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Epoxy Resin Adhesives: Modification and Applications

Jun Zhang, Hai Luo, Xiaojian Zhou and Bowen Liu

Abstract

Epoxy resin adhesives (ERAs) as easily prepared thermosetting adhesives have been extensively employed in building construction, electrical appliance manufacturing, automobile manufacturing and wood industry because of their excellent mechanical properties, water resistance, low cost, long service life and strong bonding properties. This chapter aims to introduce the synthesis, properties and development of ERAs and to illustrate how defects in their curing properties, thermal properties, brittleness and flammability affect their global development. Furthermore, this study introduces the modification of ERAs according to these defects and their development in main application fields. Lastly, the limitations and prospects of ERAs in future applications are also discussed.

Keywords: epoxy resin, adhesives, mechanical properties, curing properties, modification

1. Introduction

Epoxy resin adhesive (ERA) is the general term for polymers with two or more epoxy groups in the molecule. It is widely used in industries and is an important thermosetting resin adhesive [1, 2]. ERA is a thermosetting adhesive with strong adhesion, high cohesion, low shrinkage, low cost and low creep rate. It can be used for several materials, such as metal, cement and wood; thus, it is referred to as a 'universal and strong' glue [3]. It has a history of more than 70 years. The molecular end of epoxy resin is connected with epoxy groups. During curing, hydroxyl and ether bonds are formed, and the structure contains benzene or heterocyclic rings. Due to the presence of epoxy groups, hydroxyl groups, ether bonds, ester groups and other polar groups, it has a strong bonding effect on many substances other than non-polar polymers [4]. After the epoxy-based adhesive is cured, it forms a complex three-dimensional (3D) network structure with strong cohesion. The epoxy-based adhesive hardly generates low-molecular products during curing, has a small linear expansion coefficient, stable dimensions, small internal stress and better bonding strength. Epoxy-based adhesives meet the requirements of structural adhesives, but they also have some shortcomings. Because the curing process of epoxy-based adhesives needs a higher temperature, and it contains many rigid groups, such as a benzene or heterocyclic ring, the flexibility of the molecular chain is minimal [5].

Besides, after cross-linking to form a network structure, the deformability is further weakened, showing strong brittleness, which results in low bonding strength, poor impact strength, delamination and easy cracking resulting of epoxy-based adhesives [3]. Meanwhile, its flame retardancy is poor. As a structural adhesive, it is expected to cure quickly, have higher heat resistance and flame retardancy. Therefore, epoxy-based adhesives must be modified to expand its scope of application. This study mainly introduces the curing, heat resistance, toughening and flame-retardant modification of epoxy-based adhesives and their application in different fields.

2. Modification of ERAs

2.1 Curing modification of epoxy adhesives by curing agent

As a thermosetting adhesive, ERA must be cured at high temperatures. However, for industrial applications, it must be cured at room temperature [6, 7], so the importance of developing curing agents for epoxy-based adhesive cured at room temperature is self-evident. Especially, room-temperature fast-curing epoxy adhesives can be used in aerospace and marine engineering applications, as well as in traditional manufacturing and daily life [8, 9], because of their fast-curing speed, high strength and strong durability [10]. With the continuous development of curing agents, room-temperature fast-curing ERAs as chemical products have become indispensable in the manufacturing industry [11]. The room-temperature curing of ERAs is an energy-saving curing method. The curing process is simple, and it is suitable for various curing situations that do not require heating.

2.1.1 Classification of curing agent for ERAs

According to the curing temperature, epoxy-based adhesive curing agents can be divided into amines, acid anhydrides, synthetic resins and latent curing agents by different chemical components. Among them, amine-curing agents are often used in ambient curing at room temperature [12]. Amine-curing agents are the earliest room-temperature curing agent used. It adheres excellently to most adherents. However, amine-curing agents have high volatility and toxicity and have strong water and carbon dioxide absorption abilities. The cured surface is prone to whitening and blistering [13]. Among the amine-curing agents, there are mainly polyamides, aliphatic amines, alicyclic amines. In industrial applications, curing agents, such as aliphatic amines, polyamides and alicyclic amines, are often used [14].

