# Recent Developments on Biobased Curing Agents: A Review of Their Preparation and Use

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**ABSTRACT:** The drive toward sustainable practices and principles across the supply chain has led to an upsurge in renewable materials. Epoxy resins are used in a wide range of applications in various fields, such as coatings, adhesives, castings, modeling compounds, impregnation materials, high-performance composites, insulating materials, and encapsulating and packaging materials for electronic devices. In order to achieve the desired properties, uncured epoxy resins must be converted to hard, infusible, thermoset networks in the presence of a variety of curing agents, also known as hardeners. This paper reviews recent advances in the development of curing agents from renewable materials. Attention is given to modified plant oils, biobased acids and anhydrides, amines and their derivatives, biobased phenols, rosin acids, and terpenes and lignin as biobased curing agents for primarily epoxy resin or biobased epoxy resin systems.

**KEYWORDS:** *Biobased, Curing agents, Epoxy resins, Renewable materials*
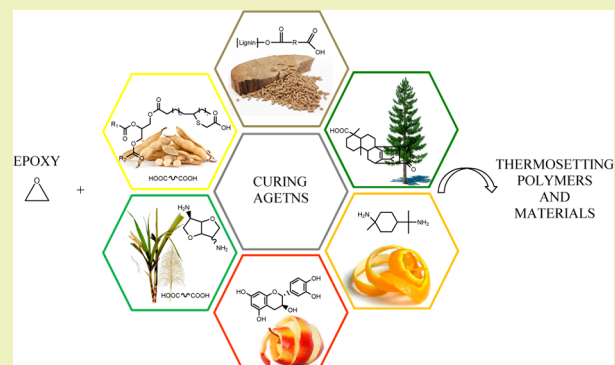


## ■ INTRODUCTION

Utilization of biomass is at best nonfood competitive and where it is produced as a waste or low value resource represents an outstanding opportunity for our next generation feedstocks for the chemical industry. According to Pike Research, green chemistry markets represented a market opportunity of $2.8 billion in 2011 and are expected to reach $98.5 billion by 2020. Judicious use of the 12 principles of green chemistry[1] (waste as a resource, biobased or renewable materials) is expected to save the chemical industry $65.5 billion by 2020. For example, thermosetting epoxy resins represent one unique opportunity for greening, and although nature already provides many biobased feedstocks such as vegetable oils and dicarboxylic acids, it is essential in the future that all components of the formulation are both renewable and sustainable.

Epoxy resins (containing at least one epoxide or oxirane functional group) find a broad range of applications as depicted in Figure 1 due to their wide-ranging dimensional, thermal, and environmental stabilities and ease of processability.[2]

In order to achieve the desired properties, curing agents (also sometimes known as hardeners, accelerants, and catalysts) are used to cross-link epoxy prepolymers and either act as catalysts or react with the epoxide group via polyaddition/copolymerization reactions to generate hard, infusible, thermoset networks.[3,4] Mika and Bauer[5] categorized epoxy curing agents into three broad types (Figure 2).

Xiao and Wong[6] highlighted the toxicity of curing agents, which is of growing concern as certain aliphatic- (diethylenetriamine, DETA, and triethylentetramine, TETA), cycloaliphatic- (isophoronediamine, IPDA), and aromatic-amines (methylene-
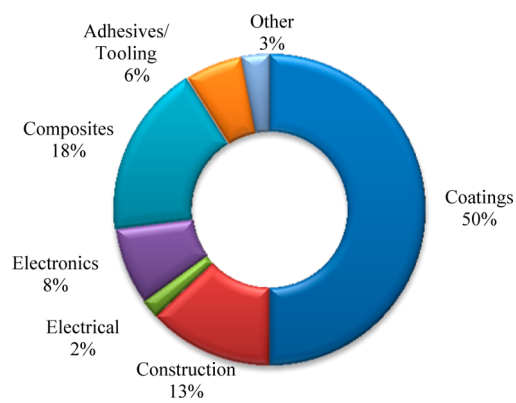


**Figure 1.** Global epoxy resin demand by sector.[2]

dianiline, MDA) are well-known skin sensitizers, and the latter are carcinogenic in animals and possibly humans.[7] As reported by the Health Council of The Netherlands, acid anhydrides, for example, hexahydrophthalic anhydride (HHPA), maleic anhydride (MA), methyl tetrahydrophthalic anhydride (MTHPA), phthalic anhydride (PA), tetrachlorophthalic anhydride (TCPA), tetrahydrophthalic anhydride (THPA), and trimellitic anhydride (TMA), cause sensitization, and in addition, PA and MTHPA cause asthma.[8] Furthermore, toxicity may still exist in

**Figure 2.** Types of curing agents.
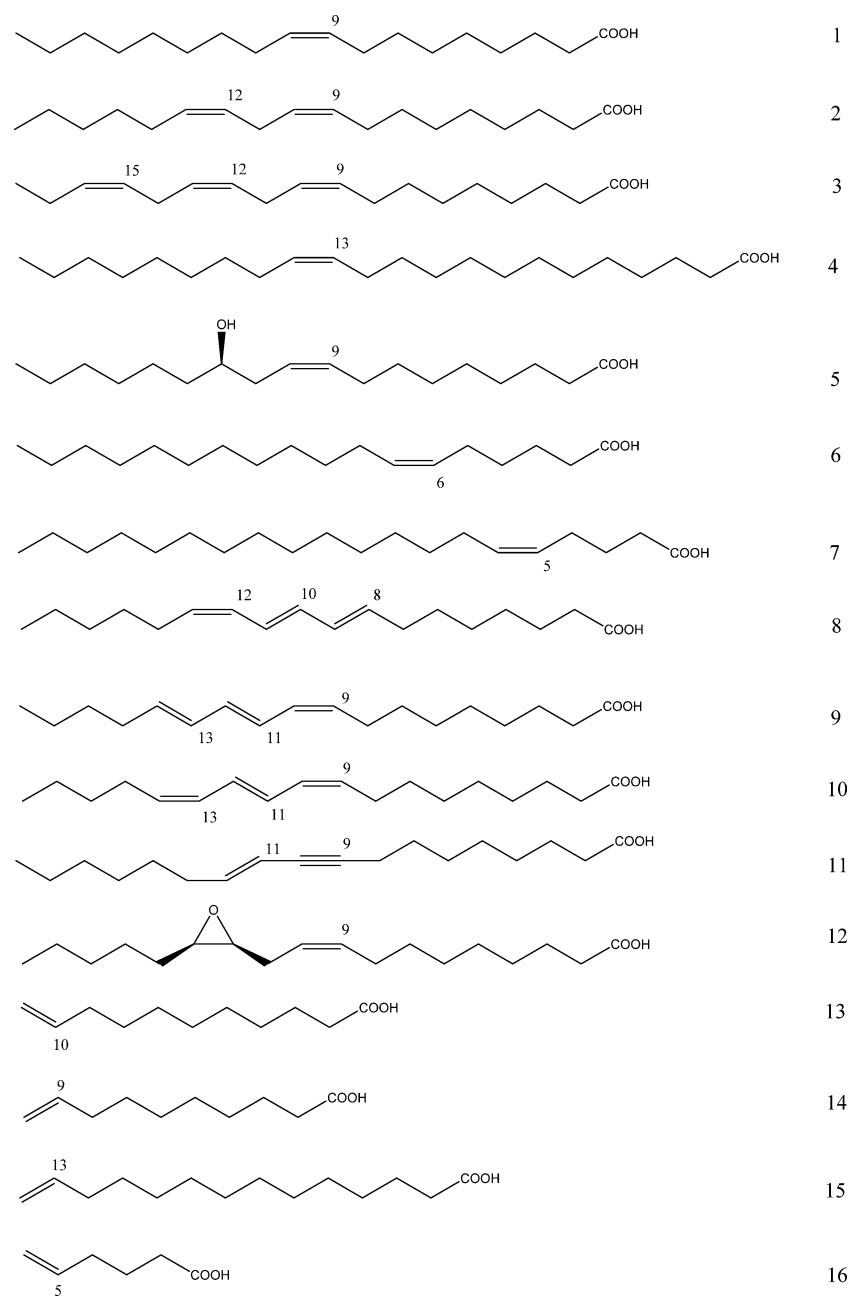


**Figure 3.** Fatty acids as potential starting materials for biobased curing agents: oleic acid (**1**), linoleic acid (**2**), linolenic acid (**3**), erucic acid (**4**), ricinoleic acid (**5**), petroselinic acid (**6**), 5-eicosenoic acid (**7**), calendic acid (**8**), a-eleostearic acid (**9**), punicic acid (**10**), santalbic acid (**11**), vernolic acid (**12**), 10-undecenoic acid (**13**), 9-decenoic (**14**), 13-tetradecenoic acid (**15**), and 5-hexenoic acid (**16**). NB: although not shown, their respective methyl esters are referred to as **1a−16a**.[11]

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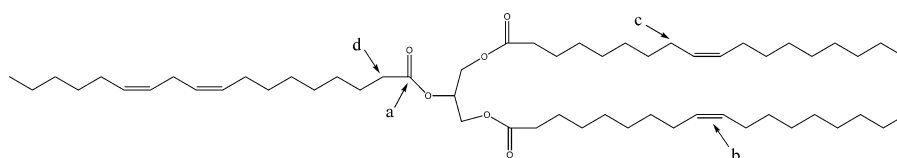dx.doi.org/10.1021/sc500478f | ACS Sustainable Chem. Eng. 2014, 2, 2217−2236

**Figure 4.** Reactive positions in triglycerides: ester groups (a), C=C double bonds (b), allylic positions (c), and α-positions of ester groups (d).[13]
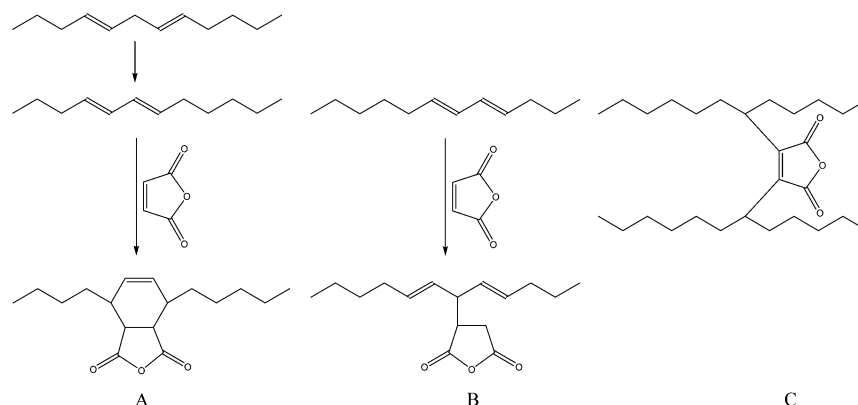


**Figure 5.** Possible addition of MA to nonconjugated double bonds. (A) Diels−Alder adduct, (B) radical addition, and (C) cross-linking.

products in the form of residual curing agents and uncured monomers due to incomplete cure.

