A REVIEW ON DEVELOPMENTS IN CURING AGENTS FOR EPOXY RESINS

Joghee Manivannan[1] and Kaliappan Kaliraj[1*]

Department of Chemistry,

V.S.B College of Engineering Technical Campus, Coimbatore, Tamil Nadu, India

[#] *Both authors contributed equally to this work. Email: klrj16@gmail.com*

**Corresponding Author*

Abstract:

Epoxy resin systems consist of two parts i.e., Part A and Part B. The Part A is the base epoxy resin and Part B is known as the curing agent which is also called as hardener .The curing agent, Part B is responsible for reacting with the epoxy groups present in the epoxy resin i.e., part A. Reaction of curing agents with epoxy resins results in hard, thermoset material suitable for industrial applications. For epoxy resins there are large number of materials that can be used as curing agents to cover the entire range of applications from very low to high curing temperature. The functional groups of curing agents are ranging from amine, mercaptan and phenol to phosphazene derivatives. The choices of curing agents and catalysts have grown due to their usage in different field of applications. Selection of the curing agent is mainly based on the performance requirements of the cured final product. Epoxy curing agents are primarily used in the construction industry's flooring, adhesives, and protective coatings. Recent advancements in epoxy curing agents for coatings focuses on improving sustainability, performance, and application ease. Developments include bio-based curing agents and those tailored for high-performance applications. The variety and the wide range of curing agents developed in the recent past for epoxy resins are overwhelming. This review mainly provides a survey on the recent developments of curing agents and their specific performance characteristics.

Key Words: Epoxy Resin, Curing Agents, Polymerization, Cross Linking, Thermoset Materials.

Introduction

Epoxy resins are one of the most significant classes of synthetic resins find broad range of industrial applications. Epoxy resin products are characterized by their durability and high protective properties. They offer solutions to industries such as chemicals, automobiles, marine, aerospace, construction, energy and electronics. The main sectors of applications of epoxy resins are shown in the figure 1. This large interest in epoxy resins originate from its excellent mechanical strength, adhesion to different kinds of surfaces, its resistance to corrosion and chemicals. Epoxy resins are of three types 1) Cycloaliphatic epoxy resins 2) Glycidated resins 3) Epoxidized oils. Among these epoxy resins, glycidated resin types prepared from bisphenol-A and epichlorohydrin constitute the most important class of resins. These epoxy resins which are diglyceryl ether of bisphenol-A (DGEBA) are prepared by condensation of bisphenol-A with epichlorohydrin in presence of an alkaline catalyst. The excellent performance properties of epoxy resins are due to the bisphenol-A moiety (toughness, rigidity and low temperature performance), the ether linkage (chemical resistance) the hydroxyl group and the three-member cyclic ether group commonly known as epoxy groups (reactivity and adhesion).

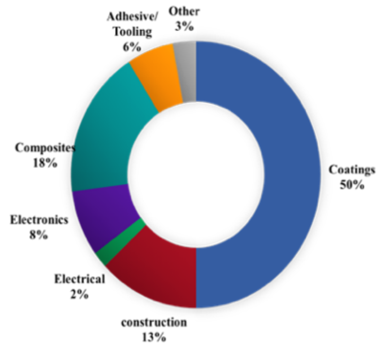

Figure 1: Global sector wise epoxy resin applications. (reproduced from ref. [1] with permission from American Chemical Society, Copyright 2014).

The cured epoxy resin itself is generally brittle in nature and to convert the epoxy resins to hard, fusible thermoset network, it is necessary to use chemical curing agents. The primary reactions arising from curing are poly addition/co-polymerization reaction with a multi-functional curing agent or by homopolymerization initiated by a catalytic curing agent.

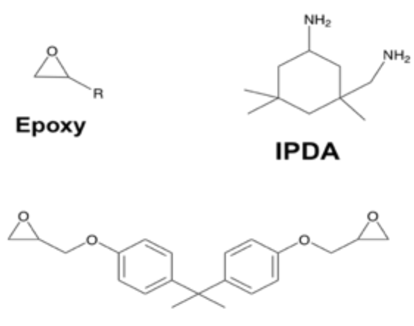

Figure 2. Structures of typical epoxy, top left, Isophorone diamine (IPDA) (Amine curing agent), top right and DGEBA, bottom [2].

The curing agents which are widely used are aliphatic and aromatic amines, aromatic amine adducts, polyamidoamines and acid anhydrides. The reaction of curing agents with epoxy resins results in formation of oxirane ring unit on the ends of the epoxy resin. The epoxy resins react with materials having active hydrogen to form an –OH pendant chains and hydroxyl group contributes to the outstanding adhesion of epoxy resins to different substrates.

There are varieties of curing agents developed in the recent past to modify the epoxy resin to hard infusible thermoset network. The tremendous development in the different types of curing agents and the catalysts are due to two reasons. First, there are various types of epoxy resins developed and which necessitated the development of suitable curing agents for these resins. This has resulted in development of polyfunctional amines, polybasic carboxylic acids, mercaptans and some organic chemicals. The second and important reason is the necessity to modify the existing curing agents to meet the specific application requirements.

The aim of this review work is to provide comprehensive theoretical information on wide range of curing agents available for epoxy resins to assist the researchers, innovators and industrial users to verify the facts and for the extension of knowledge on the developments of these curing agents. The epoxy hardeners are categorized based on their chemical structure, reactivity, curing characteristics and distinct properties needs to be tailored to specific end use applications.

2. Nitrogen-containing curing agents

2.1. Aliphatic amine curing agents

Both primary and secondary amines are used for curing the epoxy resins at room temperature, the former being more reactive than the latter [3]**.** Aliphatic amines as curing agent gives fast curing system with low viscosity, good chemical resistance, excellent solvent resistance and mechanical strength but imparts less flexibility to the applied system. The unmodified amines creates certain handling hazards because of their high basicity and comparatively high vapor pressure [4]. However, it is usually modified to eliminate problems caused by objectionable volatility of amines.

