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A Review of Curing Agents for Metal Coatings and Their Role in Corrosion Resistance and Environmental Durability

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Abstract
A comprehensive evaluation of key performance indicators such as chemical resistance, environmental durability, and adhesion strength was conducted using electrochemical impedance spectroscopy and accelerated aging experiments. This review suggests that the proposed curing agent significantly improves the protective capabilities of metal coatings, resulting in enhanced resistance to corrosion and wear. This innovation presents promising opportunities for the industrial and automotive sectors, potentially leading to prolonged service life and reduced maintenance costs. Ongoing research will further explore the scalability of the curing agent and its environmental impact in industrial applications.

Keywords: Curing agent, Metal coating, Epoxy-based system, Corrosion resistance, Mechanical performance, Thermal stability.

Introduction

Curing agents strongly affect how fast epoxy reactions happen, how long the process curing takes, and what the final material is like—whether it's strong, flexible, or durable. [1–3]. These agents usually contain reactive components like crosslinkers, ionic and cationic inhibitors, and active hydrogen compounds, all present in similar proportions [4, 5]. Techniques such as wet curing, formwork, membrane curing, heat treatment, hot mixing, and infrared techniques have been established to boost the hardness of epoxy materials [6,7]. Carbon-based nanoparticles which can react with anhydrides and amines are commonly used to improve epoxy materials [8-10]. New sensor systems, like marine depth filters, aim to reduce water absorption, lower density, and increase strength by using crosslinking curing agents [11-13]. Low-density glass microspheres combined with aliphatic and aromatic amines are often used in 3D epoxy networks, along with epoxy oligomers and high-strength resins [14-16]. These matrices are mechanically

strong, adhesive, and resistant to water. Curing systems help maintain stable temperature and humidity for different types of concrete, both indoors and outdoors [17-18]. Internal curing is being explored to improve hydration in Materials based on cement, especially those used in high-performance concrete (HPC) with low water-to-cement ratios [19-20].

Adding solid materials to lime sand can improve soil strength, increase compressive resistance, and extend durability [21–23]. Shotcrete is especially useful in underground construction due to its high safety and efficiency [24, 25]. Thermosetting concrete is widely used for its productivity, though it faces issues like poor final-stage hydration, uneven product distribution, and microstructural damage. Recent studies suggest that internal curing using fibers may help solve these problems by slowing water release [26-28]. While Portland cement is commonly used to harden clay, quicklime is gaining popularity because of its chemical versatility, simple in operation, as well as low cost. In food applications, nitrate scavengers from ethanol by-products and kimchi spices may help reduce residual nitrates in dry foods [30, 31]. Traditional amine curing agents having low-viscosity generally contain primary amines, which can cause surface dullness and staining due to CO_2 reactions [32, 33].

Bisphenol A (DGEBA) undergoes a chemical reaction with anhydride-based curing agents resulting in the formation of a robust, three-dimensional polymer network that is cost-effective, easy to produce, and has excellent insulation properties [34, 35]. This system is commonly employed in high-voltage insulation applications and phosphate ceramic coatings [36, 37]. During bonding, small reactive compounds help trigger color changes and increase pressure in epoxide reactions with various nucleophiles. Epoxy materials are ideal for creating thermostat networks that can be fine-tuned for specific treatments [38, 39]. High-performance epoxy coatings often use silicone anhydride curing agents, and silicon-sulfur compounds are essential for developing multifunctional coatings [40, 41].

A new polymer system has been developed that integrates the active curing process into the polymer chain itself. Although many crosslinking methods exist, curing agents enhance the polymerization pathway. Choosing the right curing agent is key to optimizing crosslinking chemistry and achieving the best results for different formulations.

The cross-linker completes the polymerization by reacting with the polymer, which is crucial because the material continues to harden after the initial reaction. By designing a three-dimensional binder network using specific curing agents, the system can gain additional properties. Amine-functional curing agents have shown excellent performance in water-based epoxy systems, making them increasingly popular in various applications. This new amine adducts are effective even at lower concentrations, enhancing overall performance. This review highlights recent developments in epoxy resin systems using innovative hardeners, especially for cement-based industrial uses. These systems offer faster curing, better resistance to chemicals and stains, easier handling and application, and improved cleaning of water samples. Their performance is compared with commercial products that address common failure issues in cementitious substrates.

Replacing petroleum-based epoxy thermosets with eco-friendly alternatives remains a major challenge. Bio-derived epoxy monomers often face challenges in achieving the high-performance standards set by conventional DGEBA-based systems. While aromatic structures in epoxy resins contribute to superior

mechanical strength and thermal stability, they typically require elevated processing temperatures due to their high melting points. After curing, these materials can exhibit brittleness and a tendency to crack, limiting their durability. Enhancing epoxy's suitability for manufacturing and handling matrices—particularly by lowering viscosity as well as melting temperatures—is crucial for broadening its use in the field of electronics and electrical engineering.

Epoxy resins form a solid, three-dimensional network when monomers or oligomers react with curing agents [42]. Their resistance to chemicals, along with excellent heat and strength performance, makes them highly suitable for use in aerospace, protective coatings, composite materials, and electronic devices [43]. The epoxy resin most commonly utilized, DGEBA, is derived from the reaction between bisphenol A and epichlorohydrin. While epichlorohydrin may be derived by using glycerol based on renewable-sources, BPA is petroleum-based and raises concerns about sustainability and energy use [44]. BPA also poses health risks [43]. As a result, research into biomass-derived alternatives has grown rapidly, driven by environmental and health awareness. Bio-based epoxy resins are now being developed from sources like plant oils, itaconic acid, and cardanol [46]. The aim is to develop environmentally friendly epoxy resins that can perform as well as those made from petroleum-based materials [47].