Thus, it is of great importance to develop curing agents from renewable materials rather than petroleum-derived materials for producing next generation biobased epoxy networks as highlighted recently by Auvergne et al.[9] However, it must be stressed that renewable does not always automatically imply safe.

Herein, we review recent development in Type I and Type III curing agents derived from potentially renewable biobased resources because they contribute significantly (by wt %) to the total weight of an epoxy resin system. Attention is given to modified plant oils, biobased acids, and anhydrides, amines, and their derivatives, biobased phenols, rosin acids, terpenes, and lignin as biobased curing agents for primarily epoxy resin or biobased epoxy resin systems.

## ■ MODIFIED PLANT OILS

Plant oils represent a significant renewable resource for applications such as paints, coatings, cosmetics, detergents, lubricants, biodiesel, and composites due to their wide availability, inherent biodegradability, and low toxicity.[10]

Plant oils predominantly comprise triglyceride molecules, i.e., esters derived from glycerol and fatty acids. Most common plant oils contain fatty acid groups varying in carbon chain length from 14 to 22 and comprising 0 to 3 double bonds (C= C) per chain (Figure 3).[11] Thus, plant oils are a mixture of various triglycerides with differing degrees of saturation.

The double bonds act as reactive sites for coatings and paints, but usually, additional functionalization methods need to be used for preparation of polymeric materials.[12] Figure 4 shows possible reactive sites within a triglyceride: ester groups, C=C double bonds, allylic positions, and α-positions of ester groups.[13]

**Reactions at Double Bonds: Maleinization.** Maleinization, the reaction of MA with a double bond, is a common method to introduce an anhydride group into a triglyceride. For example, Warth et al.[14] have prepared maleated plant oil (MPO) by directly reacting a triglyceride with MA in an inert

atmosphere (nitrogen) at 200 °C for 7 h. Although this review will not focus on peroxides, it is noteworthy to mention that the use of peroxide catalysts, such as benzoyl peroxide,[15] 2,5-bis(tertbutylperoxy)-2,5-dimethylhexane peroxide, and di-tert-butyl peroxide,[16] allows maleinization to proceed faster and at lower temperatures.

As shown in Figure 5, Tran et al.[16] summarized three possible product pathways for maleinization yielding either a Diels−Alder adduct, radical addition product, or cross-linking, whereby the MA links two triglyceride chains.

The long-chain carbon backbone confers flexibility, and many MPOs have been used as flexible anhydride curing agents for epoxy resins.[14,17,18] Warth et al.[14] reported the use of maleated soybean oil (MSO) and maleated linseed oil (MLO) as flexible hardeners for diglycidyl ether of bisphenol A (DGEBA) and epoxidized natural oils in the presence of aluminum acetylacetonate as catalyst to yield highly cross-linked amorphous polyesters. The thermal and mechanical properties of the resultant polyesters depended on the type and concentration of anhydride employed and in particular the epoxy to anhydride molar ratio. MLO, which has higher anhydride content than MSO, afforded better thermal and mechanical properties.

Besides reacting with triglycerides directly, modified plant oils, such as methyl soyate,[17] acrylated epoxidized soybean oil (AESO),[19] and soybean oil monoglycerides (SOMGs),[20] have been maleinized to further improve their reactivity. Tran et al.[17] compared the curing properties of maleated methyl soyate (MMS) and MSO with epoxidized soybean oil (ESO) in the presence of hexamethylenediamine (HMD) and 4-dimethylaminopyridine (DMAP), showing that MSO provided higher gel content (almost no weight loss) after Soxhlet extraction compared with MMS. Interestingly, to the best of our knowledge, maleated AESO and SOMGs have not been explored as curing agents for epoxy resins but have been reported as blends with styrene to produce thermoset copolymers.[19,20]

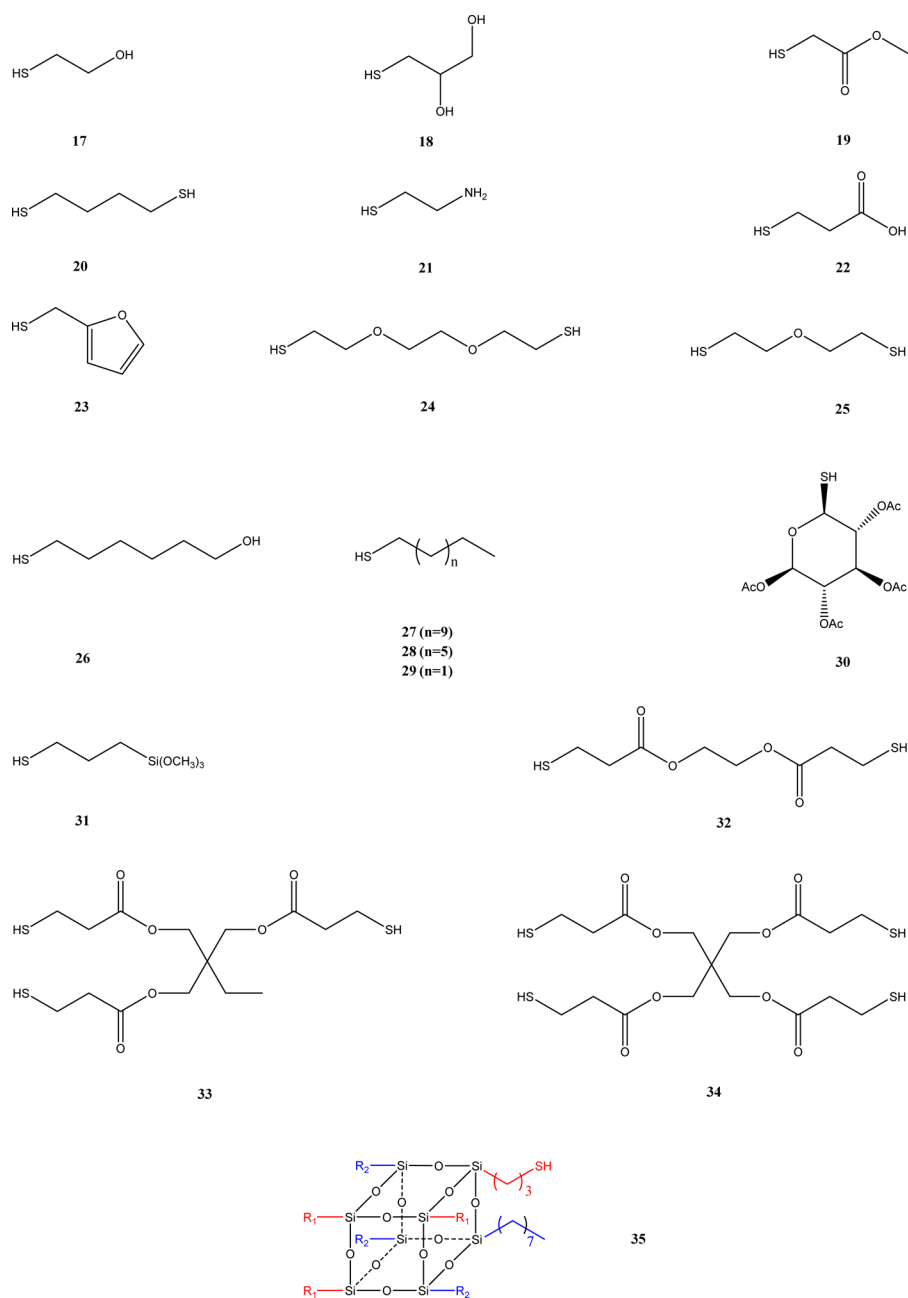Biermann et al. reported that he Diels−Alder addition of MA to methyl α-eleostearate occurred both regio- and stereo-

**Figure 6.** Chemical structures of thiols used in the transformation of oleochemicals into monomers and polymers.
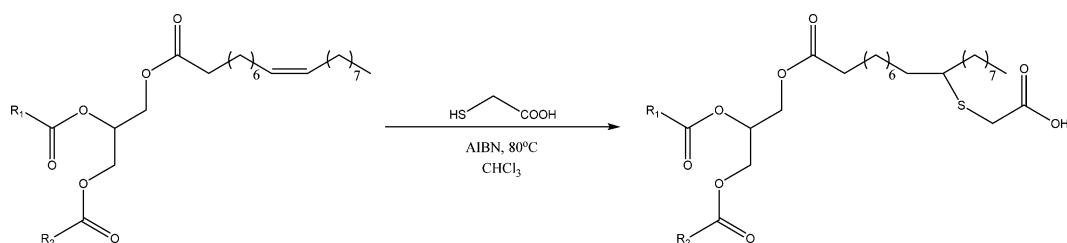


**Figure 7.** Functionalization of soybean oil with thioglycolic acid.

selectively at positions C-11 and C-14 of the ester.[21] The latter is derived from $\alpha$-eleostearic acid (9-*cis*,11,13-*trans*-octadeca-trienoic acid, **9**), a conjugated triene acid found in the oil from the nuts of the tung oil tree and, hence, is also known as tung oil.[22] Xu et al.[23] prepared nanocomposites composed of epoxy resin, tung oil anhydride (TOA), and montmorillonite (MMT).

The resultant nanocomposites were exfoliated to good effect such that the individual silicate layers were dispersed in the polymer matrix, and the glass transition temperature ($T_g$) decreased with increasing MMT content.

**Reactions at Double Bonds: Thiolation.** Thioethers are of great importance in changing the functionality of double
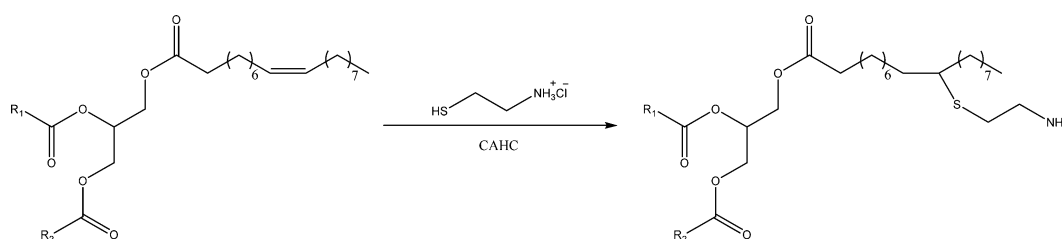
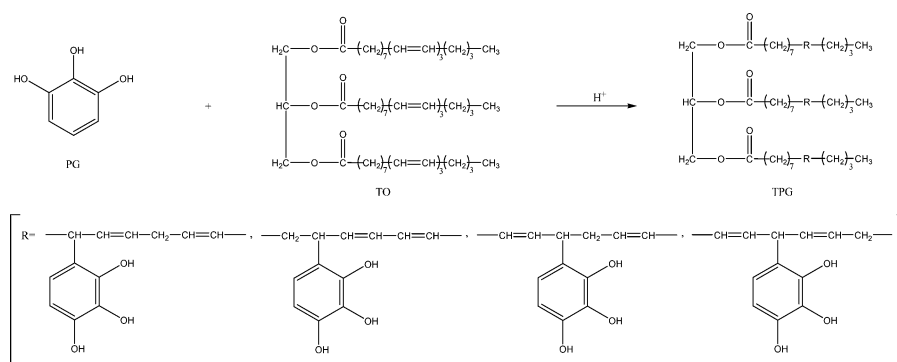**Figure 8.** Amination of GSO using CAHC by UV-initiated thiol−ene coupling.