2.2. Aromatic amine adducts based curing agents

The aromatic curing agents improve the thermal stability, chemical resistance, and mechanical properties of the cured resin. Aromatic amines are less reactive than aliphatic amines and usually require high curing temperatures [5]. Because of high cross-link density and aromatic backbone, most epoxy resins are rigid materials and fail by brittle fracture.

However, the aromatic amines holding an electron donor substituent influences the curing process of epoxy resin at lower temperature. The chemical structure of the amine, the steric restrictions towards the epoxy-amine addition reaction, physical interactions among different functional groups of the constituent components influences the cure kinetics. The effect of the modifications is to reduce the curing properties of the coating system. This aromatic amine adducts cures at slightly lower temperatures and will have better color stability. Generally aromatic amines provide higher heat resistance and chemical resistance to the cured film compared to aliphatic amine-based curing agents.

2.3. Curing agents based on Polyamides and Polyamidoamines

Amidoamines are basically mono-adducts of polyamine with fatty acids and having higher molecular weight than polyamine and therefore longer reaction rate. Polyamidoamines are polymerized unsaturated fatty acids with higher order homologues of the ethylene amine series. The various range of polyamidoamine are obtained with different fatty acid/amine ratios. The products formed differs in molecular weight, physical form, amine content and reactivity with lesser volatility. The ratio of polyamidoamines to be mixed with epoxy resins may be varied to get required cure properties. The properties obtained can be from tough and hard to flexible and soft. Hence, they are user friendly and also, they result in good adhesion to a wide variety of substrates [6]. Specifically, the amidoamines are well-known for their adhesion to concrete and good performance under humid conditions. Hence, they are widely used in civil engineering applications such as flooring, concrete bonding and crack injection. They also find use in high solids coatings, adhesives, electrical encapsulation.

Polyamide are bi-adducts with bigger molecular weight and thus, reflect higher viscosity with longer pot life. Generally, polyamides are very familiar for their water and corrosion resistance. Polyamide cured epoxy resins provides better adhesion and effective barrier protection on surfaces even if the surface is under prepared. Hence these are generally used to protect mild steel structures from corrosive environments. Polyamides are widely used in metal coatings applications particularly as primers, and also find uses in adhesives, putties, sealants, cable jointing and electrical encapsulation. But the main disadvantage of polyamide cured epoxy coating is the coating disintegration from UV radiation and also poor resistance to high-humid conditions.

Therefore, they are further modified to improve the weatherability and UV resistance [7]. In one of the studies reported epoxy polyamide resin has been modified with different ratio of Camphor oil. The physico-chemical and electrochemical properties of this film on steel in 0.5M NaCl solution have been studied. It was found that when 5wt.% of Camphor oil is incorporated in epoxy polyamide coating, it gives maximum protection for the mild steel surface [8].
Hence, the epoxy resin cured with polyamide or polyamidoamine forms well plasticized thermosetting polymer with good rigidity from its high hydrocarbon moiety in its molecules. The coating cured with this resin system also provides superior mechanical properties by forming a stiff, strong, high tensile strength, compression and bending strength film with excellent shock resistance to metal surfaces.

2.4. Curing agents based on Modified amines

Through modifications of amine curing agents the targeted properties can be enhanced such as: Chemical resistance, Blush resistance, Adhesion, improved pot life, rate of curing and reduced toxicity and irritation to skin [9]. Amine adducts are prepared by reacting excess primary amines with epoxy resin. The excess amount of polyamine consumes all the available epoxy groups forming an amine adduct containing active hydrogen of the residual amino groups. The adduct has a high molecular weight, it is less volatile, releases less amine odour and less toxic. Also, due to its increased molecular weight, these are less susceptible to blush formation than their unmodified amine precursors.

A novel butyl-glycidyl ether-modified poly(propyleneimine) dendrimer (PPIs) has been prepared which was found to be capable of curing bisphenol-A epoxy resin to an acceptable reaction extent [10]. The non-isothermal reactions, thermal stabilities and mechanical properties of their cured epoxy resin were investigated. This work offers a unique way of preparing modified aliphatic-polyamine curing agents, and gives an opportunity to learn about the amine-adduct curing agents which are commonly used in room-temperature-cure epoxy coatings and adhesives.

Paul Jones (2020) described the new series of ketamines developed for improvements in the following properties a) low free amine in supply product b) low free amine following hydration in application (when hydrolyzed) c) Improved compatibility d) Improved surface appearances e) Maintain pot-life and cure properties [11]. They outperformed their conventional counterparts in technical performance offering both long pot-life and reduced hazard, making them as useful curing agents for coating industry. The study on novel aromatic amine functional curing agents like amine functional aniline formaldehyde condensates (AFAFC) and amine functional chloroaniline formaldehyde condensates (AFCFC) as a function of concentration acting as a curing agent for diglycidyl ether of bisphenol A (DGEBA) resin has been reported [12]. Equimolecular mixture of curing agent and epoxy resin were subjected to curing reaction which showed the occurrence of effective curing and revealed that the reactions were first order. The mechanical studies showed that AFAFC of greater rigidity than AFCFC and this amine cured epoxy networks exhibited thermal stability up to around 230-240^{0}C.

2.5. Imidazoles as curing agent

Imidazoles are a type of anionic polymerizing curing agent for epoxy resin provides good adhesion on metals and forms resins with high tensile strength. Imidazoles are characterized by a comparatively long pot life and the ability to form cured resin at faster rate with a high heat deformation temperature when it is treated at a moderate temperature (80°C to 120°C) for a short time. There are also various derivatives made having moderate reactivity to improve workability. The Imidazole derivatives as latent curing materials for epoxy thermosetting resin were studied [13]. It was demonstrated that a mixture of imidazoles and latent curing agent with epoxy resins has long storage stability at room temperature, which was not accomplished with the imidazoles themselves.