2.1.1.1 Polyamide-curing agent

As one commonly used curing agent, polyamide accounts for more than 30% of the total epoxy resin-curing agents. It is mainly made of dimers or unsaturated fatty acids and polyamine as raw materials and forms amide bonds through dehydration condensation [15]. Among them, the dimerised fatty acid polyamide can overcome the shortcomings of epoxy-based adhesives' fragility and has low toxicity, good workability and high-paint film adhesion [16]. Modifying the polyamide-curing agent can effectively improve the properties of epoxy resins. For example, Bryan et al. [17] used polyamide and phthalic anhydride as the curing agent of epoxy resin to improve the

curing rate at room temperature. Gholipour et al. [18] improved the thermal properties of epoxy resins by preparing polyamidoamine (PAMAM) dendrimer-curing agents grafted with graphene oxide.

2.1.1.2 Aliphatic amine-curing agent

The amount of aliphatic amine-curing agents in various curing agents is second only to polyamide because most are liquid and have good miscibility with epoxy resin. Epoxy resin can be cured at room temperature. Modifying the aliphatic amine-curing agent can effectively improve the mechanical properties of epoxy resin. For example, Patel et al. [19] brominated unsaturated castor oil, which was the main raw material, and reacted the resulting material with excess aliphatic diamines, such as ethylenediamine, 1,3-propanediamine and 1,6-hexanediamine, to obtain an amino-functionalised castor-oil-curing agent to improve the mechanical strength of epoxy resins. Wan et al. [20] synthesised a novel low-volatility star aliphatic polyamine with extremely high-NH₂ functional groups as the curing agent of bisphenol A diglycidyl ether epoxy resin. The novel curing agent has a high reaction activity, and the reaction has autocatalytic properties. Additionally, compared with linear propylene diamine, it can significantly increase the crosslinking density and glass transition temperature (T_g) of the cured epoxy resin.

2.1.1.3 Alicyclic amine-curing agent

Alicyclic amines are amine compounds containing alicyclic rings. The alicyclic amine-curing agent has many spatial conformations and good flexibility. Most alicyclic amines are low-viscosity liquids with long pot life and excellent chroma and gloss. Alicyclic polyamine compounds are widely used as curing agents for epoxy-resin adhesives and other structure adhesives because the molecular structure contains alicyclic rings (five-membered or six-membered rings) with higher stiffness and better stability. Xu et al. [21] used alicyclic polyamines and acrylonitrile to synthesise the curing agent to improve the bonding strength of epoxy-resin-based adhesives.

2.2 Heat-resistant modification of ERAs

ERAs can withstand high temperatures up to 175°C and are compatible with all common reinforcement materials. A higher-temperature-resistant ERA can be essentially applied in many fields. In addition to having high-temperature-resistant properties, it can also show strong properties in many aspects, such as high-temperature-resistant epoxy. It has excellent mechanical properties, relatively outstanding strength and has good corrosion resistance and insulation properties [22, 23]. Therefore, research on high-temperature-resistant ERA is extremely necessary. There are two main measures in implementing the modification of high-temperature ERA. The first measure entails introducing new structures into the epoxy resin itself to improve its high-temperature properties. The second measure is blending or co-polymerisation to modify the high-temperature epoxy resin.

2.2.1 ERA itself introduces a new structure to improve its high-temperature resistance properties

The modification treatment of high-temperature-resistant ERA is mainly performed to promote the structure of ERA to be changed to a certain extent. It is more

common to improve the high-temperature resistance effect by introducing new structures. This method for introducing a new structure through the epoxy resin also involves many types of processing in actual implementation. For example, the effective use of multifunctional structures can promote the formation of ring structures [24]. The functionality of the epoxy-resin structure increases, which can promote the stability and cross-linking density of the corresponding structure and finally effectively enhance the high-temperature resistance of the epoxy resin. Furthermore, introducing rigid groups that have a good high-temperature resistance effect can promote the epoxy resin to show excellent performance, such as benzene ring, fused ring and biphenyl are some of the more commonly used rigid groups [25]. Moreover, Bismaleimide and epoxy resin may form an interpenetrating network or two-phase system during the polymerisation process, which improves the toughness and heat resistance of the epoxy resin [26].

Luo et al. [27] modified bisphenol A epoxy resin with bismaleimide and 4,4'-diaminodiphenylsulfone to produce a two-component high-strength bismaleimide modified epoxy-based adhesive with high cross-linking. The viscosity of the adhesive gradually decreases as temperature increases and can maintain good mechanical properties and storage stability. Cheng et al. [28] used 2,7-dihydroxynaphthalene and epi-chlorohydrin as raw materials to synthesise an epoxy-resin-based adhesive containing a naphthalene ring structure. Also, Yang et al. [29] used 1-naphthol and dicyclopentadiene as the main raw materials to synthesise an ERA containing naphthalene ring and dicyclopentadiene structure. The results show that the ERA has a higher heat resistance than the bisphenol A epoxy resin.