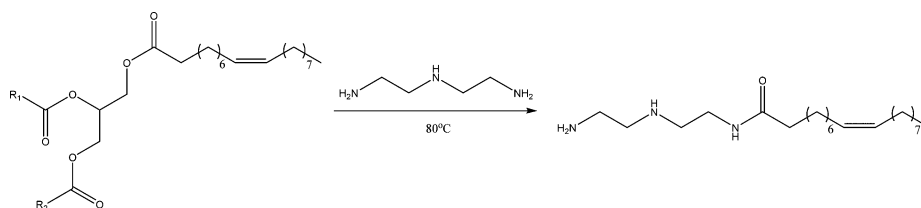**Figure 9.** Synthetic scheme of TPG.



**Figure 10.** Amine hardener by vegetable oil amidification.

bonds and have been synthesized traditionally via the thiol−ene reaction, which is the addition of a thiol to an alkene forming a thioether.

A thiol−ene reaction is high yielding, regio- and stereospecific, and able to introduce various functional groups.[24] Gerald et al.[25] summarized a wide variety of sulfur-based monomers (Figure 6) and their subsequent polymers that may be realized by the thiol−ene reactions.

Jaillet et al.[26] reported a novel biobased polyacid hardener derived from soybean oil by thiol−ene coupling with thioglycolic acid (Figure 7). ^{1}H NMR analysis revealed an acid funtionality of 3.3 per triglyceride molecule and with only 15% of thioester as byproduct. The latter and further side reactions have been investigated by Desroches et al.[27] using NMR, FT-IR, LC-MS, and iodine titration based on oleic acid as a model compound. The performance of the sulfur-containing polyacid hardener when studied with DGEBA showed increased reactivity compared to conventional amine hardeners.

Stemmelen et al.[28] have used the thiolene reaction to good effect by reacting grape seed oil (GSO) with cysteamine chloride (**21**) (Figure 8) to yield aminated grape seed oil (AGSO). In their study, GSO with 4.75 double bonds per triglyceride was modified to AGSO with 4.13 amine units per triglyceride for 87% of conversion.

**Reactions at Double Bonds: Allylic Reactions.** The allylic position (Figure 4, position c) has been modified to good effect by several researchers. For example, Shibata et al.[29]

introduced pyrogallol (PG) moieties into tung oil triglycerides to afford tung oil−pyrogallol resin (TPG) catalyzed by p-toluenesulfonic acid (Figure 9). Unlike soybean and linseed oils, which give oligomerized materials on reaction with pyrogallol, the presence of a conjugated triene moiety in tung oil triglycerides furnishes a cleaner and less troublesome reaction in acidic conditions with a degree of addition of PG to the C=C double bonds of 2.3 per triglyceride. Furthermore, Shibata et al.[29] produced biocomposites comprising sorbitol polyglycidyl ether (SPE, Figure 23) as epoxy resin, TPG as hardener, and wood flour, which showed much higher storage moduli than SPE−TPG resin alone. The tensile strength, modulus, elongation, and $T_g$ (measured by dynamic mechanical analysis, DMA) for the SPE−TPG network cured under 190 °C for 3 h were 28.2 MPa, 1070 MPa, 7.4%, and 53.5 °C, respectively.

**Reactions at the Carbonyl Group.** Desroches et al.[30] successfully produced an amido−amine hardener in a one-step reaction between DETA and the carbonyl group within vegetable oils (Figure 10) with an average functionality of 3. The monoadduct was used as amine hardener with DGEBA epoxy precursors to yield a resin with a $T_g$ of 32 °C.

Zhao et al.[31] reported amine-functionalized triglycerides via complex processes including epoxidation, reduction, bromination, substitution, and reduction. However, it is important to note in the context of biobased materials and sustainability that the reaction conditions used to obtain the corresponding triamine are not good.
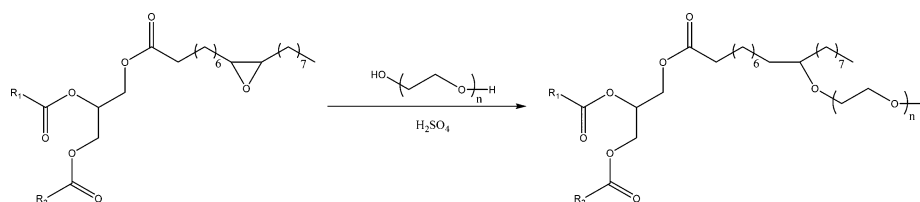
**Figure 11.** Hydroxylation of epoxidized oils.

**Biobased Polyols.** Most biobased polyols are derived from plant oils and fatty acids via a variety of methods, for example, hydroxylation of double bonds, ring opening of epoxidized plant oils (EPOs), and dimerization of fatty acids.[32,33] Polyols in the main are used to make polyurethane polymers, and relatively few papers report their use as curing agents for epoxy resins. However, Czub et al.[34] prepared hydroxylated soybean oil and rapeseed oil via ring opening of their respective epoxidized precursors, either monoethylene glycol (MEG) or diethylene glycol (DEG), in the presence of sulfuric acid as catalyst (Figure 11), which on subsequent reaction with DGEBA produced a high molecular weight epoxy resin. Ahn et al.[35] have made biobased pressure sensitive adhesive (PSA) tapes from the reaction between dihydroxyl soybean oil (DSO) and ESO in the presence of phosphoric acid, which have comparable peel strengths to commercial nonbiobased PSA tapes. The PSA tapes were produced at 110 °C within 30 s through a simple air-drying process possessing good thermal and chemical stability and optical transparency.

Alternatively, certain plant oils inherently contain hydroxyl (alcohol) groups. For example, the hydroxyl group within castor oil can be further derivatized to yield hardeners. Liu et al.[36] reacted castor oil with phosphoryl chloride to produce phosphorylated castor oil (PCO, Figure 12) in high yield (80% conversion ratio for the hydroxyl phosphorylation) followed by a reaction with ESO or ELO to give elastomers without the need for additives at 37 °C.
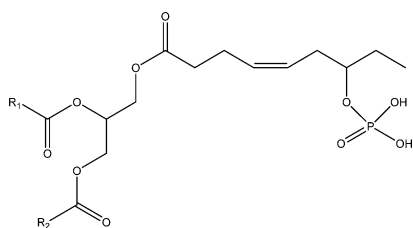


**Figure 12.** Structure of phosphorylated castor oil.

Plant oil-derived fatty acids, which can be easily obtained by either simple hydrolysis or alcoholysis of triglycerides, are potential biobased hardeners and will be discussed in next section.

### ■ BIOBASED CARBOXYLIC ACIDS AND ANHYDRIDES

**Biobased Carboxylic Acids.** Traditionally, dicarboxylic acids (DCAs, $HOOC(CH_2)_nCOOH$) are mainly derived from petrochemical feedstocks. From the view of renewable starting materials, short-chain DCAs may be obtained either by fermentation or chemical transformation of carbohydrates, while long-chain DCAs could be obtained either by chemical or enzymatic modification of fatty acids. In 2004, the U.S. Department of Energy (DOE) identified 12 sugar-derived

building blocks (Table 1), the so-called "platform molecules", eight of which are DCAs easily accessible from glucose.[37−41]

**Table 1. Top Sugar-Derived Building Blocks[37]**

| building blocks |
| --- |
| 1,4-diacids (succinic, fumaric, and malic) |
| 2,5-furan dicarboxylic acid |
| 3-hydroxypropionic acid |
| aspartic acid |
| glucaric acid |
| glutamic acid |
| itaconic acid |
| levulinic acid |
| 3-hydroxybutyrolactone |
| glycerol |
| sorbitol |
| xylitol/arabinitol |

Fatty acids are easily available by either hydrolysis or alcoholysis of animal and vegetable oils and fats. The hydrolysis process of triglycerides was summarized by Corma et al.[39] Ranges of DCAs synthesized from fatty acids by chemical or enzymatical transformations are shown in Table 2.[11]

For example, as outlined in Figure 13, ozonolysis is an efficient way of making DCAs. Ozonolysis of oleic acid (**1**) furnishes pelargonic and azelaic acid. Ozonolysis of petroselenic acid (**6**) affords adipic acid. Brassylic acid can be obtained from erucic acid (**4**). Vasishtha et al.[42] used high temperature (250 °C) alkali hydrolysis of castor oil to produce sebacic acid via ricinoleic acid (Figure 14).

Microbial methods of $\omega$-oxidation of the terminal $CH_3$ group of long-chain fatty acids to produce diacids are gaining impetus. *Candida tropicalis* is widely used in the production of DCAs of different chain lengths to good effect with yields exceeding 100 g/L.[43,44]

Ahn et al.[45] reported a biobased acid-derived acid catalyst, magnesium stearate (Mg stearate), to ring open ESO in a one-step process without using a solvent or purification process. Different products were obtained depending on the ratio of the epoxy group and Mg stearate, namely, a biogrease material for ratios of 1:1 to 1:2 and a thermoplastic-like material for a ratio of 1:4 with a $T_g$ of −27 °C and $T_m$ of 90 °C.