3. Sulphur-containing curing agents

3.1. Polymercaptan curing agent

Polymercaptans are attracting attention as a low-temperature curing agent and used when the speed of cure is important [14]. It also provides toughness, durability or strong adhesion. The other advantages of polymercaptan are their lower toxicity compared to other hardeners, light in color and excellent adhesion to metals, glass, concrete, wood. Polymercaptan is also used to accelerate other amines and polyamides.

The invention to provide a polymercaptan for the crosslinking of epoxy resins to yield thermoset polymers having particularly good resistance to the absorption of water and thereby improving the adhesion bond strength has been reported [15]. The thermoset polymer obtained has got fast-curing characteristic with commercial feasibility for production. It has also been found that more SH groups are desirable on the end of the carbon chain in order to result in good properties of a thermoset polymer. Further, it is also reported that the polymercaptan free of any other reactive functional groups is desirable for its better performance.

Multifunctional sec-thiols were prepared and used as a hardener with DGEBA and its performance were studied [16]. The cure kinetics was found to be slower than that of primary thiol hardener, but it showed increased glass transition temperature without any noticeable change in thermal stability. The slower curing of sec-thiol provided long-term stability which results in increased pot life in industrial applications.

3.2. Polysulfide resin

Polysulfides are not used exclusively as a curing agent for epoxy resin due to its slower cure rate. Polysulfide structures are used to modify epoxy resin to provide excellent flexibility, impact resistance, chemical resistance and anti-corrosive properties [17]. Since polysulfide is a highly flexible elastomer, by addition of liquid polysulfide elastomer to epoxy resin gives better flexibility and provide strength to epoxy matrix. In applications where, maximum flexibility is required the percentage of polysulfide will be higher than epoxy resin. It is the high concentration of sulphur linkages that also provides these products with their unique chemical properties. The liquid polysulfides are generally added to the liquid epoxy resin component because of possible compatibility problem. When used in combination with a tertiary amine or polyamine resin, it works as a room-temperature curing agent. Due to the good low temperature properties of epoxy-polysulfide adhesives they have found significant use in the building and construction industry.

3.3. Phenyl bis-thiourea

The curing properties of novel curing agent based on phenyl bis-thiourea for an epoxy resin system has been studied [18]. Three different phenyl bis-thioureas: 4,4′-(bis-thiourea) diphenylmethane (DTM), 4,4′-(bis-thiourea) diphenyl ether (DTE), and 4,4′-(bis-thiourea) diphenyl sulfones (DTS) were synthesized and used as curing agents for the epoxy resin di-glycidyl ether bisphenol A (DGEBA). For comparison studies, the epoxy system was also cured using the conventional aromatic amine 4,4′-diaminodiphenyl ether (DDE). From the oxidative induction temperature measured on DSC indicated that the phenyl bis-thiourea cured epoxy resins were found to be having better oxidative stability when compared to the conventional aromatic amine cured epoxy resin system. Hence sulphur-containing curing agents can be used both as pure curing agents and also as an additive to improve the curing process.

4. Oxygen containing curing agents

4.1 Anhydrides

Anhydrides used as epoxy-resin curing agents have been used widely as curing agents for electrical insulating materials due to their high electrical and thermal insulating properties. Anhydrides need severer curing requirements than amine-based curing agents, but they are suitable for making large moldings due to their long pot life and forming cured resins which are having relatively well-balanced electrical, mechanical, and chemical properties while generating a small quantity of heat [19]. Examples of some of the more commonly used acid anhydrides are phthalic, tri-mellitic, hexa-hydro phthalic and Nadic Methyl Anhydride.

The reaction mechanism of anhydrides with epoxies is complex and there are many competing reactions [20]. During the curing process an anhydride group first reacts with an aliphatic hydroxyl to provide an ester group and a free carboxylic acid. The free carboxyl group reacts

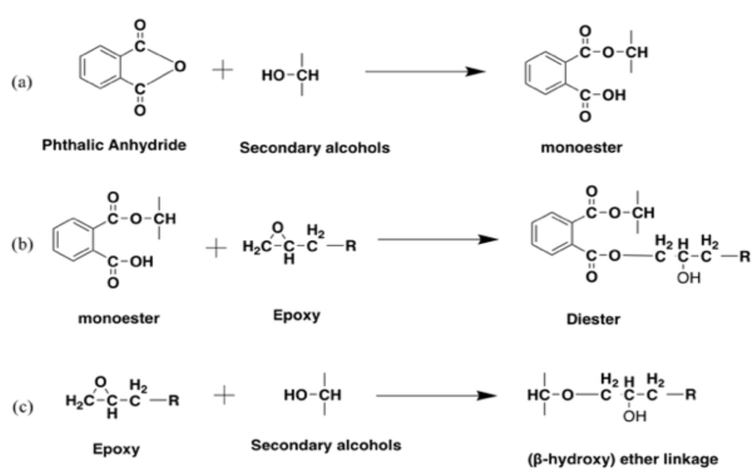

Figure.3. Scheme of reaction steps (a) formation of Ester group and free carboxylic acid. (b) Formation of Diester group (c) Formation of ether linkage

with an epoxy group to give a Diester. So, every time a carboxylic acid group reacts with an epoxy group, another aliphatic hydroxyl is created, and is then available to react with another anhydride group The carboxylic acid reacts with epoxy group forming a diester.

5. Latent curing agents

Latent curing agents are mixtures of curing agents with epoxy resin that can be stored at room temperature, and rapidly cured by heat, light, pressure and others. C. S. Chen et al**.** studied the boron trifluoride monoethyl amine (BFMEA) complex crosslinked epoxy resins [21]. The BFMEA cured epoxy resins have good strength, heat resistance, and electrical properties. BFMEA can act as a primary curing agent or a co-curing agent for epoxy resins. It reacts as a semi latent catalyst and provides long pot life for epoxy resins

Feng Wu et al. developed a novel multifunctional epoxy resin *N*,*N*,*N*′,*N*′-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) with stoichiometric latent curing agent dicyandiamide (DICY) [22]. The resulting cured TGDDM/DICY presented excellent mechanical, adhesive and dielectric properties and lower water absorption.