2.2.2 Modification of high-temperature-resistant ERA by blending or co-polymerisation

The blending and co-polymerisation methods can effectively and mainly help select an ideal material and ERA for effective combination to ensure greater high-temperature-resistant properties. Combined with the specific application and implementation of these methods, the requirements for specific blended or co-polymerised materials are relatively strict [6]. For example, the appropriate use of heat-resistant polymers, nano-materials and silicones can achieve ideal modifications. The treatment effect improves the heat resistance of the epoxy resin; besides, it can also guarantee its toughness or strength to be ideally optimised. Zhang et al. [30] modified ordinary bisphenol A epoxy resin with organic silicon active intermediates, added nitrile-40 and nano-TiO₂ active fillers to toughen and strengthen the resin. The results showed that the modified ERA that could be cured at room temperature, used for a long time at 250°C and can withstand 300°C for a short period has been developed. Hu et al. [31] used polymethyltriethoxysilane (PTS) to react with a synthetic phosphorus-containing silane coupling agent in a certain ratio to modify the bisphenol A epoxy resin. The modified ERA retained its tensile strength. However, the T_g, high-temperature thermal stability, impact strength and limiting oxygen index (LOI) were all improved. Ramirez et al. [32] combined epoxycyclohexyldimethylsilyl with the curing agent 4,4'-(1,3-phenylene diisopropylidene) diphenylamine after coordination. Due to the dispersion of the heat-resistant epoxycyclohexyldimethylsilyl in the ERA, the silicon oxide compound formed during the thermal decomposition process deposited on the surface of the unburned polymer, partially forming a protective layer, slowing down the heat transfer to a certain extent and inhibiting the flammability as the gas volatilises, thereby preventing the mixture of flammable gas and oxygen.

2.3 Toughening modification of ERAs

ERAs are cost-effective and have simple moulding and processing methods, low chemical shrinkage after curing, good chemical stability, excellent mechanical properties and good bonding properties [33]. However, due to several epoxy groups, the cured structure has a high chemical cross-link density, low-molecular chain flexibility and high internal stress, resulting in greater brittleness, poor impact resistance and fatigue resistance of the ERA. It limits its application and development in some high-tech fields that require high durability and reliability.

ERA has good compatibility with rubber and other elastomers. After the rubber is dissolved in the uncured epoxy-resin matrix, the ERA undergoes a curing reaction, separates from the rubber and is dispersed in the resin to form a 'sea island' structure, thereby improving the toughness of the epoxy resin [34]. The rubber molecules containing no reactive groups cannot react with epoxy resin and will precipitate out during curing, which has a toughening effect. However, if excessively added, it weakens the adhesion of the bonding interface. Therefore, rubber molecules with active groups are generally used to modify and toughen epoxy resins. Carboxyl-terminated liquid nitrile rubber (CTBN) and amino-terminated liquid nitrile rubber (ATBN) have been widely mixed with epoxy resins to improve their toughness. For example, Wang et al. [35] used CTBN and ERA to prepare a structural adhesive with high shear and excellent peel strength. Meanwhile, to adapt to the application in different fields and improve the toughness of the cured ERA, flexible segments are often introduced into the curing agent to control its physical and chemical properties. Lou et al. [36] used dendritic polyester polyol as the branching unit and toughening segment and imidazole-terminated diisocyanate as a functional group to synthesise a functional toughening-curing agent to improve the toughness of ERAs. In the initial curing stage, several secondary hydroxyl groups react with the isocyanate groups to form a dendritic epoxy structure, and the bisphenol A epoxy molecule acts as a long-chain polyol to react with the dendritic epoxy structure. Simultaneously, the epoxy group opens a ring to form a secondary hydroxyl group and continuously reacts with the isocyanate group in the cross-linking structure. Furthermore, NH- existing in the carbamate reacts with the epoxy group, thereby obtaining an epoxy resin-curing cross-linking system with a 3D dendritic cross-linking structure. Thus, the toughness of epoxy resin has been greatly improved. Meanwhile, Zheng et al. [37] studied the toughening effect of nano-SiO₂ on cycloaliphatic epoxy systems. They used nano-silica to improve the toughness of cycloaliphatic ERA. The coupling agent γ -glycid oxypropyltrimethoxysilane (KH-560) was used to modify the surface properties of SiO₂. The results show that adding nano-SiO₂ effectively improves the toughness and thermal stability of the cycloaliphatic ERA.