Shogren et al.[46] studied the biodegradation behavior of epoxy networks from ESO cross-linked with different aliphatic carboxylic acids (citric acid, succinic acid, adipic acid, and sebacic acid) in the presence of either aluminum acetyl acetonate or tetrabutyl ammonium bromide as catalyst. The epoxy networks showed fairly rapid degradation in soil due to the inherent polyester structure formed between reactions of epoxy groups with acid groups. Although the full mechanism is yet to be elucidated, the main reaction is considered to be the addition of the esterification reaction between epoxy and carboxylic acid groups, accompanied by several side reactions.[47]

**Table 2. Unsaturated Fatty Acids and Esters as Substrate for Synthesis of Linear Fatty Diacids**

| entry | substrate | synthesis | diacid[a] | coproduct |
|---|---|---|---|---|
| 1 | **6** | ozonolysis | 6 | dodecanoic acid |
| 2 | **7a** | cross-metathesis with methyl acrylate; hydrogenation | 7[b] | methyl heptadecanoate |
| 3 | **6a** | cross-metathesis with methyl acrylate; hydrogenation | 8[b] | methyl heptadecanoate |
| 4 | **1** | ozonolysis | 9 | nonanoic acid |
| 5 | **5** | splitting with caustic soda | 10 | 2-octanol |
| 6 | **1a** | cross-metathesis with methyl acrylate; hydrogenation | 11[b] | methyl undecanoate |
| 7 | **13a** | cross-metathesis with methyl acrylate; hydrogenation | 12[b] | ethene |
| 8 | **1a** | cross-metathesis with 2-butene; methoxycarbonylation, hydrogenation | 12[b] | methyl dodecanoate |
| 9 | **4** | ozonolysis | 13[b] | nonanoic acid |
| 10 | **13a** | cross-metathesis with 2-butene; methoxycarbonylation | 14[b] | − |
| 11 | **4a** | cross-metathesis with methyl acrylate; hydrogenation | 15[b] | methyl undecanoate |
| 12 | **4a** | cross-metathesis with 2-butene; methoxycarbonylation | 16[b] | dodecanoic acid |
| 13 | **15a** | cross metathesis with 1-butene; methoxycarbonylation | 17[b] | − |
| 14 | **1a** | self-metathesis; hydrogenation | 18[b] | octadecane |
| 15 | **14a** | self-metathesis; hydrogenation | 18[b] | ethene |
| 16 | **1** | microbial oxidation | 18 | − |
| 17 | **1** | methoxycarbonylation | 19 | − |
| 18 | **13a** | self-metathesis; hydrogenation | 20[b] | ethene |
| 19 | **7a** | methoxycarbonylation | 21[b] | − |
| 20 | **4a** | methoxycarbonylation | 23[b] | − |
| 21 | **4a** | self-metathesis; hydrogenation | 26[b] | octadecane |
| 22 | **15a** | self-metathesis; hydrogenation | 26[b] | ethene |

[a]Number of carbon atoms of diacids. [b]Dimethyl ester.

The polymerized ESO and citric acid combination was further used as coatings on Kraft paper to slow the degradation process.[48] Under certain conditions, for example, in the absence of catalysts, polyols were obtained from epoxidized vegetable oils with different biobased diacids ($C_6$–$C_{12}$)[49] or mono fatty acids (acetic acid, lactic acid, and glycolic acid).[50]

Interesting applications of biobased diacids include vulcanizing epoxidized natural rubber (ENR) using dodecanedioic acid[51] and cross-linking with liquid crystalline (LC) epoxy monomers to form liquid crystalline elastomers (LCEs, $C_6$–$C_{10}$).[52] Compared with the sulfur vulcanization process, the reaction between ENR and dibasic acids lessened the detrimental effect of heat treatment and eliminated the use of some toxic additives like zinc oxide. As for the LCEs, their properties were largely dependent on the nature of epoxy monomers and curing agents.

DCAs may also be made by dimerization of fatty acids, for example, $C_{18}$. The products obtained through this process are a
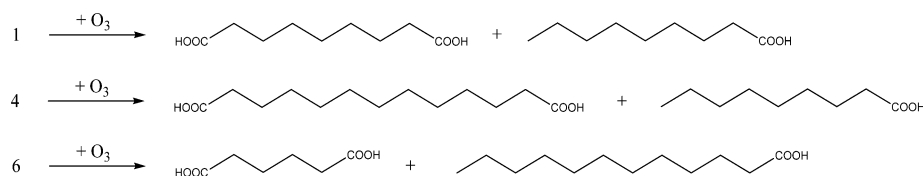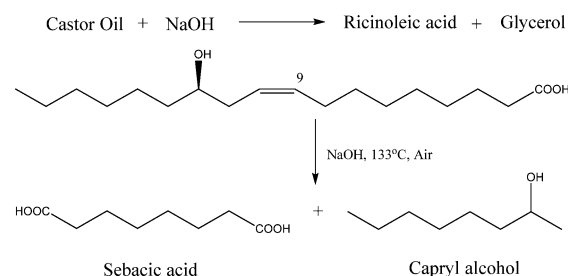
**Figure 14.** Production of sebacic acid and capryl alcohol from castor oil.

mixture of dimers, trimers, and isostearic acid due to the existence of many side reactions.[39] A range of different $C_{36}$ dimer and trimer fatty acids, namely, Pripol and Unidyme, are available from Croda and Arizona Chemical, respectively. Supanchaiyamat et al.[53] reported synthesis and properties of a fully biobased flexible and water-resistant network derived from ELO and Pripol 1009 in the presence of different catalysts, triethylamine (TEA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),1-methylimidazole (1-MI), 2-methyl-imidazole (2-MI), and DMAP.

Montarnal et al.[54] amidated Pripol 1040 (70 wt % trimer acids) with aminoethylimidazolidone (UDETA) and subsequently cross-linked it with DGEBA in the presence of 2-MI to generate cross-linked materials combining the supramolecular chemistry of urea with the chemistry of epoxies. The presence of H-bonding groups in the material improved matrix−filler interactions thus producing composites with better mechanical properties. Leibler et al.[55−57] reported a new concept of epoxy networks termed "vitrimers", which are strong organic glass covalent formers able to change their topology through thermoactivated bond exchange reactions. Vitrimers were obtained from the cross-linking reactions between DGEBA and Pripol 1040 or anhydrides in the presence of different transesterification catalysts. Different temperature welding experiments[56] and effects of catalyst types and concentrations[57] were also studied. The welding process was achieved in different time−temperature windows without any changes of the dimensions of the materials. Faster welds were achieved at higher temperatures. The higher the catalyst concentration, the higher force at break was obtained. Zinc acetate (Zn(OAc)$_2$) and triazobicyclodecene (TBD) were found to be more efficient transesterification catalysts compared with triphenylphosphine (PPh$_3$).

On the basis of the concept of vitrimers, Pei et al.[58] developed liquid crystal elastomers with exchangeable links (xLCEs) from the reaction of DGEBA or diglycidyl ether of 4,4′-dihydroxybiphenol (DGE-DHBP) with sebacic acid in the presence of triazobicyclodecene as catalyst. The resultant LCEs were easily processable with monodomain alignment making them useful as actuators and artificial muscles.
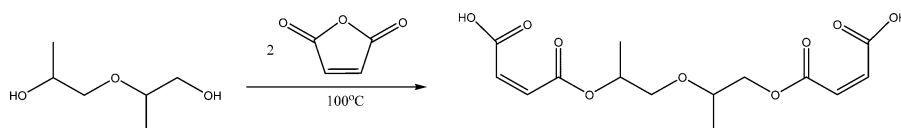
**Figure 13.** Oxidative scission of oleic acid (**1**) with ozone to give azelaic acid and pelargonic acid. Erucic acid (**4**) gives brassylic acid and pelargonic acid. Petroselinic acid (**6**) gives adipic acid and lauric acid.

**Figure 15.** Schematic synthesis of maleic monoester used to cross-link ELO.
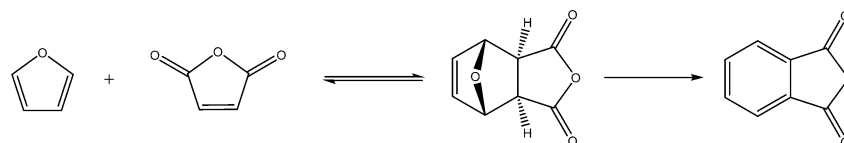


**Figure 16.** Route to renewable PA from biomass-derived furan and MA.

Carter et al.[59] reported a carboxyl-terminated polyester (Figure 15) for potential use in heavy duty flooring applications synthesized from the reaction of dipropylene glycol and MA followed by cross-linking with ELO.

**Biobased Anhydrides.** Hu et al.[60] reported an efficient and convenient method to synthesize DCAs from carboxylic acids with sulfated zirconia by phase transfer catalysis (PTC), which on heating give five- or six-membered cyclic anhydrides, succinic anhydride, and glutaric anhydride. MA can be obtained renewably, for example, by the dehydrogenation of succinic anhydride using iron phosphate based catalysts,[61] oxidation of furfural using a $VO_x/Al_2O_3$ catalyst,[62] oxidation of 5-hydroxymethylfurfural in the liquid phase,[63] and fermentation containing butanol using a catalyst based on oxides of vanadium and/or molybdenum.[64] Biobased PA (Figure 16) can be made via Diels−Alder addition between biobased furan and MA followed by dehydration of the resultant adduct.[65]

Vitrimers were also obtained from the cross-linking reaction between glutaric anhydride and DGEBA in the presence of zinc acetylacetonate dehydrate $(Zn(acac)_2)$.[55] Compared with acid cured samples, harder networks with much higher stress and modulus were obtained. The effects of anhydride types (MA, succinic anhydride, PA, HHPA, and dodecenylsuccinic anhydride (DDS)) on dynamic mechanical and thermal behavior of epoxy resin based on ESO were studied by Gerbase et al.,[12] who showed that anhydrides with rigid structures like MA, PA, and HHPA gave higher $T_g$ and cross-linking densities. Whereas, thermosets obtained from DDS produced lower thermal stability because that the side chain of the molecule started decomposition at lower temperature.

## BIOBASED AMINES AND THEIR DERIVATIVES

**Amino Acids and Their Homopolymers.** Amino acids and their homopolymers, e.g., polylysine, represent an important class of biobased amines and their derivatives. Currently, amino acids are mainly manufactured either by fermentation or enzymatic methods.[66]

Lysine[67] and tryptophan[6] (Figure 17) are two amino acids reported as ecofriendly cross-linking agents for epoxy resins in the electronics industry. Both the amino and carboxyl functional groups are able to ring open an epoxy moiety with the former being slightly less reactive than the latter due to absence of an active hydrogen. Li et al.[67] reported the $T_g$ and thermal degradation temperatures for lysine comprising networks with a cycloaliphatic-type epoxy of 91.37 and 195.49 °C, respectively. In comparison, the network between the cycloaliphatic-type epoxy and methylhexahydrophthalic anhydride (MHHPA) gave temperatures of 127.36 °C ($T_g$)
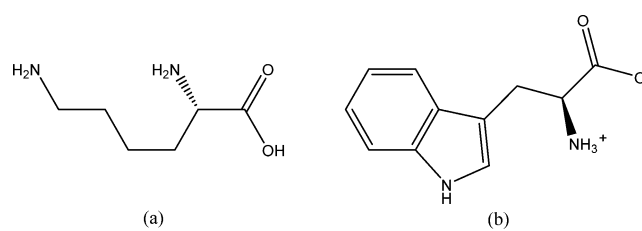


**Figure 17.** Chemical structures of (a) lysine and (b) tryptophan.

and 367.03 °C (degradation temperature), respectively. Tryptophan cross-linked with DGEBA in the presence of an imidazole catalyst yields networks with reasonably high $T_g$ (107 °C) and thermal stability (284 °C).