Adrian M. Tomuta et al. studied the use of dihydrazides as latent curing agents in diglycidyl ether of bisphenol-A coatings. A series of dihydrazides were prepared and these compounds were studied as latent curing agents [23]. The formulation was made with the ratio DGEBA/dihydrazide 2:1 (mol/mol). The thermomechanical characteristics, microhardness and toughness values obtained in the specimens could be related to the flexibility introduced by the dihydrazide structure.

The latent curing agents are significantly important to develop one-component epoxy resins [24]. As these latent curing agents are from unsustainable fossil resources, a new type of latent curing agent has been developed from bioresources and studied [25]. The bio-based amino acid containing amide bond was synthesized from 1,5-pentanediamine and maleic anhydride (PDA-MAH), and used together with a bio-based epoxy monomer from itaconic acid to achieve a fully bio-based one-component epoxy system. The obtained epoxy network exhibited significantly enhanced glass transition temperature, tensile strength and young's modulus.

5.1. Light-curing and ultraviolet-curing agents

Light curing of Epoxy Resin by UV-polymerization mechanism is an effective method of curing because it gives best performance, eco-friendly and good compatibility. Epoxy Resin and photo initiator or photo curing agents are combined together and then the mixtures are cured. The curing agents are decomposed by exposure to UV light to cure the resin [26]. These are considered as latent curing agents. These are attracting attention as a potential ingredient of non-polluting paints, since these agents are dissolved in liquid resins without using solvent and it does not pollute the environment. Photo cured Epoxy Resin are reported to be providing outstanding working performance, enhanced flexibility, excellent adhesion and resistance to many environmental hazards [27].

6. Phosphorus containing curing agents

Phosphorus containing curing agents have been synthesized through Mannich type reaction. They contain polyamino groups which improves the cure characteristics at lower temperature.

These Mannich bases were thermally cured with diglyceryl base epoxy resin and were compared with the conventional curing agents EDA, TTA. It was observed that the phosphorus containing epoxy resins (DGEBA/PEDA and DGEBA/PTTA) showed longer gel time and higher glass transition temperature [28].

Table 1. Gel times of epoxide/curing agents (equivalent ratio of 1:1) at different temperatures

Temperature (°C)	Gel time (hr)			
	DGEBA/EDA	DGEBA/PEDA	DGEBA/TTA	DGEBA/PTTA
25	100	–	72	–
50	17	21.5	10	13
80	4	9	2	6
120	0.3	0.5	0.2	0.5

Xiaojun Gu et al. have synthesized novel curing agent for epoxy resin based on phosphazene derivatives [29]. The study showed a lower starting curing temperature and a wider range of curing temperature that can help reduce the internal stress of epoxy materials. Phosphazenes with alternating nitrogen and phosphorus atoms in the main chains as its backbone had indicated that the flame-retardant efficiency increased in the curing system of epoxy resin. This novel curing agent with flame retardancy has broaden the potential application of Epoxy phosphazenes in many fields.

Lucie Zarybnicka et al. in his report on halogenophosphazene as curing agent for epoxy resin described the synthesis and characterization of hexachloro-cyclo-triphosphazene derivative and its subsequent use for curing epoxy resins [30]. The derivative was synthesized from hexachloro-cyclo-triphosphazene by nucleophilic substitution with isophorone diamine. The curing capability has been compared with original isophorone diamine. The derivative hexaisophorone diamino-cyclo-triphosphazene (HICTP) providing improved mechanical properties and also the flame resistance. The epoxy resin cured with the phosphorus containing HICTP exhibited lesser heat release, smoke release and amount of oxygen consumed, which resulted in slower flame spread.

Isocyanate Type Curing Agents

Polyisocyanates are very effective and versatile curing agents. They can react with hydroxyl or amine functionalities to form polyurethane or polyurea chains. But the disadvantage of using isocyanates is their sensitivity to moisture and also, they cause health hazards due to the availability of free isocyanate. Hence, they are used as blocked isocyanate to control the chemical reactivity. Blocked isocyanate enables 1K polyurethane systems with reduced free isocyanates and extends storage stability [31]. When unblocked, they react fast and reduces the pot-life significantly. Polyisocyanate can enhance many parameters such as mechanical properties and also improves chemical resistance of the system. As the isocyanate reacts primarily with the hydroxyl group, the higher molecular weight solid resins (in which the hydroxyl group predominates) are used in isocyanate cured compositions and there is a simultaneous reaction between epoxy and isocyanate to form heterocyclic oxazolidone rings [32].

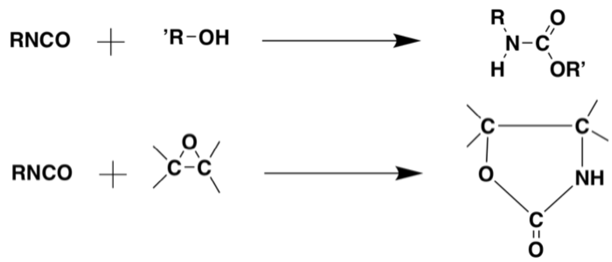

Figure 4. Scheme of reaction steps. (a) Formation of Ester. (b) Formation of heterocyclic oxazolidone rings

The polyurethane and epoxy resins are joined both by physical penetration of the chain (entanglement) and the chemical binding which has a significant influence on the properties of the product. The ambient cure, two component paint involving the reaction of epoxy resin with isocyanate system expected to produce high performance coating for a variety of special application including underground pipelines, structures and equipment in chemical industries.

7. Bio-based epoxy curing agent

Chemicals and materials derived from renewable resources have received considerable attention in recent years as the petroleum depletion and environmental problem become increasingly serious. Because of this, various bio-based epoxy curing agents have been prepared and studied. For instance, a novel vegetable-oil-based polyamine was derived from grape seed oil combing cysteamine chloride by thiol-ene coupling [33]. The outcome of this study led to the synthesis of a polyepoxide system in which both resin and hardener are based on the modified natural oils.

