical insulation, and strong bonding properties [4,5]. The epoxy resin market is led by countries in the Asian region, including India, Korea, China, and Japan, and their share reaches a whopping 41.8%. This has the influence of relatively low environmental regulations and national policies encouraging manufacturing compared to North America and Europe, and is widely used in developing and emerging countries on the Asian continent due to the nature of the product, which is largely required in the construction sector such as roads and buildings. The average annual growth rate between 2019 and 2024 was also the highest in Asia at 6.9%, followed by the Middle East and Africa, South America, North America, and Europe. In 2022, the global capacity of EPs reached 4.69 million tons. Global demand for EPs is expected to continually increase with the growth of end-use industries, such as transportation, aerospace, marine coatings, composite materials, etc. Undoubtedly, epoxy matrix has become indispensable basic materials in various industrial fields. In this paper, the existing epoxy resin systems are reviewed in detail. In addition, the latest technologies of epoxy resin are discussed, including ways to improve existing epoxy resin systems. Finally, the main application of epoxy resins is briefly described.

Mono-functional epoxy resin

Mono-functional epoxy resins contain only one epoxy group, and they are primarily used as reactive diluents. They improve processability and workability by reducing the cross-linking density of epoxy resins, and for this reason, they are mainly used as textile sizing agents and epoxy resin softeners [6].

Di-functional epoxy resin

Di-functional epoxy resins contain two epoxy groups in their molecular structures, and commercially, they are among the most widely available epoxy resins. Among them, bisphenol-A epoxy resin, a Diglycidylether of Bisphenol-A (DGEBA), is produced by reacting epichlorohydrine with Bisphenol-A (BPA). DGEBA exhibits low curing shrinkage compared to those of other epoxy resins. Various bonds exist in the DGEBA structure, among which the benzene ring imparts heat resistance and rigidity, ether bond imparts chemical resistance, hydroxyl group imparts adhesion and reactivity, and epoxy group imparts reactivity [7]. Compared to DGEBA, Diglycidylether of Bisphenol F (DGEBF) offers the advantages of low viscosity and strong mechanical properties, and it is widely used in various engineering fields, for example, to produce matrixes for composite materials.

Cycloaliphatic epoxy resin

Cycloaliphatic-type epoxy resin is synthesized through the polymerization of diene compounds, and it possesses excellent chemical resistance, thermal stability, and electrical properties. The cured epoxy resin exhibits high hardness and high brittleness. It appears more yellow than other resins, and it is used in applications that require weathering resistance [8]. Representative cycloaliphatic epoxy resins are 3,4-epoxycyclohexylmethyl-3',4'-Epoxycyclohexane Carboxylate (CAE) and diglycidyl 1,2-cyclohexanedicarboxylate.

Multifunctional epoxy resin

Multifunctional epoxy resins contain three or more epoxy groups, and they are used as high-functional materials. The thermal and mechanical properties of multifunctional epoxy resins are superior to those of other epoxy resins because of their high cross-linking density. These resins are used as matrixes in the preparation of advanced materials (such as aircraft, missiles) that require high performance and flame retardancy. Representative multifunctional epoxy resins are trimethylol propan-N-triglycidyl ether and N,N,N',N'-Tetraglycidyl-4,4′-Diaminodipehnylmethane (TGDDM) [9].

Biodegradable epoxy resins

At present, approximately 90% of commercially available epoxy resins are produced from petroleum-based BPA and epichlorohydrin. The use of BPA in food packaging, baby bottles, and other industries is prohibited in the European Union and the United States. In addition, over-exploitation of non-renewable fossil resources has led to energy shortages, and non-degradable waste plastics have caused environmental pollution. Considering the increasing severity of environmental problems, global warming, and the depletion of petroleum resources, the development of new bio-based epoxy resins has emerged as a research hotspot. For example, Liu [10] synthesized a series of Lignin-based Epoxy Resins (LEPs) by reacting epichlorohydrin with lignin oligomers and blending the reaction products with renewable Epoxidized Cardanol Glycidyl Ether (ECGE). As a result, the MTHPA-cured LEP system exhibits good thermal and mechanical properties. In addition, the tensile, flexural, and impact strengths of a system containing 20wt.% ECGE are 77MPa, 115MPa, and 14Kj/m2, respectively, which are comparable to those of commercial DGEBA epoxy resin.

Flame-retardant epoxy resins

Similar to most polymer materials, epoxy resins have high flammability, which severely limits their application in fields requiring high levels of fire resistance. To solve this problem, flame retardants containing phosphorus, nitrogen, or silicon have been developed and blended with epoxy resins to improve their flame retardancy. In terms of the mechanisms of flame retardants, the flame retardant containing phosphorus can capture free radicals or facilitate catalytic carbonization, that containing silicon can form a high-temperature-resistant char residue layer, and that containing nitrogen can produce an inflammable gas to inhibit polymer decomposition. For example, Zhou [11] synthesized a eugenol-based intrinsically flame-retardant epoxy monomer bis (2-methoxy-4- (oxirane-2-ylmethyl) phenyl) phenyl phosphonate (BEEP). Their results indicated that the flexural strength and flexural modulus of the DGEBA/BEEP/DDM system containing 20wt.% BEEP increased from 69.4MPa and 1.57GPa to 74.5MPa and 3.60GPa, respectively, compared to those of the DGEBA/DDM system. Moreover, the DGEBA/BEEP/DDM system with 1.0% phosphorus achieved the V-0 rating in the UL-94 test with an LOI of 27.5%.

Conclusion

In this paper, the existing epoxy resin systems were reviewed in detail. To overcome the shortcomings of the existing epoxy resin systems, the latest epoxy resin technologies, such as bio-based epoxy resins and flame-retardant epoxy resins, were described. Currently, the primary raw materials for epoxy resins, such as BPA, are predominantly sourced from nonrenewable fossil-based resources, with over 90% of epoxy polymers, including DGEBA resins, being derived from BPA. It is necessary to develop fully bio or flame-retardant epoxy resins with facile fabrication and excellent physicochemical properties. Future studies should focus on the following aspects

a) Development of a new type of bio-based epoxy resin that can be cured rapidly at low temperatures to reduce the curing temperature and curing time.

b) Sustained development of epoxy resins and curing agents with high flame retardancy and strong mechanical properties to reduce the flammability of epoxy-based materials.

c) Development of appropriate surface-treatment technologies to improve adhesion between epoxy resins and crystalline polymers or nonpolar polymers.

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