$\varepsilon$-Polylysine (PL) obtained by aerobic bacterial fermentation of a broth comprising *Streptomyces albulus*, glucose, citric acid, and ammonium sulfate has also been exploited as an example of an amino acid/homoploymer curing agent.[68,69] Scholl and co-workers[70,71] reported dendrimers of PL (Figure 18) obtained via homopolymerization of lysine chlorohydrate in the presence of KOH at 150 °C. The existence of multiple pendant $\alpha$-amino groups makes the resultant dendrimer potentially a very reactive cross-linking agent.

Takada et al.[72] employed PL as cross-linking agent with glycerol polyglycidyl ether (GPE) and polyglycidyl ether of polyglycerol (PGPE) epoxy prepolymers to form GPE−PL and PGPE−PL networks, respectively. The latter possessed a greater $T_g$ compared with GPE−PL due to higher epoxy content. The incorporation of 15 wt % MMT in to the formulation significantly increased both tensile strength from 4 to 42 MPa and modulus from 6 MPa compared with its counterpart neat PGPE−PL network.

**Biobased Amines.** Biobased amines can be made via either biotechnological or traditional chemical routes. For example, 1,5-diaminopentane, an important industrial platform chemical, may be bioengineered from *Corynebacterium glutamicum* or *Escherichia coli*.[73] Biobased amines can also be derived from isosorbides via conversion of isosorbide hydroxyl groups into cyano groups followed by hydrogenation.[74−77] Decamethylene diamine (DDA) can be obtained from castor oil-derived sebaconitrile under harsh conditions.[78] Wang et al.[79] made a new series of poly(epoxidized soybean oil-*co*-decamethylene diamine) (PESD) elastomers from the cross-linking reaction of ESO and DDA. Further cross-linking with succinic anhydride produced materials of higher $T_g$ and tunable tensile strength (0.8 to 8.5 MPa) compared its uncross-linked counterparts, which possessed low $T_g$ (−30 to −17 °C). The crossed-linked elastomers showed good damping property, water resistance,
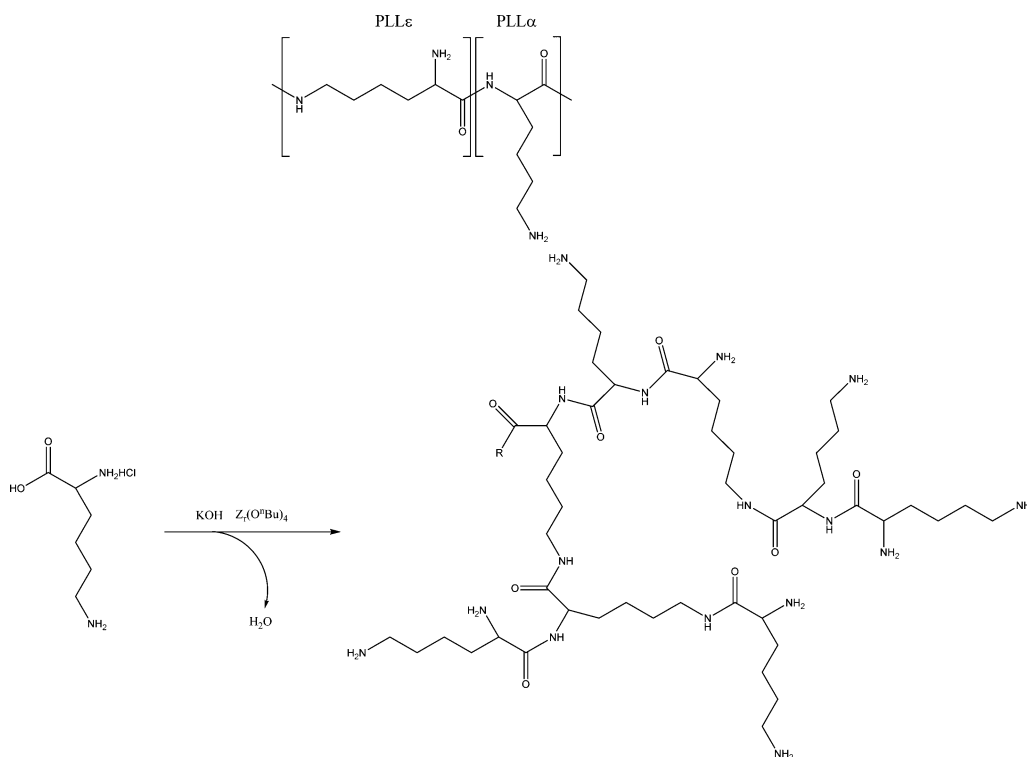
**Figure 18.** Synthesis and structure of polylysine (PL).

and degradation resistance in phosphate buffer solution, making them potentially useful as biomaterials, e.g., actuators.

Phenalkamines are an interesting set of hardeners derived from cardanol, a component of cashew nut shell liquid (CNSL), which is a byproduct from the cashew industry.[80−84]

The main component of solvent-extracted CNSL is anacardic acid with a smaller amount of cardanol, cardol, and its methyl derivatives;[82] whereas, CNSL produced by roasting (high temperature) is rich in cardanol because the anacardic acid readily decarboxylates.[81]

Phenalkamines are prepared by the Mannich reaction occurring between cardanol, formaldehyde, and appropriate diamines (Figure 19).[85] The resultant Mannich-based curing
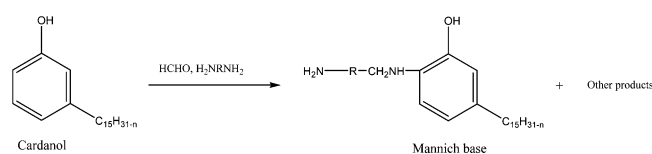


**Figure 19.** Synthesis of phenalkamine from cardanol.

agents are advantageous because of speed, low temperature of the cure, and excellent chemical and physical properties. Some phenalkamines are food contact approved and some are used in potable water coatings.[86]

Furthermore, phenalkamines blended with polyamine salts[87] and phenalkamines comprising at least one aromatic or alicyclic ring in the diamine side chain[88] have also been developed to give coatings with reduced Gardner color index compared to phenalkamines.

**Biobased Polyamides.** Polyamides may also be used as curing agents. Polyamides are condensation products of dimerized fatty acids and polyamines and are commercially available from Arizona Chemical under the trade name Uni-

Rez. Vijayalakshmi et al.[89] reported polyamides prepared from $C_{21}$ cycloaliphatic dicarboxylic acid or $C_{36}$ dimer acids with various amines, namely, DETA, TETA, and tetrathylenepentamine (TEPA), which subsequently were reacted with epoxy resins at different weight ratios. The cured product (binder) derived from an equivalent weight ratio of polyamide to epoxy showed better binding properties. Furthermore, $C_{21}$ DCAs-derived binders were better than $C_{36}$ DCAs-derived binders. Biobased amides can also be derived either from sugars such as isosorbide, isomannide, and isoidide or fatty acids as reported by Fenouillot et al.[90] and Fomina et al.[91]

Similar to phenalkamines discussed earlier, phenalkamides derived from the chemical combination of phenalkamines and polyamides can be used as curing agents for epoxy systems. The chemical and physical properties of phenalkamides are similar to phenalkamines, for example, excellent anticorrosion properties, good color stability, and extended overcoatability.[92]

## ■ BIOBASED PHENOLS

Phenolics are a group of epoxy curing agents that are cross-linked with epoxy groups via the phenolic hydroxyl group such as in phenol-, cresol-, and bisphenol A-terminated. Campaner et al.[93] synthesized cardanol-based Novolac resins by the condensation reaction of cardanol and paraformaldehyde using oxalic acid as catalyst (Figure 20). By varying the ratio of cardanol to catalyst, two different types of novolacs (Nov-I and Nov-II) were obtained. The average number of cardanol
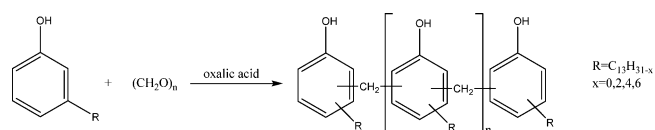


**Figure 20.** Synthesis of the cardanol-based novolacs.

units and the amount of unreacted cardanol in Nov-I and Nov-II were 3.8, 35%, and 5.2, 20%, respectively. The curing properties of these two novolacs were studied with different ratios of DGEBA, and the results showed that higher cross-linking density was obtained with higher amounts of epoxy resin. Compared with Nov-I, the cured resin using Nov-II had higher a $T_g$ and better mechanical properties but similar thermal degradation properties due to the higher molecular weight and lower unreacted cardanol content.

Biobased polyphenols are abundant in nature albeit in low concentrations. Quideau et al.[94] summarized the chemical properties, biological activities, and synthesis of a wide variety of plant polyphenols. Polyphenols may also be recovered or isolated from biproducts during food processing processes as reported by Schieber et al.[95] For example, apple pomace has potential to be exploited to produce polyphenols including catechins (Figure 21a), hydroxycinnamates (Figure 21b), procyanidins (Figure 21c), phloretin glycosides (Figure 21d), and quercetin glycosides (Figure 24).
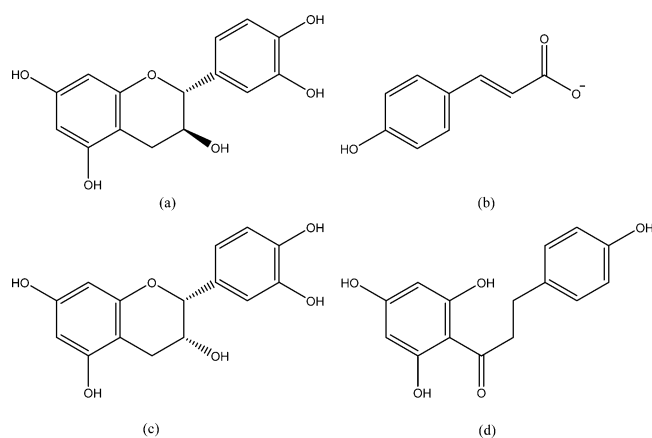


**Figure 21.** Structures of (a) catechin, (b) hydroxycinnamates, (c) procyanidins, and (d) phloretin.

Tannins are defined as chemicals mainly composed of phenolic structures, including condensed or polyflavonoid tannins and hydrolyzable tannins.[96] Commercial tannic acid (TA, $C_{76}H_{52}O_{46}$, Figure 22) is based mainly on glucose ester of gallic acid.