One example of a bio-based epoxy monomer is TEIA, which is made from itaconic acid (IA) and has three epoxy groups. TEIA is easy to process because it's a liquid having a viscosity as low as 0.92 Pa·s at 25 °C. It cured using methylhexahydrophthalic anhydride, while the resin itself was based on a petroleum-based epoxy compound. As compared to traditional DGEBA system, the TEIA-based epoxy showed better performance, including superior flexural strength and a higher glass transition temperature (135.2 °C vs. 109.5 °C) [48].

Research into bio-based epoxy resins has grown rapidly, with improvements in material properties. Many studies show that bio-based epoxies can outperform sourced from petroleum feedstocks with respect to Tg, degradation temperature, tensile stability, as well as elastic energy retention capacity [49]. These resins are often made from natural compounds like magnolol, resveratrol, vanillin, and ferulic acid [50].

However, producing bio-based epoxy resins on a large scale is still difficult due to high costs and challenges with biomass compatibility [51]. To overcome these issues, future bio-based epoxies should be designed not only for better thermal and mechanical properties but also for specific functions like flame resistance [52], biodegradability, recyclability [53], shape memory [54], antibacterial effects [55], and more [56]. Because of these unique features, epoxies derived from renewable biological sources has attracted too much research consideration [57].

Despite many studies, most reviews focus only on performance and often highlight just one property, such as flame retardancy. A complete and practical evaluation of epoxy resin compounds based renewable biological sources is yet missing. Goal of the mentioned study is clarifying the summary of overview of the latest advancements in bio-based epoxy resins materials made from biomass for various applications (Scheme 1).

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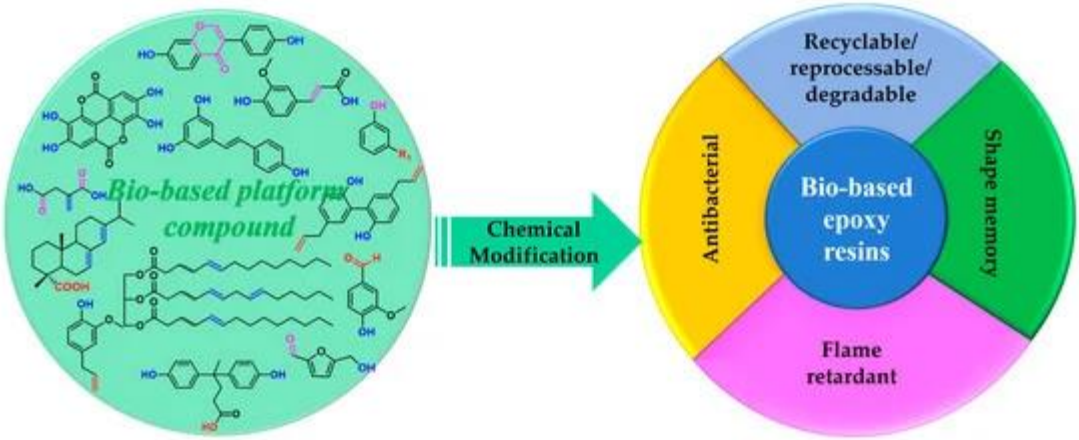
Scheme 1. The transformation of epoxy resins based on renewable biological sources into bio-derived platform compounds.



A. Purpose of curing

Curing is a chemical process where the hardener mixes with the epoxy resin and helps it form a strong, solid structure. This structure is like a tight 3D web that doesn't melt or dissolve. The process starts when a special part of the epoxy (called the ring) opens up and connects with other molecules, making the material tough and stable.

One of the most studied properties in epoxy systems is fracture toughness, especially at the edge between epoxy resin as well as thermoplastic materials. However, the long-term durability of bonds between epoxy and flexible carrier sheets used in integrated sensors has received limited attention. To measure bonding strength, interlaminar shear tests are recommended, while tensile tests are used to evaluate contact strength between epoxy and thermoplastics.

The bond at the interface between epoxy resin and PES film is relatively weak. When PEI film is used instead, the interface strength improves and matches that of reference samples. However, cracks tend to form in the surrounding epoxy resin, meaning the measured strength mainly reflects the interface itself. Tensile curve comparisons show that both reference samples and those with PEI films follow similar stress paths, forming an arc before failure—indicating that the epoxy resin near the interface is the weak point. Figure 1 illustrates how differences in clamping and specimen grinding during tensile testing can affect results, especially in tapered versus non-tapered specimens [57].

Additionally, a self-curative epoxy structure was explored. Nanofibers based on amine were electrospun utilizing PAN (polyacrylonitrile) as a curing agent and epoxy encapsulant. The resulting nanofibers had diameters between 406–483 nm. Chemical analysis confirmed successful integration of the curing system, and thermal studies showed that 24% and 37% of the epoxy resin's weight was retained. This system forms the basis of self-curative epoxy resins, which are mostly useful at room temperature [58].