Rosin, a natural product derived from pine trees contains mixture high molecular weight organic acids and small percentage of other neutral materials. Rosin acids and their derivatives are important biobased alternatives to petroleum- derived materials. The acids, anhydrides, amines and amides derived from rosin which could be used as curing agents for epoxy resins. Maleopimaric acid is an important rosin derivative which can be modified with acids and amines to form new categories of curing agents. Rosin derived amine curing agent containing an imide structure displayed similar modulus but higher glass transition temperature than the commercial aromatic amine curing agent [34, 35].

Xuejuan Yang et al. synthesized bio-based epoxy crosslinking agent which is derived from myrcene and castor oil and studied the performance of the cured products [36]. Two different curing agents were synthesized and their cured properties were tested. Myrcene, a monoterpene is derived from the cracking of β-pinene, which is extracted from turpentine oil. The curing agent has been synthesized through Diels-Alder reaction of myrcene and maleic anhydride as an adduct (MMY) to crosslink epoxy resin. The crosslinked epoxy resin has shown better strength and modulus, but the impact property was poor and shown very low elongation at break. However, the toughness of epoxy resins could be enhanced by combining a flexible epoxy resin, curing agent or reactive additive into the network during curing [37].

The second curing agent has been synthesized to improve the flexibility of the cured film using Castor oil which is widely used in coatings, varnishes, paints and various types of other products. Due the long aliphatic chains in the triglyceride section, the products obtained from castor oil results in excellent flexibility. The myrcene-based adduct is modified by hydrolysis of castor oil to produce Ricinoleic acid. The modified myrcene-based adduct (CMMY) also utilized as the crosslinking agent for epoxy resin. Though the cured epoxy resins produced excellent flexibility, the poor strength limited their applications.

The crosslinked epoxy material expected to have both strength and flexibility when the two curing agents were mixed at different weight ratios and used to co-cure epoxy resin. When the weight ratio of CMMY was increased, the tensile strength has decreased but the elongation at break increased. The mixing of two curing agents was optimized to get the balanced properties of both strength and flexibility. The significantly improved toughness of the crosslinked epoxy resins showed that vegetable-oil-based curing agents could be utilized in preparation of flexible epoxy products.

The study of cationic UV-crosslinking of epoxidized bio-based resins has been found to be having numerous advantages over conventional thermal curing [38]. In particular, the photopolymerization has low volatile emissions, fast curing speed, and no shrinkage. Moreover, since this technique does not require any additional heating, it can be cost-effective. However, the properties achieved by bio-based UV-cured thermosets can match the requirements needed in the fields of coatings, films or adhesives only.

7.1. Phenalkamines

Phenalkamines are synthesized form cardanol, a derivative of Cashew nut shell liquid CNSL, formaldehyde and amines by Mannich reaction [39]. Cashew nut shell liquid (CNSL) is a by-product from the cashew processing contains cardanol as one of the components. It is abundantly available at low cost and contains cardanol, 2-methyl cardol and anacardic acid. Cardanol can be easily modified to make it suitable for coating applications [40].

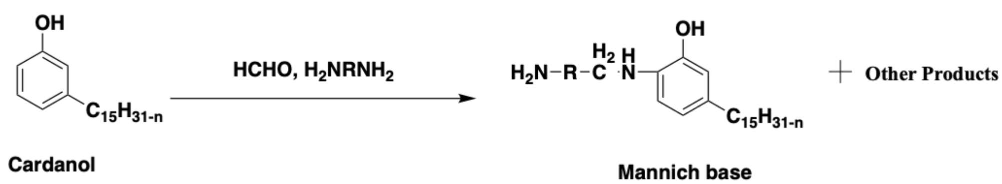

Figure 5. Synthesis of Phenalkamine from cardanol.

As it is a phenolic compound with aliphatic long chain at meta position it provides the required balance of hardness and flexibility required for various polymer and coating applications [41]. Phenalkamines are now emerging as a new class of curing agents for epoxies and have gained significant attention due to their numerous advantages, including fast and low temperature curing even in wet and humid conditions and show excellent chemical properties [42-44]. Coating properties majorly depend on amine value, structure of diamines (aliphatic, aromatic or cycloaliphatic), functionality and molecular weight of resultant Phenalkamine [45]. Literature has suggested that phenalkamines exhibit excellent wear resistance, impact strength and elongation than that of the polyamine curing agent used for curing epoxies [46].

The light color cardanol based epoxy curing agent prepared from cardanol butyl ether, formaldehyde and diethylenetriamine found to be less reactive than normal phenalkamine and showed much higher impact strength and sheer strength. It could be due to the cavities formed in the curing process [47].

Kunal Wazarkar et al. have synthesized structurally different phenalkamines based on cardanol and evaluated their effect on performance properties of the coatings [48]. They have synthesized various phenalkamines by choosing different polyamines, including hexamethylene diamine (HMDA), diamino diphenyl methane (DDM) and other amines containing aliphatic chains. All these phenalkamines were mixed with commercial epoxy resin to prepare coatings which were then evaluated for mechanical, chemical, thermal, optical and anticorrosive properties. Commercial phenalkamine was used for comparison purpose. The presence of aliphatic chains allowed easy permeation of water and oxygen, therefore increasing the rate of electrochemical reactions at surfaces and showed poor electrochemical properties. It was observed that anticorrosive properties evaluated using a salt spray test and electrochemical impedance spectroscopy revealed significant improvement in anticorrosive performance of coatings cured with synthesized phenalkamines based on Diamino diphenyl methane (DDM) compared to the coatings based on commercial Phenalkamines. The corrosion rate of epoxy-phenalkamine systems were analyzed by DC polarization method, it showed that EP-DDM coatings having lowest corrosion current, which is indicated in Tafel parameters shown in Table 2. It was inferred that to obtain optimum performance properties of the coatings, a combination of phenalkamines can be used.