The Mitsuhiro group[29,97−100] have explored several biobased polyphenols as curing agents. For example, they have used TA as a curing agent with GPE, SPE (Figure 23), and ESO to form biobased resins.[97,98] The most balanced thermal and mechanical properties were obtained for a 1:1 epoxy (either GPE or SPE) to hydroxyl (TA) ratio; whereas, a slightly higher ratio was needed for ESO (1:1.4) because of the additional steric hindrance of the epoxy groups in ESO. Consequently, $T_g$, tensile strength, and modulus of the ESO epoxy resin system was lower than those of GPE and SPE. Shibata et al.[97,98] also investigated the effect of adding microfibrillated cellulose (MFC) to the epoxy resins, which significantly enhanced both thermal and mechanical properties of the resultant network.

Quercetin (QC, 3,3′,4′,5,7-pentahydroxyflavone, Figure 24) occurs naturally in many plants such as apples, cranberries, blueberries, onions, and tea. QC can be obtained via extraction of the quercetin glycosides followed by hydrolysis to release the aglycone and subsequent purification.[101]
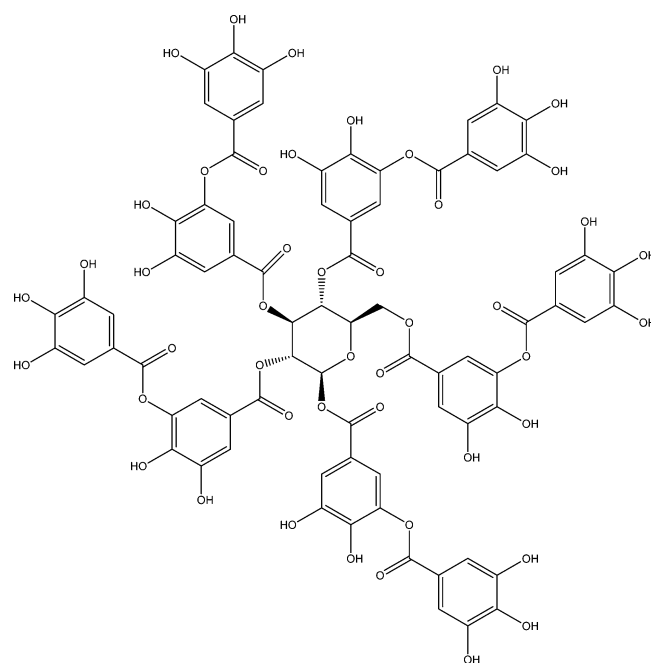


**Figure 22.** Structure of tannic acid (TA).

Shimasaki et al.[99] reported the synthesis of a pyrogallol−vanillin calixarene (PGVNC) via the reaction of PG and vanillin (VN) catalyzed by p-toluenesulfonic acid in moderate yield (51%) (Figure 25). PGVNC has a high biobased content because PG is prepared via decarboxylation of gallic acid, which is found in gallnuts, sumac, witch hazel, tea leaves, oak bark, and other plants; and VN exists in the essential oil of clove or vanilla or can be prepared from biobased eugenol or guaiacol. Spectral analyses revealed that PGVNC was mainly composed of guaiacyl pyrogallol arenes. In contrast to other calixarenes formed by PG, for example, with benzaldehyde, p-methyl-benzaldehyde, and p-methoxybenzaldehyde, PGVNC is able to dissolve in common organic solvents for ease of processing.

Compared with TA, QC and PGVNC have lower hydroxyl values but higher aromatic contents.[99,100] When cured with SPE, higher $T_g$ and thermal degradation temperatures were obtained as expected, but tensile stress and modulus were decreased. When compared with petroleum-derived phenol Novolac (PN), the thermal and mechanical properties of the SPE−QC epoxy network had slightly higher $T_g$ but comparable mechanical properties than that of SPE-PN, while the SPE−PGVNC epoxy network possessed much higher $T_g$ and thermal degradation temperature but lower tensile strength and elongation than that of SPE−PN. Later, Shibata et al.[100] prepared SPE−QC biocomposites with wood flour that showed increased tensile strength and modulus due to additional hydrogen-bonding interactions between the unsaturated carbonyl group of QC (Figure 24) with the lignocellulose component of wood flour.

The thermal and mechanical properties of some phenolic cross-linked SPE networks are summarized in Table 3, which all show high tensile modulus and good thermal stability.

## ROSIN- AND TERPENE-BASED CURING AGENTS

Terpenes and rosin (a mixture of unsaturated polycyclic carboxylic acids, of which abietic acid is the major component) are a typical class of "natural resins" (Figure 26).[102]
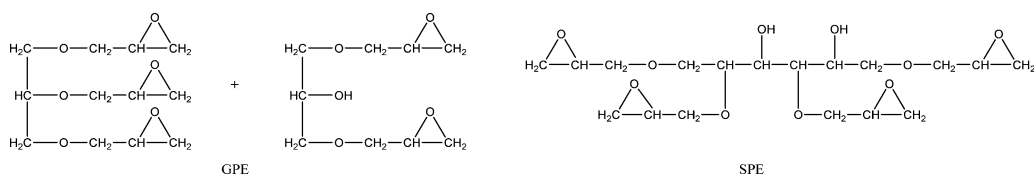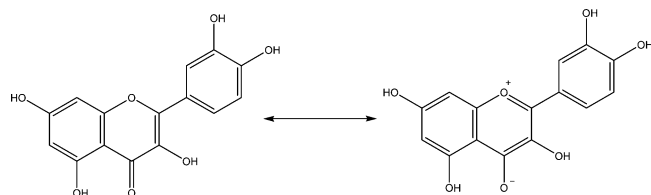
**Figure 23.** Structure of GPE and SPE.



**Figure 24.** Resonance structure of QC.

**Rosin-Based Curing Agents.** Rosin, obtained directly from pine and conifer exudates or as a byproduct from the pulping process, is an abundantly available natural product with annual production of 1−1.2 million tons.[103] Rosin is a complex mixture of naturally occurring high molecular weight organic acids (~90%, generally named rosin acids) and related neutral materials (~10%). Rosin acids are mainly composed of isomeric abietic-type acids and pimaric-type acids.[104] Rosin acids and their derivatives could become important biobased alternatives to current petroleum-derived cyclic aliphatic and aromatic monomers in polymers due to the presence of a hydrogenated phenanthrene ring structure.

Figure 27 summarizes rosin-derived acids, anhydrides, amines, and amides that were explored to be used as curing agents in epoxy resins.[105−117] Maleopimaric acid (MPA), obtained via Diels−Alder reaction between levopimaric acid and MA, is probably one of the most important and abundantly available rosin derivatives. MPA itself can be used as curing agent or easily modified with acids and amines to form new types of curing agents.

Zhang's group have synthesized several epoxy curing agents derived from rosin, namely, MPA, methyl maleopimarate (MMP), rosin maleic anhydride imidodicarboxylic acid (RMID), di-RMID (D-RMID), and MPA-terminated poly-caprolactones (MPA-PCL).[105−109] The thermal mechanical properties and thermal stability of the epoxy systems cured by MPA and MMP were compared with their petrochemical analogues, i.e., 1,2-cyclohexanedicarboxylic anhydride (CHDB) and 1,2,4-benzenetricarboxylic anhydride (BTCA), respectively.[106] The existence of a hydrogenated phenanthrene ring into the molecule led to higher $T_g$ and modulus but slightly lower thermal stability. In order to improve the flexibility of rosin-based anhydride curing agents, different chain lengths of PCLs were introduced between two terminal maleopimarate entities.[108] An increase in the chain length reduced the stress, modulus, and thermal stability due to lower cross-link density. Furthermore, rosin-based imide−diacids (RMID, D-RMID) were synthesized, and the cross-linked resins showed higher thermal stability compared with that of resins cured by MPA and MMP.[109]

Atta et al.[110,111] investigated the influence of introducing amine groups into MPA. Acryloabietic acid (APA), maleodiabietyl ketone (MA/DAK), acrylodiabietyl ketone (AA/DAK), and MPA were modified with TETA and pentaethylene hexamine (PEHA). The resultant amino-curing agents were cross-linked with rosin-derived epoxies to give cured networks with good mechanical properties and high chemical and solvent resistance.

Recently, Zhen et al.[112] reported the synthesis of a rosin-based polyamide (RMPA) from MPA with DETA as a potential curing agent for epoxy systems. The cured epoxy resin had comparable properties with petrochemical-cured epoxies: shear strength of 21.6 MPa, thermal decomposition temperature of 343.0 °C, and $T_g$ of 146.6 °C. Wang et al.[113] compared the curing behavior of rosin-based imidoamine (RMIA) with MPA and a commercial aromatic amine curing agent diaminodiphenylmethane (DDM) in order to investigate structure−property relationships. They found that epoxies cured with RMIA produced the highest $T_g$ and higher moduli and thermal stability compared with MPA but slightly lower moduli and thermal stability compared with DDM, which revealed the importance of the structure of curing agents.
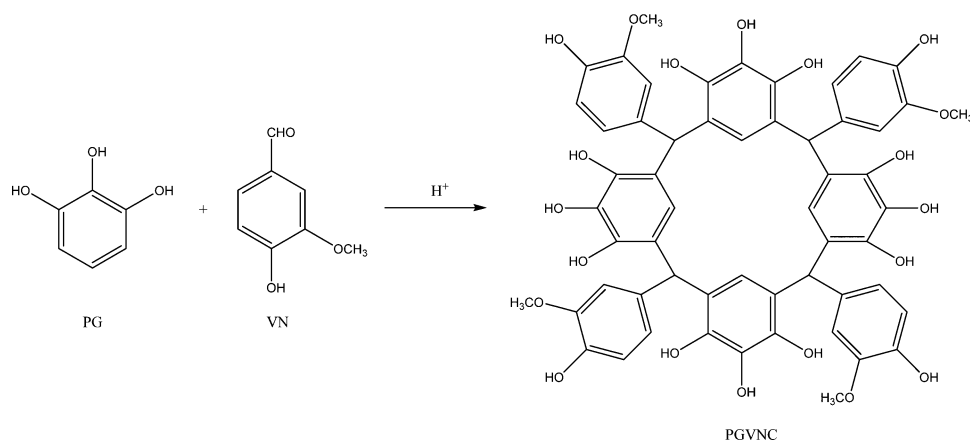


**Figure 25.** Synthetic scheme of PGVNC.

**Table 3. Thermal and Mechanical Properties of SPE-Based Epoxy Networks**

| curing agent | $R^a$ | $T_g^b$ (°C) | $T_{5\%}^c$ (°C) | tensile strength (MPa) | tensile modulus (MPa) | elongation at break (%) | ref |
|---|---|---|---|---|---|---|---|
| TA | 1 | 95 | 314.0 | 60 | 1700 | − | 97 |
| QC | 1.2 | 85.5 | 342.5 | 45 | 1380 | 4.3 | 100 |
| PGVNC | 2.65 | 148.1 | 319.2 | 15 | 1700 | 0.9 | 99 |
| TPG | 1 | 53.5 | 361.1 | 28.2 | 1070 | 7.4 | 29 |

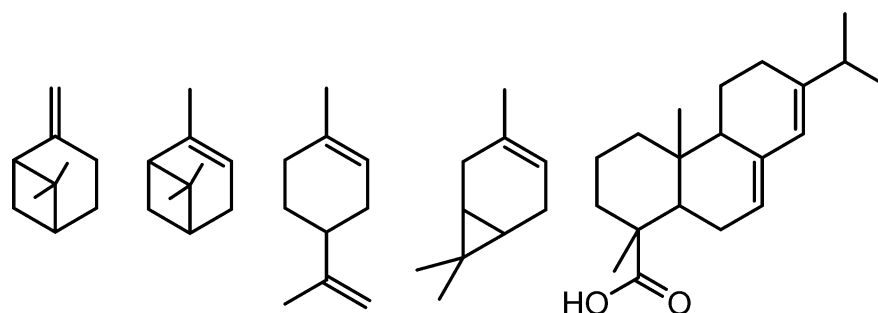$^a$Hydroxyl group/epoxy group. $^b$Glass transition temperature measured by DMA. $^c$The 5% weight loss temperature.