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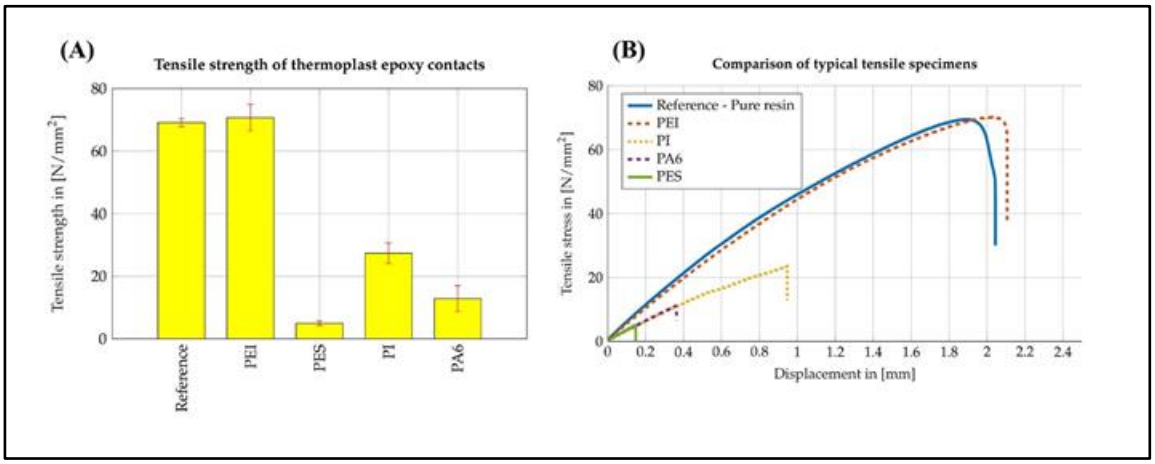
Figure 1: (A) Tensile strength comparison among various thermoplastic films. (B) Illustrations of various curve-shaped specimen types. (Modified from Kyriazis et al. [57], 2022)

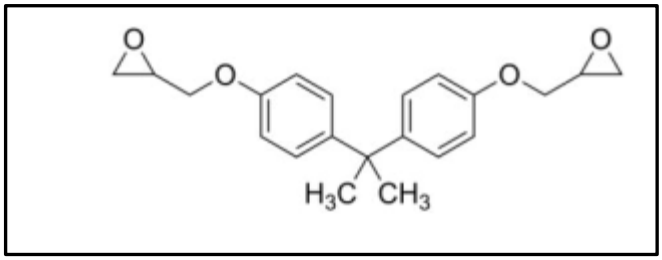


EPOXY RESINS TYPES:

1. Diglycidyl Ether Resins-

BPA (Bisphenol A) and epichlorohydrin are the primary components in among the widely utilized epoxy resins, which vary in molecular weight. DGEBA (Diglycidyl ether of bisphenol A) is synthesized through the reaction of bisphenol A with epichlorohydrin using basic catalytic reagent. The DGEBA structure is illustrated in Figure 2. The DGEBA resin characteristics are determined by the quantity of repeating structural elements present in its molecular structure. Additionally, the molecular weight of solid or more viscous DGEBA is greater than that of liquid DGEBA [59].

Figure. 2 Structure of DGEBA



2. Flame (FIRE) Resistant Epoxy system –

Flame (Fire) Resistant Epoxy Resins system are developed by incorporating flame-retardant additives or chemically modifying the resin structure. These resins are designed to reduce flammability**,** suppress smoke formation, and limit heat release during combustion.

Nitrogen-Containing Epoxy Resins –

Non-toxic, smoke-reducing flame retardant resins that are safe for the environment. Wang et al. [60] created phosphorus-based epoxy resins use as flame resistant. A significant improvement in flame retardant behaviour was seen when the epoxy resin, which contains phosphorus, and the curing agent,

which contains nitrogen, worked together. The novel phosphazene-based epoxy resins were synthesised by reacting hexakis(4-hydroxyphenoxy)-cyclotriphosphazene with DGEBA. The resulting product had a high Tg, outstanding flame resistance, as well as low decomposition temperatures (Lie et al., [61]).

Phosphorus-Containing Epoxy Resins

Phosphorous chemicals have the potential to provide epoxy resins a high flame-retardant quality by inhibiting flames in the gas phase and increasing char in the condensed phase. Compared to compounds containing halogens, epoxy resins containing phosphorus produce less harmful gas and smoke. Epoxy resins may have covalently bound phosphorus added to them using oxirane molecules that contain phosphorus [62]. Liu et al. [63] synthesised environmentally acceptable electronic packaging materials using epoxy resins that include phosphorus.

3.Cycloaliphatic Epoxy Resins

These resins outperform bisphenol-A epoxies in terms of UV stability because they lack aromatic groups. A cycloaliphatic epoxy resin (CAE) called 3,4-epoxycyclohexylmethyl ester of 3,4-epoxycyclohexanecarboxylic acid is produced by reacting 3-Cyclohexene-1-carboxylic acid, 3-cyclohexen-1-ylmethyl ester Diene 221, with peroxyacetic acid. The excellent UV durability, strong heat resistance, and outstanding electrical characteristics of this CAE are all due to its saturated backbone and aliphatic backbone. For structural components that are subjected to high temperatures in the environment, these properties are crucial for the resins used in their production [64].

4.Phenoxy Resins

Coatings and mouldings benefit from the high heat stability of higher molecular weight epoxies. Epoxy resins made from phenolic novolac resin and epichlorohydrin are called phenolic novolacglycidyl ethers resins. Thanks to their abundance of epoxide groups, novolac epoxy resins exhibit remarkable chemical, solvent-resistance, and thermal characteristics, as well as high cross-linking densities [65]. Epoxy resins containing phosphorus that serve several purposes are produced by reacting epoxy resin derived from novolac and DOPO (a phosphorus-containing heterocyclic compound). A remarkable Classified as V-0 according to UL-94 vertical flammability standards was attained by these Phosphorus-modified multifunctional epoxy systems that were synthesised as reported by Lin and colleagues [66]. They showed excellent resistance to thermal degradation along with a high glass transition temperature (Tg).