Table 2. Tafel parameters of epoxy-phenalkmines coatings.

Coatings	Corrosion Potential (mv)	Current (A)	Corrosion rate (mmpy)
EP-D400*	202.17	1.345E-09	3.89E-08
EP-DDM	51.32	0.634E-09	1.05E-09
EP-HMDA	–327.61	3.085E-08	5.13E-08
EP-T403*	–469.57	0.877E-09	1.45E-09
EP-AG141*	–297.45	1.025E-09	1.70E-08

*D400, T403 & Ag141-Commercial Phenalkmines

The protective performance of the coatings was studied by incorporating polyaniline nanowire into epoxy polyurethane resin combination [49]. It showed excellent protection while evaluated using electron impedance spectroscopy. The polyaniline addition was carried out in different weight ratios and the coating containing 2% polyaniline showed the maximum corrosion resistance.

The Influence of cross-linking agents and curing condition on the performance of epoxy coating has been studied with five cross-linking agents including phenalkamine have been investigated by evaluating their physico-mechanical characteristics, thermal properties and anticorrosion performances [50]. The cross-linking agents used are 1) Modified cycloaliphatic amine 2) Polyamine adduct 3) Modified aliphatic ketimine 4) Phenalkamine 5) Phenalkamide. Phenalkamine and Polyamine adduct-based curing agents showed superior drying and mechanical properties compared to others. The phenalkamine-based coatings showed excellent anticorrosive properties at low temperature when evaluated by EIS. Table 3 shows the comparison of physico-mechanical and anti-corrosion performance properties when cured at C1 (1:0.6), C2 (1:0.8) and C3 (1:1) concentrations indicated that coating concentration with C2 combination produced optimum properties to provide long-term corrosion protection to the mild steel substrate at low temperature application. It is evident from this study that the unique balance of coating performance was obtained by phenalkamine curing agent at the concentration of 1:0.8.

Table 3. Coating properties at varying concentration of Phenalkamine

	Phenalkamine curing agent, Concentration		
Properties	**C1, (1:0.6)**	**C2, (1:0.8)**	**C3, (1:1)**
Physical Properties			
Set to touch dry (hours)	3	2.15	2
Mechanical Properties			
Adhesion strength (Mpa)	6.6	8.8	9.4
Tensile strength, (Mpa)	5.4	5.9	11.1
Elongation at break, (%)	9.1	3.1	1.9
Scratch hardness, (Kg)	3.5	3.1	4.7
Thermal Properties			
Tg, (^oC)	30.2	52.8	68.4
Cross-link density, (10^3 mole/cc)	3.8	4.6	6.1
Coating resistance			
After 1020 h, Ohm.cm^2	1.2×10^7	1.4×10^8	3.9×10^8

Phenalkamines derived from cashew nut shell liquid, though provide better performance characteristics to epoxy coatings, it produces dark color coatings which limits its applications to primers & undercoats and surfaces where color is not critical. The phenalkamines blended with polyamine salts and phenalkamines comprising at least one aromatic or alicyclic ring in the diamine side chain have been developed to give coatings with reduced Gardner color index compared to phenalkamines [51]. Hence, the synthesis of the curing agents for epoxy resins from bio-based cardanol with its specific performance characteristics has opened up a new strategy for large-scale preparation of these materials. These natural renewable resources meet the critical demand for reducing the consumption of petrochemical products yet providing similar or better performance characteristics required for specific applications.

7.2. Phenalkamide

Phenalkamides are new hybrid molecule and has unique coating properties. This novel class of epoxy curing agents were developed to fill a gap between polyamide and phenalkamine chemistries. By chemically combining these two materials and forming the product as phenalkamides will offer the benefits of both, while mitigating their limitations [53]. Coatings formulations based on phenalkamides have the desired color stability, overcoatability and flexibility of polyamides, but with the outstanding corrosion protection and fast low temperature cure of phenalkamines. Further, the improved color stability and extended overcoatability solves the problem of longer intervals between application coats. The combined properties as reported above makes phenalkamides an efficient curing agent for multi-purpose epoxy coatings. The phenalkamide curing agent is considered as an advancement of phanalkamine technology which can provide a broader range of performance properties to epoxy resins for applications as industrial protective coating.

Conclusions

In order to enhance the specific properties, improve processing and to address limitations of existing curing agents, new curing agents are developed which can lead to better performance in various applications. In this study, we have reviewed different types of curing agents for epoxy resin which includes Aliphatic amine, Aromatic amine, Modified amines, Polyamides, Imidazole, Polymercaptan, Polysulfide resin, Anhydrides, Latent curing agents and Bio based curing agents. The specific performances of these curing agents and their suitability to different surface applications were reviewed. The curing agents imparting better performance properties for some specific application includes Amine adducts and Modified amines for low temperature cure and color stability, Anhydrides for electrical insulation, Phosphorus containing curing agents for fire retardancy, Isocyanate cured epoxy for high chemical resistance, Phenalkamine & Phenalkamide curing agents for low temperature cure, excellent chemical & mechanical properties and for its origin from renewable resource etc., The large choice of curing agents offers numerous possibilities to the selection of the right material. Hence, the most suitable curing agent can be selected considering the nature of surface, application conditions, workability and other specific factors. In this review, only the developments of different types of curing agents for epoxy resins and their corresponding specific performances were discussed. In practical use, they are mixed with diluents, coupling agents, fillers and other additives to improve the curing properties, workability, stability etc., and these materials will also have considerable additional impact on their performance.

Conflicts of interest

There are no conflicts of interest to declare.