2.4 Flame-retardant modification of ERA

ERAs have been widely used due to their excellent properties [38]. However, the conventional ERA is formed from reacting bisphenol A and epi-chlorohydrin [39]. It is flammable when cured, which could cause a high fire risk when ERAs are used in certain applications, such as printed manufacture, furniture, aircraft and train interiors [40]. Serious consequences could occur due to the high release rate of heat and smoke accompanied by the combustion of epoxy resins. Therefore, it is very important to enhance the flame retardancy of ERA for expanding their application in this field. Many studies have reported improving the flame retardancy of epoxy resins

via structural modification or adding various flame retardants [41, 42]. Structural modification introduces the elements with flame-retardant functions into the molecular structure of ERAs. The representative of structural modification is brominated ERA, which is the reaction product of epi-chlorohydrin and brominated bisphenol A, such as tetrabromo diphenylolpropane. The brominated ERA has an outstanding flame ignition resistance, whereas the bromine content is ~18–20% in the finished adhesive. When the product is thermally decomposed at the temperature generated in the fire, it will release acid halide gas, which protects the product from fire. These halide gases act as extinguishers to significantly increase the ignition temperature of the cured ERA. The addition of flame retardants in ERA shows good properties, such as simple processing, low cost, wide source of raw materials and obvious flame-retardant effect. It is one of the most popular strategies for flame-retardant modification of ERA. Flame retardants could be an integral part of the ERA by reacting chemically with the polymers or simply mixed with the ERA without any reaction. All kinds of flame retardants work by acting chemically and/or physically either in the vapour phase and/or condensed phase to interfere with the combustion process during heating, pyrolysis, ignition or flame spread [43]. The types of flame retardants and their operating characteristics are described as follows [38]: (1) char formers: usually, phosphorus compounds, which remove the carbon fuel source and provide an insulation layer against the fire's heat. (2) Heat absorbers: usually metal hydrates, such as aluminium trihydrate (ATH) or magnesium hydroxide, which remove heat by evaporating the water in their structure. (3) Flame quenchers: usually, bromine- or chlorine-based halogen systems that interfere with the reactions in a flame. (4) synergists: Usually, antimony compounds, which enhance the performance of the flame quencher. The flame-retarding action of ERA could be divided into physical and chemical actions. Physical action includes cooling, barrier action via the formed protective layer and fuel dilution. For the cooling action, flame retardants absorb the heat when they decompose, and the endothermic decomposition may consume the released heat from the combustion of ERA, then the burning adhesive is cooled. Generally, most inorganic-hydrated compounds, such as aluminium and magnesium hydroxides, may play a role via this mode. For the barrier action, the decomposition products of some flame retardants shield the surface of the adhesive and form a protective layer that may act as a barrier to resist oxygen and the produced heat. Consequently, the burning process is difficult to sustain. For fuel dilution, some flame retardants may release water vapour, carbon dioxide, or other inert gases, thereby decreasing the concentration of free radicals and combustible gases in the burning adhesive. Chemical action includes gas-phase and condensed-phase reactions. The gas-phase reaction mechanism is generally regarded as the interruption of the chain reaction of the ERA structural system during burning. The flame retardant that provides the flame-retarding action via the gas-phase reaction action may capture free radicals to decrease the concentration of free radicals than the combustion threshold and then prevent or delay burning, in which halogen-containing flame retardants are the most representative. During burning, the halogen-containing flame retardants release the hydrogen halide, which may react with the free radicals formed during burning to inhibit the combustion of substrates. For the condensed-phase reaction, the flame retardant that provides the flame-retarding action via the condensed-phase reaction may promote the formation of a carbonised or vitreous layer by cross-linking, aromatising, catalytic dehydration of polymers or reacting with the ERA. In this flame-retardant mode, intumescent flame retardants may form an intumescent char layer by some chemical reactions during burning, and generally, the formed char

layer may promote the barrier action and improve the flame retardancy of the ERA. Furthermore, some flame retardants can accelerate the rupture of the chains of the ERA, and several droplets are produced under this condition. Then, a large amount of heat may be taken away when these droplets move away from the burning zone [44]. Flame retardants can be classified into several families, including halogen-based compounds, phosphorus-based compounds, silicon-based compounds, nano-composites and metal-based compounds. Among them, halogen-based and phosphorus-based flame retardants are widely used.