5. Epoxy Resins with Multifunctionalities

These resins improve chemical and heat resistance; they include aromatic glycidyl ether resins (such epoxy phenolic novolacs) and aromatic glycidyl amine resins. Novolacs, which are phenol/cresol-formaldehyde condensates, are glycidylated to produce epoxidised epoxy phenolic (EPN) and epoxy cresol novolac (ECN) resins, which are of commercial importance. produced by the acid-catalyzed reaction of formaldehyde with phenol/cresol. Para methylene bridges and ortho bridges are generated at random. By reducing the interaction between phenolic hydroxyl groups and glycidylated phenol groups, epoxidation of novolacs with an excess of epichlorohydrin inhibits branching. Only a few number of multifunctional epoxies with aromatic amine backbones have achieved significant commercial success. Combining bis (3- aminophenyl) methyl phosphine oxide (BAPO) or diaminodiphenyl methane (PM)

with epichlorohydrin yielded a multifunctional epoxy resin, also known as tetraglycidyl-3, 3'-diaminodiphenyl methyl phosphine oxide (TGBAP) or tetra glycidyl-4,4'- diaminodiphenyl methane.

6.Modified Epoxy Resins

Contains epoxies and epoxy esters that have been treated with silane to enhance their resistance, adhesion, and flexibility.

Non-Glycidyl Ether Epoxides

It contains aliphatic epoxies, both cyclic and acyclic, and each has its own set of characteristics.

Epoxides that do not include glycoside may be categorised into two types: cyclic aliphatic resins, which have an epoxide group in the molecule, and cyclic aliphatic (saturated) epoxy resins, which have a linear structure to which epoxide groups are linked. Commercially accessible cyclic aliphatic (saturated) epoxy resins include vinyl-substituted cyclohexene dioxide and epoxidized dicyclopentadiene derivative, among others. Few examples of acyclic aliphatic resins are polyglycol diepoxides, epoxidized oils, and epoxidized diene polymers. The peroxidation of glycerol esters and unsaturated fatty acids is influenced by acids. Polyvinyl chloride stabilisers such as epoxidized soyabean and linseed oils have been on the market for quite some time.

Glycidyl Esters

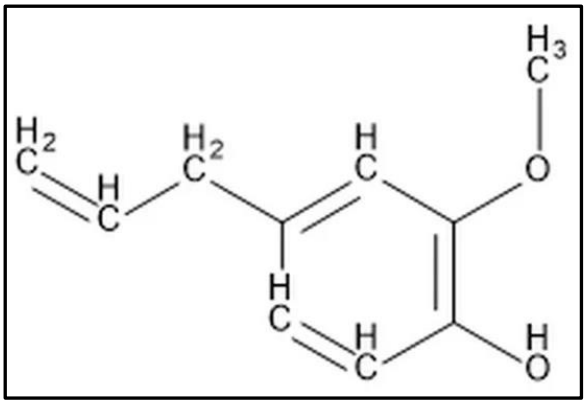
An ingredient with specialised uses, derived from dicarboxylic acids. Diglycidyl esters (VIII) were produced by treating intermediate diimide acids with epichlorohydrin, which were themselves produced by combining benzophenone tetracarboxylic acid dianhydride (BTDA) with amino acids.

BIO BASED EPOXY RESINS

Eugenol, a phenolic compound known for its volatility, is extracted from clove oil obtained from the Eugenia plant and belongs to the category of organic chemical compounds known as terpenes [67]. Its characteristics make it a favourite ingredient in cosmetics, but it has recently found new life in biopolymer manufacturing. “Santiago and colleagues introduced a technique for synthesizing a bio-based epoxy resin using a trifunctional eugenol-derived monomer” [68]; Wan and co-researchers developed an epoxy polymer with enhanced rigidity and reduced flammability, utilizing eugenol as a key precursor [69]; Jiang and collaborators produced thermosetting epoxy resins using eugenol and vanillin as renewable feedstocks [70]; Chen and team synthesized epoxy compounds through the esterification of eugenol and carried out a self-curing process to form thermosetting resins [71]; Liu and co-authors reported the synthesis of epoxy compound based on eugenol through a reaction involving succinic anhydride along with zinc-based catalytic systems

[72]; Kumar and co-authors provided a comprehensive summary of the preparation of eugenol-derived resins and their utilization in coating applications [73], Mainly, epoxy compounds made from eugenol showed good qualities such as resistance to corrosion, increased adhesion, and a stiff structure [74]”.

Figure. 3 Structure of eugenol.