References

[1] *C. Ding and A.S. Matharu, "Recent Developments on Biobased Curing Agents: A Review of Their Preparation and Use", ACS Sustainable Chem. Eng, **(2014)**, 2, pp. 2217-2236.*

[2] *E.A. Baroncini, S. Kumar Yadav, G.R. Palmese, J.F. Stanzione, "Recent advances in bio-based epoxy resins and bio-based epoxy curing agents", J. Appl. Polym. Sci., **(2016)**, 133, pp. 44103.*

[3] *D J Glover, J V Duffy and B Hartmann, "Steric hindrance in the amine - epoxide reaction". J. Polym. Sci. Poly. Chem. Ed. **(1998)**, 26:79.*

[4] *F. X. Perrin, T. M. H. Nguyen and J. L. Vernet, "Chemico - diffusion kinetics". European Polymer Journal, **(2007)**, 43, pp. 5107-5120.*

[5] *J. L. Massingill and R. S. Bauer, "Epoxy Resins – Reactions of Epoxides and Curing Mechanisms". Applied Polymer Science, **(2000)** 21st Century.*

[6] *W. R. Ashcroft, "Chemistry & Technology of Epoxy Resins- Curing Agents for Epoxy Resins". Chapman & Hall., **(1993)**, pp. 37-71.*

[7] *Sukanya Pradhana, Priyanka Pandeya, Smita Mohanty and Sanjay Kumar Nayak "Insight on the Chemistry of Epoxy and Its Curing for Coating Applications: A Detailed Investigation and Future Perspectives". Polymer-Plastics Technology and Engineering., **(2016)**, 55, pp.862–877.*

[8] *M. Selvaraj; K. Maruthan; G. Venkatachari, "Studies on enhancement of surface durability for steel surface by camphor oil modified epoxy polyamide coating" Corrosion Science, **(2006)**, 48, pp. 4365–437.*

[9] *Bruce Burton L "Amine Curing of Epoxy Resins". Paints & Coatings Industry Magazine, **(2006)**, 22, pp. 68-77.*

[10] *Jintao Wan, Zhi-Yang Bu, Cun-Jin Xu, Bo-Geng Li and Hong Fan "Novel Amine Adduct Curing Agent". Thermochemica Acta, **(2011)**, 519, pp. 72–82.*

[11] *Paul Jones "A New Generation of REACH- Compliant Ketamine Epoxy Curing Agents". Paint & Coatings Industry **(2020)**, 1, pp. 1-7.*

[12] *T. Maity, B. C. Saman, S. Dalai and A. K. Banthia. "New Aromatic Amine Functional Curing Agents" Materials Science and Engineering, **(2007)**, 464, pp. 38-46.*

[13] *K. Arimitsu, S. Fuse, K. Kudo and M. Furutani, "Imidazole derivatives as latent curing agents for epoxy thermosetting resins". Materials Letters, (2015), 161, pp. 408–410.*

[14] *Polymercaptans /define mercaptan Wiki / **Wikipedia**.*

[15] *Richard. L. Harris, Paul H. Globe "Polymercaptans for curing epoxy resins" United States Patent., **(1978)**, 4,092,293, May 30.*

[16] *Seung-Mo, Hong and Seok, Ho Hwang, "Synthesis and Characterization of Multifunctional Secondary Thiol Hardeners Using 3-Mercapto butanoic Acid and Their Thiol−Epoxy Curing Behavior". ACS Omega, **(2022)**, 7, pp. 21987−21993.*

[17] *Chempedia.info/info/epoxy polysulfide/ **(2019)**.*

[18] *P. Ramesh, L. Ravikumar and A. Burkanudeen "Curing properties of novel curing agent based on phenyl bisthiourea for an epoxy resin system" Journal of Thermal Analysis and Calorimetry, **(2014)**, 115, pp. 713-722.*

[19] *Bryan Ellis "Chemistry and Technology of Epoxy Resins" Springer-Science-Business Media BV, 1st edition, **(1993)**.*

[20] *"Anhydride Cured-Epoxy Matrices" **Applied Poleramic Inc**. – Technical Note (3) BSH-2/14*

[21] *C. S. Chen and E. M. Pearce "The boron trifluoride monomethyl amine complex cured epoxy resins". Journal of Applied Polymer Science., **(1989)**, 37, pp. 1105–1124.*

[22] *Feng Wu, Xingping Zhou and Xinhai Yu "Reaction mechanism, cure behaviour and properties of a multifunctional epoxy resin, TGDDM, with latent curing agent dicyandiamide". RSC advances, **(2018)**, 8, pp. 8248-8258.*

[23] *A. M. Tomuta, Xavier Ramis, Francesc Ferrando and Angels Serra "The use of dihydrazides as latent curing agents in diglycidyl ether in bisphenol A coatings". Progress in Organic Coatings, **(2012)**, 74, pp. 59-66.*

[24] *Yukai Ito, Daisuke Aoki, and Koji Arimitsu, "Novel Thermal Latent Curing Agents for Epoxy Resins Basedon Dual-Locked Aminopyridines by Amidation and N-Oxidation". Macromolecules, **(2025)**, 58, pp. 2870−2878.*

[25] *Zhen Yu, Songqi Ma, Zhaobin Tang, Yanlin Liu and Xiwei Xu "Amino acids as latent curing agents and their application in fully bio-based epoxy resins" Green Chem, **(2021)**, 23, pp. 6566-6575.*

[26] *M. Fazal-ur-Rehman, Hira Naseer and Muhammad Atif "A Review on Photo-curing of Epoxy resins". International Journal of Technical Research & Science., **(2017)**, 2, pp. 441-446.*

[27] *T. Aziz, , F. Haq, A. Farid et al., "The epoxy resin system: function and role of curing agents". Carbon Lett., **(2024)**, 34, pp. 477–494.*

[28] *H. Liu, K. Xu, H Ai, L. Zhang, M. Chen, "Preparation and characterization of phosphorus-containing mannich-type bases as curing agents for epoxy resin". Polym Adv Technol. **(2010)**, 20, pp. 753-758.*