For halogen-containing flame retardants, the flammability of ERA can be greatly reduced by incorporating a halogen into the molecule. The best known are the halogen-containing ERAs based on chlorinated, brominated and fluorinated bisphenol A. They often comprise blends of two or more epoxy-resin systems, one of which is a halogenated resin, and the other of which perhaps contains a halogenated curing agent, such as chloric anhydride. These halogen-containing ERAs have been developed over decades and are still used widely due to the obvious advantages of low cost, processability, miscibility and low reduction in physical/mechanical features of the flame-retardant systems. Halogen-containing flame retardants function by liberating acid halide gases as the product thermally breaks down at the high temperatures incurred in a fire. These halide gases act as extinguishers to significantly increase the ignition temperature of the cured ERA. The mechanism of these flame retardants is the release of hydrogen halides (HCl and HBr) during the thermal decomposition of the ERA. The chemical reaction during burning is a free radical chain reaction, and the continuous growth of free radicals is important for maintaining the burning process for the ERA. Several chemical halide intermediates form during the burning of ERAs. These halide species are carried into the flame front of the burning polymer where they inhibit key free radical reactions of combustion. This inhibition results in flames becoming unsteady and extinguishing and lowers the release of heat overall [10, 11]. Generally, alicyclic or aliphatic halogen-containing flame retardants are more efficient than aromatic halogen compounds. Alicyclic or aliphatic halogen-containing flame retardants burn at low temperatures for most polyolefins because of lower carbon-halogen bond energies and easier halogen release [45]. Beach et al. [46] synthesised brominated polybutadiene-polystyrene (BrPBPS) flame retardant from styrene-butadiene-styrene triblock architecture by bromination. The BrPBPS flame retardant contains similar aliphatic bromine as in hexabromocyclododecane, but with a higher-molecular-weight structure. It provides similar flame-retardant activity as hexabromocyclododecane in polystyrene blends, where both release HBr to provide the gas-phase activity. Both also provide enhanced ERA degradation as another major pathway for condensed flame-retardant activity. Jiang et al. [47] added BrPBPS into epoxy asphalt adhesive to enhance its flame resistance. Meanwhile, the T_g of the epoxy asphalt adhesive was notably enhanced with the inclusion of BrPBPS. Wu et al. [48] synthesised liquid-oxygen-compatible bromine-containing ERA by the polycondensation of tetrabromobisphenol A and epoxy resins. The bromine element was introduced into the ERA to improve the liquid oxygen compatibility and enhance flame retardancy. The results showed that limiting oxygen index increased drastically when the bromine content was increased from 0% to 21.20%.

Phosphorus-containing flame retardants are identified as one of the most promising halogen-free flame retardants [49, 50] since they possess excellent properties, such as low-smoke emission, low toxicity, form a stable carbonised layer after burning effectively [44, 46, 51, 52] and are environmentally friendly [35]. For preparing organophosphorus epoxides-based adhesive, three general methods were employed.

First, the condensation of 1-chloro-2,3-epoxypropane and organophosphorus compounds containing two or more hydroxyl groups. Second, the Michaelis-Arbuzov reaction of phosphites with 1-halogeno-2,3-epoxypropanes. Finally, the epoxidation of tertiary phosphine oxides by peroxy acids [53]. Phosphorus-containing flame retardants can be generally classified into three categories: (1) simple reactive phosphate monomers; (2) linear polyphosphazenes; (3) aromatic cyclic phosphazenes. They may be integrated into the ERA chains through co-polymerisation, homo-polymerisation, surface modification or blending; simple inorganic or organic additives are excluded [25, 53–55]. During the burning of ERAs, most of the current phosphorus-containing flame retardants may act simultaneously in the condensed and gaseous phases [56]. In the condensed phase, phosphorous-containing flame retardants can make the amount of carbonaceous residue or char, which acts as the thermal insulation, and a barrier of oxygen to transfer to the burning adhesive increase. Afterwards, a carbonised layer is formed. The carbonised layer prevents further pyrolysis of the corresponding ERA [57]. In the gaseous phase, some phosphorus-based additive flame retardants may produce several free radicals during the thermal decomposition process, and they may react with the free radicals which are generated from the ERA. Then, the free-radicals-supported combustion of polymers might be stopped due to the lack of fuel [58–60]. Wazarkar et al. [61] synthesised phosphorus–sulphur-containing di and tetra functional carboxyl curing agents and used them in preparing high-performance ERA and coating. The anticorrosive and flame-retardant properties of the adhesives and coatings were improved as the concentration of the flame-retardant-curing agents increased, and they exhibited excellent mechanical and chemical properties and thermal stability. Ma et al. [62] synthesised a phosphorus-containing bio-based ERA from itaconic acid and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. As the matrix, its cured epoxy network with methyl hexahydrophthalic anhydride as the curing agent showed comparable Tg and mechanical properties to diglycidyl ether in a bisphenol A system, as well as good flame retardancy with UL94 V-0 grade during a vertical burning test.