Epoxy polymers are widely utilized as matrix components in multiple composite applications Which are attributed to their ease of processing and excellent compatibility with many kinds of fillers. Curing conditions, the chemical make-up of the curing agent, and the impact and reactivity of modifiers all contribute to the final epoxy resin's qualities. As a result, scientists continue to place a premium on finding the optimal filler to achieve the desired chemical and heat resistance in composites and desirable mechanical qualities. There has been a surge in applied and industrial research into new materials and processing technologies for polymer composites due to their increasing use as lightweight, highly durable construction materials in the transportation, building, and automotive sectors. Once cured, epoxy has exceptional resilience to chemical and environmental stresses. Construction materials with great stiffness and endurance are achieved by blending these very brittle elements by several fillers, for example fiber and cloth. "Much research has focused on using plant-based fibers used as structural enhancement in composites system to reduce the environmental effect of epoxy materials [75]". Using bio-based curing agents, such as those derived from vegetable oils, is another way to make ecological epoxy composites.
Biodegradable or naturally occurring polymers and fillers are a part of green composites. Composite materials synthesized from natural sources, composites with recyclable or compostable by-products, and composites with environmentally friendly manufacturing processes are the three main categories into which bio composites fall [76]. It would be ideal if the composite material only uses materials that come from sustainable sources. This highlights the critical need to study eugenol's potential as a natural element in epoxy-based composites materials for industry usage. Articles about epoxy composites that used eugenol as a modifier or hardener and a polymer matrix or filler were chosen for the review. Because of its strong chemical reactivity, eugenol has many potential applications, such as the modification of fillers or incorporation into the production of polymer monomers. Li et al. detailed the process of linking silicone modified with bio-derived compounds to create crosslinked network formed by the silicone and epoxy resin. "Formation of glycidyl ethers through the reaction between a phenolic –OH group and epichlorohydrin exposed eugenol to the epoxidation process. Hydroxylated epoxidized eugenol (EPEU) was used to create silicone-linked epoxy monomers, resulting in SIEPEP, SIEEP2 and SIEEP4." Diaminodiphenyl sulfone (DDS) was used to harden the resulting monomers. Adding phenylsiloxane and methylsiloxane components to the epoxy system enhanced the composite material characteristics,

enhancing flame retardancy and dielectric permittivity. The composites exhibited a Limiting Oxygen Index (LOI) of 31, among other benefits.

CARVACROL AND THYMOL AS EPOXY RESIN

Incorporating reactive diluents into thermoset materials is a common practice in the epoxy resin industry. These diluents typically have low molecular weights, reduced viscosities at ambient temperatures, and at least one reactive functional group. The use of reactive diluents is essential as they enable the development of processes and products with lower viscosities and enhanced mechanical performance, such as improved flexibility, elongation, as well as resistance to mechanical shock [77]. Recent emphasis on reducing carbon footprints and volatile organic compound (VOC) emissions has led to a focus on novel series of biobased reactive diluents. Examples of commonly used bio based reactive diluents based on glycidyl ether contain compounds such as glycidyl ethers of dodecyl as well as tetradecyl (C12-C14 MGE), monoglycidyl ether derived from cardanol (CMGE), and diglycidyl ether of butanediol (BDGE). CMGE and BDGE may be synthesized from renewable and sustainable raw materials like
vegetable oil and cashew nutshell-based oil (cardanol), while BDGE can also be produced from 1,4-butanediol and sugar fermentation.

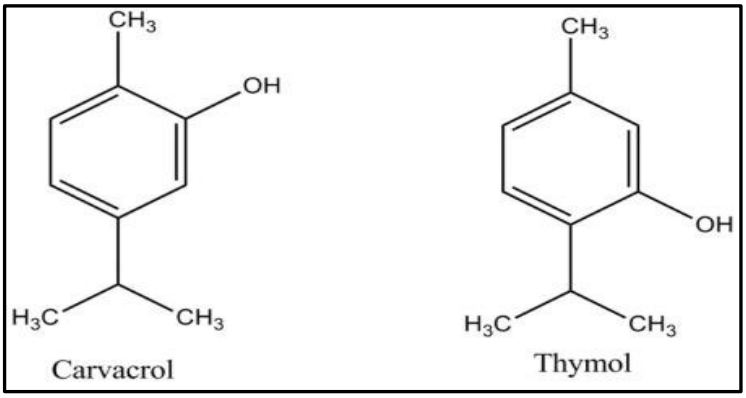
Although these biobased reactive diluents are manufactured on an industrial scale, their limited availability and aliphatic structure may result in thermoset polymers exhibiting poor stability and thermomechanical characteristics. To remain competitive with current market alternatives and create new opportunities, there is a need to development of alternative bio-derived reactive diluents suitable for epoxy formulations with enhanced characteristics [78] [79]. Due to their abundance, cheap cost, and significant variety, vegetable-based oils provide among the most advanced alternatives to the synthesis of sustainably sourced epoxy-compatible reactive diluents in this context [80]. Two different studies looked at how soybean oil based epoxidized compound (ESO) affected on mechanical, thermal characteristics of materials derived by DGEBA; one by S. Kumar et al. [81] and the other by F. I. Altuna et al. [82].

An anhydride hardener and a catalyst based on imidazole were used in both instances. Thermoset materials having a lower glass transition temperature, less thermal stability, and more reactivity may have their impact strength and fracture toughness increased by as much as 38% when the ESO concentration is increased, according to the overall findings [83]. The discussion omitted, however, The effect of varying ESO levels on formulation viscosity. Moreover, as mentioned before, VOs still display lengthy aliphatic chains, which may give rise to other concerns. A study conducted by Ding and colleagues [84] detailed the process of synthesizing glycidyl ether derivative of furfuryl alcohol (FGE), examined how the thermomechanical characteristics of formulations derived from DGEBA were affected by its concentration. The optimal ratio of FGE, according to the evaluation, is between 10 and 15 weight percent. This enhances the flexural rigidity and tensile capacity by around 16% and does not influence on the thermosetting polymer (Tg).. Similarly, Z. Karami et al. [85] used a weight concentration of up to 30% when they coupled FGE with DGEBA. Curiously, it was suggested that FGE had a more potent capacity to reduce viscosity than Cardura E10P, a commercial reactive diluent manufactured by Momentive. Incorporating 20 wt% of furfuryl glycidyl ether (FGE) into the formulation, when cured with

diethylene triamine (DETA), results in enhanced material properties—showing up to a 300% improvement in adhesion, a 40% increase in tensile strength, and a 60% rise in flexural strength. Chen and co-authors [86] explored the feasibility of utilizing glycidyl ether of polyepoxidized cardanol (PECGE) as an innovative bio-derived reactive diluent for diglycidyl ether of bisphenol A (DGEBA)-based epoxy systems and described the manufacture and use of its. Lastly, eugenol's availability and unique structure made it a strong contender for producing a biobased reactive diluent with a range of desirable characteristics [87]. For example, in their research on the preparation of eugenol based monoglycidyl ether (MGEu), A. Maiorana et al. [88] suggested a possible DGEBA alternative by combining MGEu with DGEDP-Pe (Diglycidyl Ether of Diphenolate Pentyl Ester). Isophorone diamine (IPDA) curing transformed this mixture into a thermoset material having a low glass-transition temperature of 65 °C.