**Figure 26.** Four common polymerizable terpenes (from left to right: β-pinene, α-pinene, limonene, and 3-carene) and abietic acid.

Wang et al.[114] prepared a novel vinyl ester of MPA (AMPA) with high purity by sequential reaction of MPA with oxalyl chloride and allyl alcohol. Lactic ester of MPA (MPALA) was synthesized by Mustata et al.[115] to give resins of moderate $T_g$ and good thermal stability. Importantly, the cured resins were potentially biodegradable because of the existence of lactic ester groups in the molecule.

**Terpene-Based Curing Agents.** Terpenes comprise repeat isoprene units (2-methyl-1,4-butadiene) and are secondary metabolites synthesized by many fauna and flora. For example, turpentine is a generic name given to the volatile fraction isolated from pine resin. The major components of turpentine are a few unsaturated hydrocarbon monoterpenes ($C_{10}H_{16}$), namely, α-pinene (45−97%) and β-pinene (0.5−28%), with smaller amounts of other monoterpenes.[118]

As shown in Figure 28, Milks and Lancaster[119] synthesized a terpene-based acid anhydride (TPA) via Diels−Alder reaction of MA and alloocimene (obtained by the isomerization of α-pinene). The resultant TPA network possessed higher $T_g$ and tensile strength and modulus than those of networks formed between conventional anhydride HHPA and MLO.[120] Recently, Chang et al.[121] compared the curing properties of TPA with MPA and a petroleum-based curing agent methyl nadic anhydride (MNA) based on an isosorbide epoxy system. Their results showed that epoxy resin obtained with MPA had higher $T_g$ and better thermal stability due to the high functionality of MPA. TPA derivatives with amine or hydroxyl groups were obtained by further modification of TPA with amines or amino alcohols.[122]

Auvergne et al.[9] have recently summarized terpenes containing amine or phenol groups, which include menthane diamines (Figure 29a) synthesized from limonene,[123] terpene diphenol (TPD, Figure 29b),[124] and polyphenol-based terpene synthesized from terpene, phenol and formaldehyde.[125]

TPD was further reacted with formaldehyde and aniline to form terpenediphenol-based benzoxazine (TPDB) by Kimura et al.[126] Good heat stability, mechanical properties, electrical insulation, and especially low water absorption were obtained for DGEBA networks cured with TPDB.

## LIGNIN-BASED CURING AGENTS

After cellulose, lignin is the second most abundant biopolymer from renewable materials viewpoint. The annual production of lignin on Earth ranges from 5−36 × 10^8 tons.[127] Lignin is very important because it is considered as a potential source of aromatic compounds and renewable feedstock. Lignin is a complex phenolic polymer (Figure 30) comprising three hydroxycinnamyl alcohols or monolignols: p-coumaryl alcohol (MH), coniferyl alcohol (MG), and sinapyl alcohol (MS) in the main.[128]

Different methods used to synthesize lignin-based cross-linking agents for epoxy systems have been summarized.[9,128,129] On the whole, lignin-based curing agents are prepared by two different methods, either the reaction of lignin with ozone in the presence of NaOH to give lignin with unsaturated carboxyl groups[130−132] or via reaction of modified lignin (partially depolymerized lignin or polyol solutions of alcoholysis lignin) with anhydrides or trimellitic anhydride chloride (Figure 31).[133−138] Qin et al.[133] reported that epoxy resins cured by partially depolymerized lignin-based poly(carboxylic acid) (LPCA) (acid value of 229 g/mol) exhibited comparable $T_g$ and storage modulus to that cured with a commercial anhydride curing agent.

## MISCELLANEOUS

Chitosan (Figure 32), the partially deacetylated derivative of chitin, is mainly composed of two kinds of structural units: N-acetylglucosamine and D-glucosamine. Due to the presence of primary amine and acetamido groups in the structure, chitiosan has the potential to cross-link with epoxy prepolymers. Few studies used chitosan as an epoxy hardener to react with poly(ethylene glycol) diglycidyl ether (PEGDE),[139] ethylene glycol diglycidyl ether(EGDE),[140] or with DGEBA[141,142] for different applications including hydrogels,[139] polymeric stents,[140] cement slurry,[141] and waterborne epoxy dispersions.[142]

Liu et al.[143] used dextrin, a hydrolyzate from starch, modified with TMA as the curing agent for waterborne epoxy systems used to bond wood. The adhesion properties were comparable with that of a phenol−formaldehyde resin reinforcing the use of
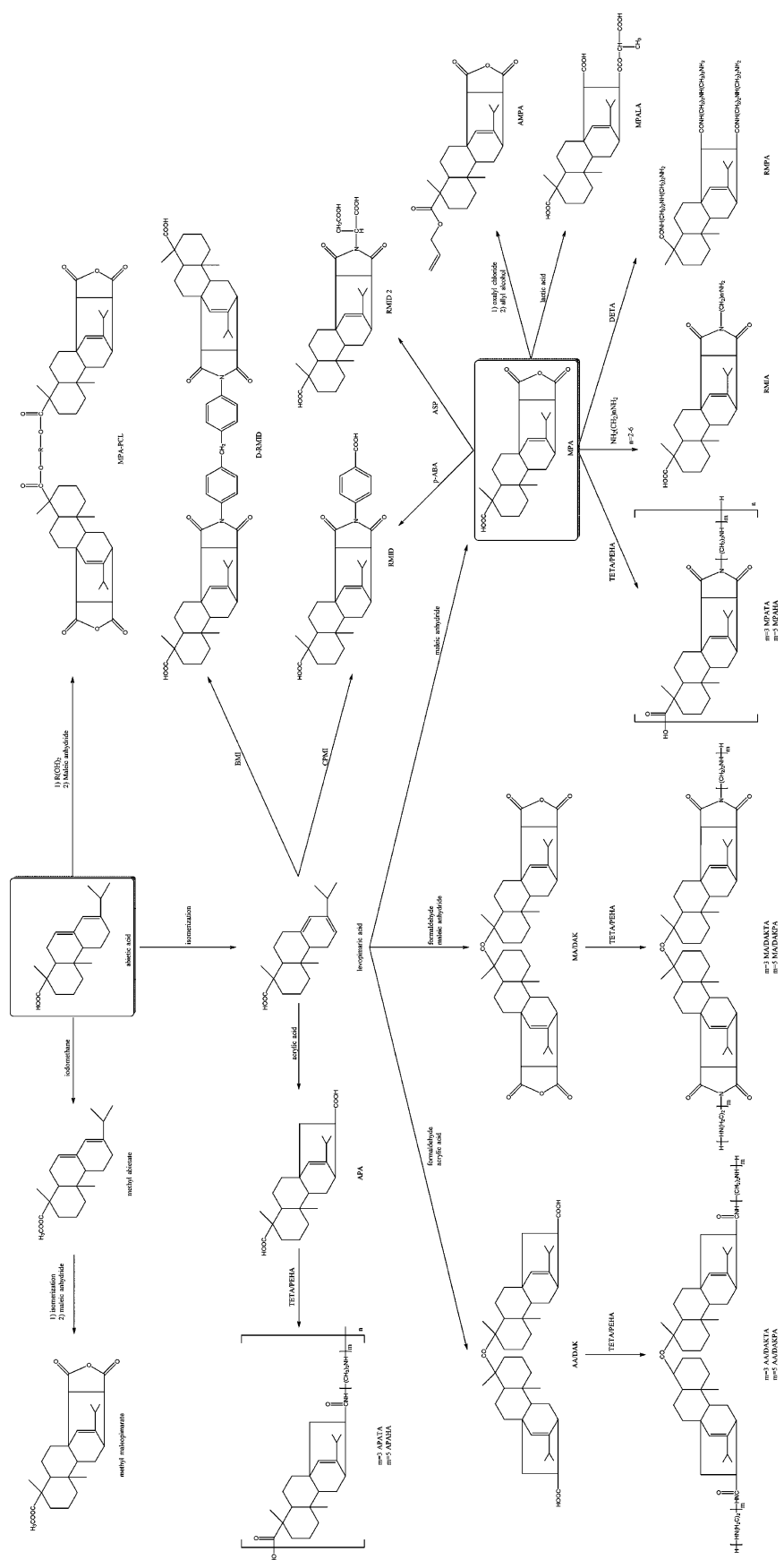
**Figure 27.** Chemical transitions of rosin acid to biobased amino and carboxyl curing agents.
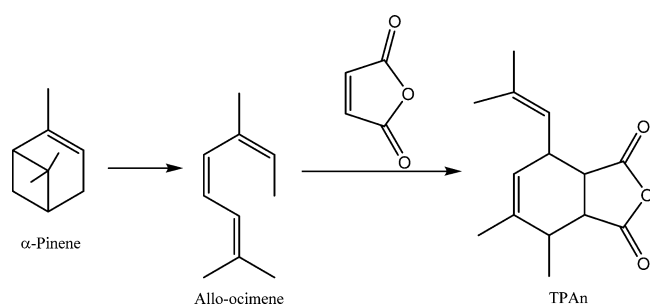
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**Figure 28.** Synthesis of terpene-based acid anhydride (TPA).
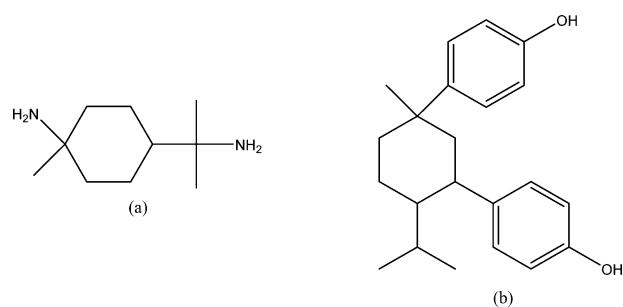


**Figure 29.** Formula of (a) menthane diamines and (b) terpene diphenol (TPD).



**Figure 31.** Synthesis of carboxylic acid from lignin.
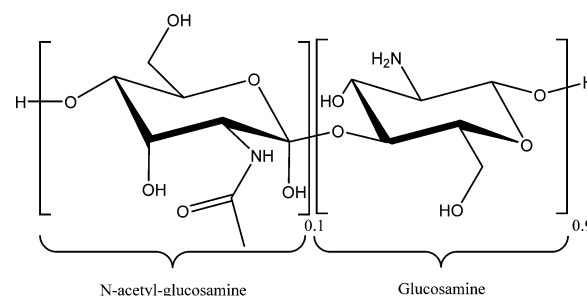


**Figure 32.** Structure of chitosan.

starch, another large amount of renewable materials, as curing agents possible.