3. Application of ERAs

ERA is often used mainly because it has the advantages of low-temperature curing, good bonding performance and improved engineering efficiency. ERAs are usually used for metal bonding, concrete bonding and wood adhesive.

3.1 Application of ERA for metals

Several studies have been conducted on the use of ERAs for metal bonding. In a previous study, polyurethane 1,2-polyethylene oxide was first cured onto the metal surface and then used 1,1-polyoxyethylene ether. The adhesive adheres the polyurethane resin material to the metal [63]. Subsequently, another study prepared a novel high-temperature curing epoxy adhesive using polysulfone as a raw material. Studies have shown that the tackifier resin accelerates the bonding of ERA and steel and promotes the bonding and vulcanisation of fluorine rubber [64]. Uehara et al. [65] prepared a monolithic ERA layer with a porous structure on the surface of a stainless steel (SUS) plate through a polymerisation-induced phase separation process, as a mediator for bonding SUS and various thermoplastic resin plates. The research results show that the bond strength of the apparent bond area between SUS and ERA is two to three times higher than those for direct metal-resin bonding.

3.2 Application of ERA for concrete bonding

Concrete is the most widely used worldwide building material. Traditional cement is used as a binding material for concrete. Cement concrete also has some shortcomings, such as low tensile and flexural strength, high porosity, low durability and abrasion resistance and longer solidification time. The mechanism of epoxy concrete is such that ERA forms a 3D structure through cross-linking in the combination of masonry mortar and concrete [66]. Afterwards, the ERA particles are dispersed into the system. Then, a part of the adhesive particles settle on the surface of the aggregate particles and participate in the cross-linking reaction. Finally, the ERA particles form a cured network structure, and the aggregates are bonded in the cured epoxy network structure. In ERA/mortar/concrete composites, the adhesive network forms a bridge between aggregates, so that the epoxy-based composites have higher mechanical properties and impermeability [67]. Also, it was found that the resin bond concrete has great advantages in the manufacture of machine tool beds. Kim et al. [68] studied ERA as the matrix material of resin concrete. The reinforced aggregate of resin concrete comprises pebbles and sand. The results showed that when the mass fraction of resin in the resin concrete is 7.5%, the thermal expansion coefficient of the resin concrete is the same as that of cast iron. In this case, the specific heat of resin concrete is 63% larger than that of cast iron. Beutel et al. [69] added epoxy resin-based adhesive concrete and coarse aggregate to the mixture and found that adding the aggregate did not affect the strength of the mixture. Additionally, the specimens exhibited much higher tensile and flexural strength than ordinary concrete, and the compressive strength was similar to ordinary high-strength concrete.

3.3 Application of ERA for wood bonding

Lei et al. [70] modified soy protein isolate with a surfactant grafted with maleic anhydride and blended with epoxy resin to prepare wood adhesives with higher bonding strength and good water resistance. Zhang et al. [71–73] prepared wood adhesive with good water and heat resistance by the co-polycondensation of tannin or lignin or starch with furfuryl alcohol and blending with epoxy resin. After bonding with wood, the adhesive was cured at high temperature under pressing to prepare a wood-based panel. After testing, the material showed good shear strength.

4. Conclusions

Although research activities on modifying ERAs have greatly progressed, several problems still need urgent resolution. For example, most of the toughening methods of ERAs are at the expense of the rigidity and strength of the modified product, and it is difficult to increase the toughness and strength of the ERA simultaneously. The ERA modified with rubber or nano-particles, due to the large specific surface area of nano-particles or rubber, is very easy to agglomerate. Therefore, how to uniformly disperse it in the ERA system to obtain a reinforced and toughened high-performance ERA remains an important research topic. Therefore, the future development direction of ERAs should be towards low-temperature fast curing, high performance, green environmental protection and multifunctional development. ERAs have developed in a more stable, safe and scientific direction.

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Conflict of interest

The authors declared that they have no conflicts of interest.

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