There is lack of study into the creation and evaluation of novel classes of epoxy-based reactive diluents, despite the fact that the literature does include some intriguing data. It can be demonstrated that certain molecular structures exhibit non-aromatic chains and contain reactive epoxy groups within those segments. Not only can this cause a discrepancy in reactivity, which in turn can cause structural non-uniformity or partial reaction of epoxy groups, consequently, can lead to reduced network formation within the cured matrix, however, this may adversely affect the thermal resistance of the material and thermomechanical properties. As a phase transfer catalyst, tetraethylammonium bromide (TEAB) was used to bring phenol derivatives (carvacrol and thymol as shown in Figure 6) into contact with an excess of epichlorohydrin at 90 °C. At 15 °C, a NaOH alkaline solution was added. Two primary reactions may coexist in the first reaction step, as shown in earlier work by S. Caillol's group [89]. In the initial case, the phenolate ion participates in a nucleophilic substitution (SN2) reaction with the carbon bonded to chlorine, resulting directly in the formation of the target epoxide compound. In this case, second step involves employing an alkaline solution to seal the oxirane ring internally while keeping its configuration. We were able to get epoxide yields of 79–99% using this method, which is comparable to or even better than previously published values [90].

Figure 4 Chemical structure of carvacrol and thymol.



APPLICATIONS OF EPOXY RESINS

By selection the right epoxy resin, hardener, and extra ingredients, we can make materials that work exactly how we want—strong, flexible, heat-resistant, or more. What we choose depends on how it's made, how much it costs, and what it's supposed to do. These materials are used in many things, like Paints and coatings, Adhesives and bonding, Composites and laminates, Molding, casting and tooling, Construction, Electricals and electronic systems and so on.

EPOXY RESIN SYSTEM BEFORE CURING

Unfortunately, most commercial polymers do not exist in their purest, most homogenous form, with the exact structure described on the packaging. Products made from epoxy resins may include trace quantities of components, including isomers, oligomers, and others. Key properties commonly evaluated in epoxy resins include epoxy value, appearance (such as color), specific gravity, presence of hydrolyzable chlorine, and the amount of volatile substances. Furthermore, analytical techniques like NMR, IR, gel permeation chromatography, and HPLC are employed to assess molecular weight, its distribution, the presence of oligomers, functional group types, and trace impurities in epoxy resin formulations. Depending on how they interact with the resin system—particularly with components like a basic catalyst (such as a tertiary amine) or an amine-based curing agent—the reactivity and formulation of the resin can be influenced, which consists of α-glycol and chlorine, may be affected. It is helpful to know the kind and concentration of chlorine to achieve the desired reactivity and flow rate in a formulation [91].

One of the most typical ways to measure epoxy resin is by looking at its epoxy content. Epoxy group content is determined through the measurement of epoxide equivalent weight (EEW); the mass of the resin in grams corresponds to one gram of the epoxy group. If you want to make thermoset epoxy, you need to know how many stoichiometrically balanced cross-links to use, and EEW is a prerequisite for that. In order to characterize the thermoset epoxy structure, understanding the level of secondary -OH groups in the epoxy matrix is essential for evaluating its reactivity and performance, Conventional techniques for evaluating epoxy content include reacting the epoxy ring with halogen-containing acids, leading to the formation of halohydrin compounds [92]. The amount of hydroxyl functionalities present controls the stoichiometric balance between epoxy resin and curing agent because they can react with curing agents or hardeners. When the hardener and epoxy group react, these secondary alcohol compounds speed up the process. There are other types of hydroxyl groups, such as α-glycol, which is occurs when the reactive oxirane ring undergoes hydrolysis, forming hydroxyl groups, and when epoxy resins synthesized from bisphenol A at elevated concentrations generate phenolic hydroxyl groups due to incomplete reactions involving phenol. $LiAlH_4$, selectively reacts with compounds containing labile hydrogen atoms. the periodic acid technique, may be used to estimate the α-glycol content [93]. It is important to use caution while measuring α-glycol to get an accurate result since it often exists in minute quantities. Low quantities and concentrations of phenolic hydroxyl are often obtained. A solution of pyridinium chloride may be used to estimate this concentration by acetylation with acetic anhydrides. The hydroxyl functional group converts to ester moiety as the oxirane reacts with two acid groups.

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Reduced thermal stability is possible with high chloride concentration epoxy system, particularly when cured with an amine hardener. At the same time, flame retardancy is now a standard feature of thermoset epoxy resin; as a result, designers and manufacturers of epoxy resin need to know how to create compositions that work well in hot environments. When used as coating materials for semiconductors, bisphenol A epoxy resins' electrical characteristics are severely compromised by chloride. Because chloride is present, the resin might also have an undesirable and reactive colour. If active chloride is present, epoxy resins react poorly catalyzed by tertiary amines, which exhibit low basic strength. Epoxy resins lose some of their functionality and the strength of their cross-link networks when organic chloride linkages appear.