[29] *Xiaojun Gu ,Hao Wei, Xiaobin Huang and Xiaozhen Tang "Synthesis & Characterization of Novel Curing Agent for Epoxy Resin Based on Phosphazene Derivatives". Journal of Macromolecular Science, **(2010)**, 47, pp. 828-832.*

[30] *Lucie Zarybnicka, Radka Bacovska, Vacera M, Snuparek J,.Alberti M, Rychly J. and Kalenda P "Synthesis of Curing Agents for Epoxy Resins based on halogenophosphazene" -Wiley Periodicals, Inc. J. Appl. Polym. Sci., **(2015)**, 132, pp. 42917(1-9).*

[31] *Ryszard Pilawka, Krzysztof Goracy and Katarzyna Wilpiszewska "High-performance isocyanate-epoxy materials" Pigment & Resin Technology, **(2014)**, 43, pp. 332-340.*

[32] *J Manivannan, S Kalaiselvan & N Velmani, "Study of Epoxy – Isocyanate Coating System for High Performance Application in Chemical Industries". GEDRAG & ORGANISATIE REVIEW, **(2020)**, 33, pp. 2539-2548.*

[33] *M. Stemmelen, F. Pessel, V. Lapinte, S. Caillol, J. P. Habas and J. J. Robin "A Fully Biobased Epoxy Resin from Vegetable Oils". J. Polym. Sci., Part A: Polym. Chem., **(2011)**, 49, pp. 2434 -2444.*

[34] *Honghua Wang, Heiwei Wang and Gaungyuan Zhou "Synthesis of Rosin Based Curing Agents"- Polym. Int., **(2011)**, 60, pp. 557 -563.*

[35] *R. Chang, J. Qin and J. Gao, "Fully biobased epoxy from isosorbide diglycidyl ether cured by biobased curing agents with enhanced properties". J. Polym. Res., **(2014)**, 21, pp. 1-7.*

[36] *Xuejuan Yang, Chunpeng Wang and Shouhai Li "Biobased curing agents derived from Myrcene and Castor Oil". RSC Adv., **(2017)**, 7, pp. 238-247.*

[37] *H. Miyagawa, M. Misra, L. T. Drzal and A. K. Mohanty, "Fracture toughness and impact strength of anhydride-cured biobased epoxy". Polym. Eng. Sci., **(2005)**, 45, pp. 487-495.*

[38] *Camilla Noe, Minna Hakkarainen and Marco Sangermano "Cationic UV-Curing of Epoxidized Biobased Resins" Polymers, **(2021)**, 13, pp. 89(1-16).*

[39] *M. Kathalewar and A. Sabnis "Effect of molecular weight of phenalkamines on the curing, mechanical, thermal and anticorrosive properties of Epoxy based coatings", Progress in Organic Coatings., **(2015)**, 84, pp. 79-88.*

[40] *Voirin C, Caillol S, Sadavarte N, Tawade B V, Boutevin B, Wadgaonkar P P "Functionalization of cardanol: towards biobased polymers and additives". Polymer Chemistry, **(2014)**, 5, pp. 3142-3162.*

[41] *D. Balgude and A. Sabnis, "CNSL an ecofriendly alternative for the modern coating industry". Journal of Coatings Technology and Research, **(2014)**, 11, pp. 169-183.*

[42] *C. Cheng, D. Bender and H. Wang, "Phenalkamine curing agents and epoxy resin compositions containing the same" **(2001)**, US Patent 6262148B1, July 17.*

[43] *D. Balgude, A. Sabnis and S. K. Ghosh, "Synthesis and characterization of cardanol based aqueous 2 K Polyurethane coatings". European Polymer Journal, **(2016)**, 85, pp. 620-634.*

[44] *Changhao Wu, Jixiao Wang, Fengrui Yang, Zhi Wang, Zhiye Sun, Full bio-based phenalkamine prepared by one-pot process used for preparing solvent-free protective coating, Progress in Organic Coating, **(2024)**, 188, pp. 108257.*

[45] *Mukesh Kathalewar, Kunal Wazarka and AnaghaSabnis "High performance polyurea coatings based on cardanol". Progress in Organic Coatings, **(2017)**, 1016**,** pp, 96-110.*

[46] *Panda R, Tjong J, Nayak S K, and Sain M M "Effect of Alkyl Phenol from CNSL on mechanical and dry sliding wear behavior of Epoxy Resin" J. BioResources., **(2015)**, 10, pp. 4126-4136.*

[47] *K. Huang, Y. Zhang, M. Li, J. Lian, X. Yang and J. Xia "Preparation of a light color cardanol-based curing agent and epoxy resin composite: Cure-induced phase separation and its effect on properties".* Prog. Org. Coat., ***(2012)****, 74, pp. 240 -247.*

[48] *K. Wazarkar and A. Sabnis "Phenalkamine curing agents for epoxy resin: characterization and structure property relationship" Material Science, Chemistry". Pigment &Resin Technology.* ***(2018)****, 47, pp. 281-289.*

[49] *D. Chu, J. Wang, Y. Han, Q. Ma and Z.Wang, "High performance epoxy protective coatingsincorporated with polyaniline nanowires using cardanol-based phenalkamine as the curing agent". RSC Advances,* ***(2015)****, 5, pp. 11378–11384.*

[50] *P. Shekhar, D. Tambe Shwetambari, N. Jagtap Ramakant, Choudhari. B.P. Mallik, "Influence of cross-linking agents and curing condition on the performance of epoxy coating", Pigment & Resin Technology.,* ***(2016)****, 45, pp. 354 –362.*

[51] *R. C. Bueno, A. Ferreira, R. M. Moon, S. Sato, S. C. Shah, "Phenalkamine and Salted Amine Blends as Curing Agents for Epoxy Resins".* ***(2009)****, U.S. Patent US20100286345 A1, July 2.*

[52] *Y. M. Kim, F. Tavares, L. Donald, and C. Mengjiu. "Phenalkamide - new hybrid molecule and its unique coating properties, Polymers Paint Color Journal,* ***(2013)****, 4586, pp. 25-27.*