Interestingly, due to the high percentage of carboxylic acid and phenolic groups in graphene oxide (GO), Ahn et al.[144] have reacted GO with epoxidized methyl oleate (EMO) using a one-step process without catalyst or solvent to obtain oleo-functionalized GO (oleo-GO) dispersible in a wide range of solvents. Puig et al.[145] have prepared superparamagnetic nanocomposites by dispersing oleic acid (OA)-coated magnetite nanoparticles in an epoxy compound based on DGEBA modified with OA. By modification with OA, a large mass fraction (at least up to 8 wt %) of OA-stabilized magnetite nanoparticles was homogeneously dispersed in a DGEBA-based epoxy matrix. The obtained nanocomposites showed a shape memory effect.

## ■ CONCLUDING REMARKS

In conclusion, the desire for sustainable materials, in particular biobased polymers, will see an upsurge in curing agents from renewable materials. The demand for biobased products is growing; current annual growth of the market for biobased plastics is at 20% with the worldwide production capacity of biopolymers forecast to increase from 3.5 million tonnes (2011) to 12 million tonnes by 2020.[146]

Biobased curing agents most likely arise from within a biorefinery concept and are not produced on an individual basis *per se*. The biorefinery is a concept that integrates biomass



**Figure 30.** Schematic model of lignin structure.

conversion processes and equipment to produce fuels, power, and chemicals from biomass. Waste biomass will become an important feedstock for biobased curing agents. For example, 1.3 billion tonnes of unavoidable food waste is generated globally,[147] with approximately 89 million tonnes generated in the EU each year. Food supply chain wastes are a rich source of triglycerides, lipids, terpenes, amines, amino acids, peptides, proteins, carbohydrates, and polyphenols such as catechins, hydroxycinnamates, procyanidins, phloretin glycosides, and quercetin glycosides.[95,148−150] Coupled with utilization of waste carbon dioxide, which can be sourced from flue gases, alkene-rich biobased feedstocks, for example, triglycerides, will have an important role to play as they offer opportunities for biobased polycarbonates and polyurethanes as shown in Figure 33.[151]
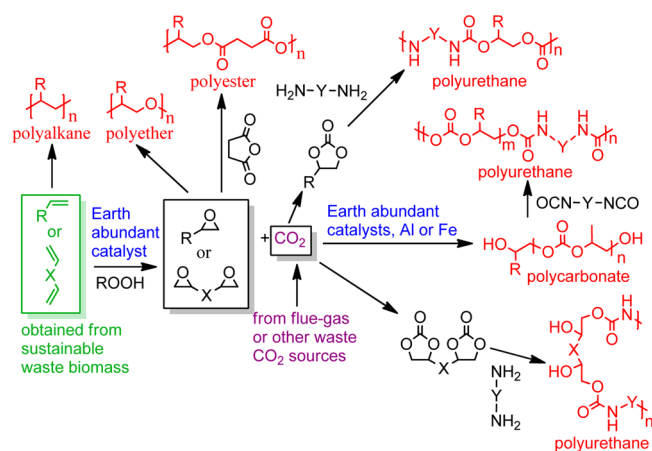


**Figure 33.** General overview of potential routes for biobased polymers from waste biomass, including carbon dioxide.

Plant oils will continue to be an interesting source of biobased curing agents due to their vast availability, array of functionalities, and ease of modification. However, utilization of lignin and its scope for modification to biobased curing agents represents a huge future opportunity within the framework of either a lignin or lignocellulosic biorefinery.

Lignin serves as an important renewable resource to produce phenols and phenol derivatives and aromatic chemicals,[152] which can be further exploited as biobased curing agents. Biorefineries do sound like an attractive proposition for sourcing biobased curing agents, but challenges in separation and purification science will need to be addressed, especially where the feedstock may be highly heterogeneous.

However, with the development of curing agents from renewable materials, two important factors must not be neglected: (i) Biobased content, the percentage of carbon in a product that is derived from biobased materials relative to the total amount of carbon (bio plus fossil) in the product (i.e., BIO% = $[C_{bio}]/[C_{bio} + C_{petro}]$), determined by $^{14}C$ analysis, needs to be considered.[153] (ii) Future biobased curing agents should have minimal harmful effects to human health and the environment. The best materials will be benign by design, nontoxic, and use renewable feedstocks. The end of life of fate of biobased curing agents will come under greater scrutiny in the future.

Finally, although Type II curing agents have not been discussed in this review, where biobased curing agents are reliant on metals, then elemental sustainability will become an

issue.[154] The EU has recently revised its list of critical raw materials from 14 to 20.[155] The list includes antimony, beryllium, and cobalt the salts, which have been used as catalysts in epoxy−carboxyl reactions.[156]

Thus, to conclude, biobased curing agents should not be viewed alone but should be viewed holistically across the entire supply chain from feedstock to final products to ensure best sustainability gains achieved. This is a very exciting period in the development of biobased materials, in particular, biobased epoxy resins.

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**Notes**

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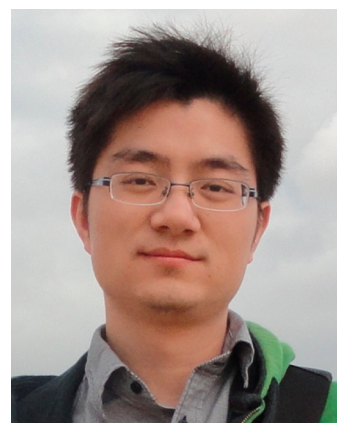


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renewable and recycling technologies and processes allied to biowastes.

## ■ ABBREVIATIONS

AESO, acrylated epoxidized soybean oil; AGSO, polyamine grapeseed oil; AMPA, vinyl ester of MPA; APA, acryloabietic acid; ASP, aspartic acid; BMI, 1,1′-(methylenedi-4,1-phenylene)bismaleimide; BTCA, 1,2,4-benzenetricarboxylic anhydride; CAHC, cysteamine hydrochloride; CHDB, 1,2-cyclohexanedicarboxylic anhydride; CNSL, cashew nut shell liquid; CPMI, carboxyphenylmaleimide; DAK, diabietyl ketone; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DCAs, dicarboxylic acids; DDA, decamethylene diamines; DDM, diaminodiphenylmethane; DDS, dodecenylsuccinic anhydride; DEG, diethylene glycol; DETA, diethylenetri-amine; DGEBA, diglycidyl ether of bisphenol A; DGE-DHBP, diglycidyl ether of 4,4′-di-hydroxybiphenol; DMA, dynamic mechanical analysis; DMAP, 4-dimethylaminoyridine; DOE, U.S. Department of Energy; D-RMID, di-RMID; DSO, dihydroxyl soybean oil; EGDE, ethylene glycol diglycidyl ether; ELO, epoxidized linseed oil; EMO, epoxidized methyl oleate; ENR, epoxidized natural rubber; EPOs, epoxidized plant oils; ESO, epoxidized soybean oil; GO, grapheme oxide; GPE, glycerol polyglycidyl ether; HHPA, hexahydrophthalic anhydride; HMD, hexamethylenediamine; IPDA, isophoronediamine; LC, liquid crystalline; LCEs, liquid crystalline elastomers; MA, maleic anhydride; MDA, methylenedianiline; MEG, monoethylene glycol; MFC, microfibrillated cellulose; MG, coniferyl alcohol; MH, p-coumaryl alcohol; MHHPA, methylhexahydrophthalic anhydride; 1-MI, 1-methylimidazole; 2-MI, 2-methylimidazole; MLO, maleated linseed oil; MMP, methyl maleopimarate; MMS, maleated methyl soyate; MNA, methyl nadic anhydride; MPA, maleopimaric acid; MPALA, lactic ester of MPA; MPA-PCL, MPA terminated polycaprolactones; MPO, maleated plant oil; MS, sinapyl alcohol; MSO, maleated soybean oil; MTHPA, methyl tetrahydrophthalic anhydride; OA, oleic acid; oleo-GO, oleo-functionalized reduced GO; PA, phthalic anhydride; p-ABA, p-aminobenzoic acid; PCO, phosphorylated castor oil; PEGDE, poly(ethylene glycol) diglycidyl ether; PEHA, pentaethylene hexamine; PESD, poly(epoxidized soybean oil-co-decamethylene diamine); PG, pyrogallol; PGPE, polyglycidyl ether of polyglycerol; PGVNC, pyrogallol–vanillin calixarene; PL, ε-polylysine; PN, petroleum-based phenol novolac; PPh3, triphenylphosphine; PSA, pressure sensitive adhesive; PTC, phase transfer catalysis; QC, quercetin; RMIA, rosin-based imidoamine; RMID, rosin maleic anhydride imidodicarboxylic acid; RMPA, rosin-based polyamide; SOMGs, soybean oil monoglycerides; SPE, sorbitol polyglycidyl ether; TBD, triazobicyclodecene; TCPA, tetrachlorophthalic anhydride; TEA, triethylamine; TEPA, tetrathylenepentamine; TETA, triethylenetetramine; $T_g$, glass transition temperature; THPA, tetrahydrophthalic anhydride; TMA, trimellitic anhydride; TOA, tung oil anhydride; TPA, terpene-based acid anhydride; TPD, terpene diphenol; TPDB, terpenediphenol-based benzoxazine; TPG, tung oil–pyrogallol resin; UDETA, aminoethylimidazolidone; VN, vanillin; xLCEs, liquid crystal elastomers with exchangeable links; Zn(acac)2, zinc acetylacetonate dehydrate; Zn(OAc)2, zinc acetate

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