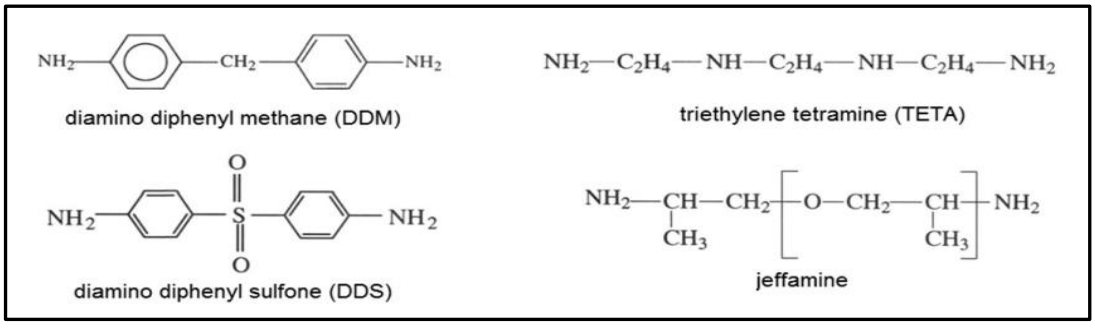
EPOXY SYSTEM CURING MATERIALS/AGENTS:

Curing forms a rigid, insoluble, and heat-resistant epoxy network. Epoxy resins can't form cross-links during curing without auxiliary compounds, it called curing agents or hardeners. The curing agent controls the epoxy resin's reactivity, viscosity, chemical bond type, and cross-link level. The curing process often alters the epoxy crystal structure, forming a compact, non-crystalline polymer network [94]. Epoxy resins can be effectively cured using amine-based hardeners, thiol, and alcohol molecules. According to their chemical makeup, epoxy-curing agents are further classified into Amines (aliphatic, aromatic and cycloaliphatic), Anhydrides, Polyamidoamines, Polyamides, Polysulphides, Dicyandiamine (DICY). Composites often make use of the first two curing materials or agents.

A. Curing agents based on Amines

Amine compounds are frequently used curing agent to create epoxy resin thermosets. The nucleophilic reactivity of amine compounds determines whether they are aliphatic, cycloaliphatic, or aromatic. "By selecting appropriate epoxy monomers and amine hardeners, the density of the cross-linked network in cured epoxy resins can be precisely regulated once stoichiometric balance is achieved". When cured with amine compounds, low molecular weight, highly functional epoxy resins tend to form a densely cross-linked polymer network. Figure 5 illustrates the chemical structures of four distinct types of amine curing agents.

Figure 5 Organic structure of various amines-based curing agents [68].



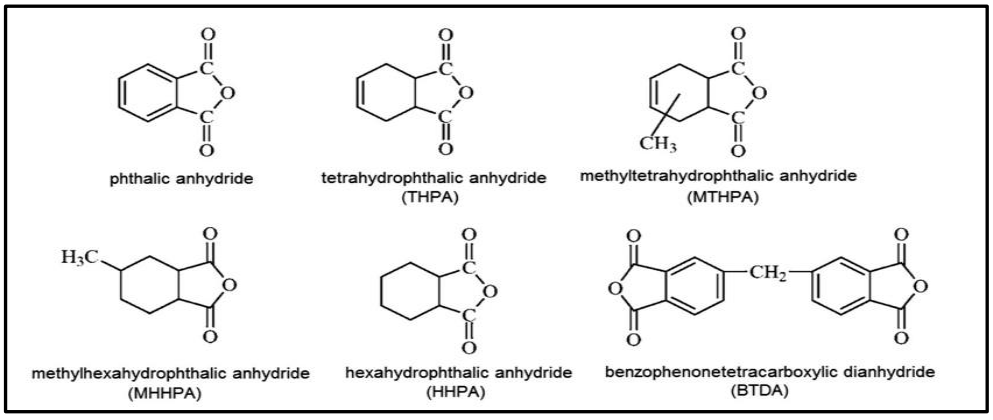
Amines' functionalities are defined by the amount of hydrogen atoms in their molecules. "Compared to secondary amines, which typically react with only one epoxy group, primary amines are more reactive due to the presence of two hydrogen atoms bonded to nitrogen. Although Tertiary amines do not react directly with epoxy groups due to the absence of active hydrogen atoms, but they serve as efficient catalysts that help accelerate the curing process [95]."

Aliphatic amine is an energy-efficient alternative because it cures epoxy resins at normal temperatures. It is very advantageous for coating and adhesion operations when dealing with complicated structures. Some structures may not be able to withstand the heat required by other amine curing agents, and this might lead to wasted energy. To achieve an ideal curing reaction with aliphatic amines, however, high temperatures are needed during the post-curing period [96]. Epoxy resins that use an aliphatic amine as a curing agent have one major drawback: they can't create the crosslinked polymer matrix when the temperature glass of transition (Tg) rises over 120°C. To overcome this weakness, aromatic amines are used as curing agents. "Aromatic amine curing agents typically require elevated temperatures, often ranging between 250°C and 300°C, to initiate and complete the curing process [97], Epoxy resins that harden with heat can handle high temperatures, which is why they are often used in strong composite materials.

B. Curing agents based on Anhydride

Typical properties of thermosetting polymer networks, including epoxy and anhydride, include a long working time, doesn't produce heat during curing, and shows very little shrinkage even at high temperatures. The curing process is often supported by additives such as Lewis bases, acids, or tertiary amines, which help accelerate the reaction, or acid molecule and occurs slowly at 200°C. To get epoxy resin that can withstand high temperatures, the catalyst concentration must be accurate control depends on the specific type of anhydride curing agent used. A mixture of one-part epoxy and eighty-five percent anhydride may generate an epoxy thermoset with outstanding thermal, mechanical, and electrical characteristics [98]. Several anhydride curing agents with different chemical structures are available for purchase, as seen in Figure 4. The curing procedure necessitates meticulous environmental coding of all anhydrides since they are hygroscopic to moisture.

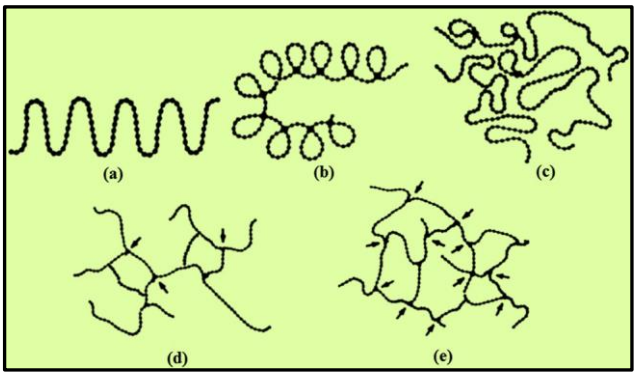
Fig. 6 Chemical structure of anhydride epoxy resins [99].



Curing behavior of epoxy systems

Epoxy resins are polymers that consist of a lengthy series of carbon-carbon bonds. They also include two valence bonds crucial for attaching hydrogen and other tiny hydrocarbon components. A linear polymer construction scheme is devoid of cross-linkages, as often seen in thermoplastic structures, as shown in Figure 7. Polymer networks can form either through chemical bonding between long, straight polymer chains or by combining resin monomers that naturally build into a three-dimensional structure, as shown in Figure 7. The cross-linking process involves complex interactions within thermoset resin compounds, setting them apart from other types of polymers. This procedure is essential to the formation of materials with enhanced durability and stability. Notably, certain cross-linking reactions can be initiated by thermal energy, and interestingly, some of these reactions can take place even at ambient temperature (around 25°C). This occurs because of the unique curing cross-linking behavior in epoxy matrices, which transforms the material into a robust, three-dimensional network, ultimately improving its thermal and mechanical properties.

Fig. 7 Diagrams of linear configuration polymers (a–c), a network polymer with mild cross-linking (d), and a network polymer with heavy cross-linking (e).



CURING AGENTS IN BIO-BASED EPOXY RESIN

Polymers have attracted attention from natural sources like plant oils because of their inexpensive cost and simplicity of epoxidation. This epoxy is biobased, manufactured from renewable resources, and is less harmful to the environment. A diverse range of bio-based curing agents has emerged as sustainable alternatives to conventional petrochemical hardeners in epoxy systems. These include naturally occurring acids like citric acid and tannic acid, amino acids such as L-arginine and L-tryptophan, and renewable phenolic compounds derived from cashew nutshell liquid (cardanol) and lignin. Their functional groups—ranging from carboxylic acids and phenolic hydroxyls to primary amines—enable effective crosslinking, contributing to properties like thermal robustness, mechanical toughness, and anti-corrosion behavior. Additionally, rosin-based amines, terpene derivatives, and polyamidations synthesized from fatty acids offer tailored performance for coatings and adhesives. The integration of these curing agents supports the development of environmentally friendly epoxy systems with reduced toxicity and improved biodegradability [100] [101] [102].

MGOL-EP, a thermosetting precursor derived from magnolol, was formulated into bio-rich epoxy thermosets. When the curing temperature was lowered to 61 °C, the resulting MGOL-EP/DDM system—cured with 4,4′-methylenedianiline (DDM)—exhibited a notable decrease in both cross-linking density and biphenyl structural content [103].” Many bio-based epoxy thermosets are available, as well as the monomers and curing agents needed for epoxy. When applied to well-cured epoxies, it dramatically changes their behaviour. It is still challenging to achieve adequate overall performance with high-performance epoxy thermosets with aromatic structures.

This magnolol and MGOL-EP show promise for future industrial scalability. After curing, the epoxy thermoset MGOL-EP-SC outperformed MGOL-EP/ DDM in every respect [104].

The basic biomass ingredients used to make bio-based thermosets have a major impact on their final characteristics. Bio-based epoxy thermosets are often synthesized from renewable feedstocks such as vegetable oils, which gives flexibility to the polymer backbone. Thermally cured epoxy systems depend on heavily on their aromatic backbone. The structural similarities between natural monomeric phenols and high-performance thermosetting polymers make them very promising for this use.

CONCLUSION

This review introduces a brief idea curing agents for epoxy metal coatings that significantly enhances adhesion strength, corrosion resistance, and longevity through a novel formulation of organ silane, advanced amine chemistry, and nanoparticles. Extensive testing reveals this curing agent outperforms traditional options in strength and environmental resilience, making metal surfaces more durable against wear and corrosive damage, especially in demanding industries like manufacturing and automotive. The improved properties reduce maintenance costs and downtime, thereby increasing the service life of critical infrastructure. While the research primarily focuses on laboratory-scale development, promising results suggest potential for scalability and real-world applications. Future investigations may explore the curing agent's versatility for other substrates, optimization for specific conditions, and integration with emerging technologies like self-healing coatings. Overall, this review article contributes to both technical advancements in curing agent design and broader sustainability goals by minimizing resource consumption and material waste, with the potential to redefine performance standards in metal coatings for years to come.

Data Availability: The data that support the findings of this study are available on within the article.

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