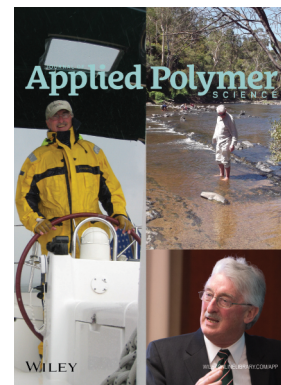


Special Issue: Sustainable Polymers and Polymer Science  
Dedicated to the Life and Work of Richard P. Wool

Guest Editors: Dr Joseph F. Stanzione III (Rowan University, U.S.A.)  
and Dr John J. La Scala (U.S. Army Research Laboratory, U.S.A.)



#### EDITORIAL

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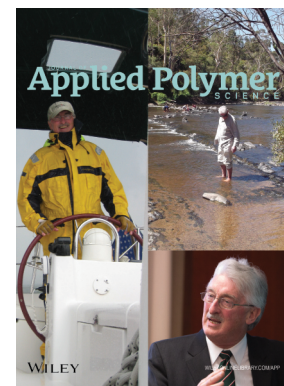
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## Recent advances in bio-based epoxy resins and bio-based epoxy curing agents

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**ABSTRACT:** The combination of awareness of harmful industrial processes and environmental issues and depleting petroleum-based resources has spurred much research in developing materials from renewable sources. Epoxy resins are common pre-polymers used in a variety of industries, such as adhesives, coatings, insulations, and high performance composites. To transform epoxy resins into crosslinked networks with desirable thermal and mechanical properties, the resins must be cured with a curing agent. This review encompasses recent developments using bio-based epoxy resins and bio-based epoxy curing agents. Resins and curing agents synthesized from modified plant oils, sugars, polyphenols, terpenes, rosin, natural rubber, and lignin are highlighted and their thermal and mechanical properties reviewed. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44103.

**KEYWORDS:** biopolymers and renewable polymers; cellulose and other wood products; resins; structure-property relations; thermosets

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### INTRODUCTION

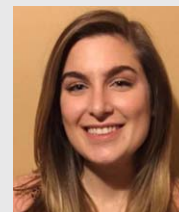
Growing environmental and economic concerns as well as the uncertainty that accompanies finite petrochemical resources has caused a rapid increase in the research and development of bio-based polymers in recent years. Manufacturers are looking to replace petroleum-based materials with polymers derived from naturally-occurring feedstocks to satisfy the industrial need for processes and products that are compatible with the environment and that enhance sustainable development.<sup>1</sup> Additionally, developing safer methods of polymer production, including the use of safer building blocks and additives, are of great interest.

A pinnacle example of a controversial petroleum-based building block and additive utilized in the polymer industry is bisphenol A (BPA, 4,4'-(propane-2,2-diyl)diphenol). Despite being classified as a reprotoxic and banned for use in children's bottles and cups in Canada, the European Union, as well as in more than ten states in the United States of America, BPA is still widely used.<sup>2,3</sup> The monomer BPA is a chemical precursor in the production of many vinyl ester resins, unsaturated polyester resins and cyanate esters.<sup>4</sup> BPA also serves as a basis for 85% of the world's production of epoxy resins, which are industrially common prepolymers that contain oxirane groups (Figure 1).<sup>5-7</sup> Epoxy resins account for about 8% of the thermosetting resins that are used in resin production.<sup>1</sup> Thermosets that contain the core BPA structure in the polymer network display excellent

mechanical properties and provide sturdy materials for use in the construction, transportation, and furniture industries.<sup>1,8</sup> Thermosetting resins are expected to contribute 13.6% of total revenue of the plastics and resins industry or ~\$14 billion in 2016.<sup>9</sup> Epoxy resins in particular afford high adhesiveness and excellent chemical and heat resistance, making them a common material for adhesives and high-performance coatings.<sup>8</sup> Globally, 41% of liquid epoxy resins that are produced are used for coatings and 31% are for adhesives with the remaining 28% used in a variety of other applications.<sup>10</sup> In 2014, U.S. production of epoxy resins was at 254,465 metric tons making it a formidable and highly valued market.<sup>11</sup>

Epoxy resins are cured with the addition of a curing agent, or hardener, which can be a variety of compounds, such as, polyamines, acid anhydrides, or Lewis acids or bases.<sup>12</sup> The properties of the cured resins depend greatly on the type of epoxy and type of curing agent employed. As with the epoxy resins, the curing agents that are commonly used today are derived from petroleum sources as well.<sup>13</sup> Additionally, common curing agents, such as isophorone diamine (IPDA) and other polyamines, polyamides, and anhydrides, are toxic before being cured, which poses additional environmental and health issues.<sup>14,15</sup> For example, the resin that is based on BPA consists of the epoxidized compound diglycidyl ether of bisphenol-A (DGEBA) mixed with a diamine hardener, such as IPDA (Figure

After receiving her B.A. in Physics from Franklin & Marshall College, **Elyse A. Baroncini** worked for a small company north of Philadelphia manufacturing analytical instrumentation. She spent 2.5 years traveling the globe as an applications engineer before leaving her position to enroll in Rowan University's Chemical Engineering graduate program. Currently, she is completing her Ph.D. research investigating lignin as an alternative feedstock for petroleum-based plastics. Her other areas of interest include bio-based materials for lithium-ion batteries.



**Santosh Kumar Yadav** received his M.Sc. at the University of Allahabad, India in organic chemistry and his Ph.D. at the Konkuk University Seoul, Korea. He worked as visiting scientist at Korea Institute of Science and Technology (KIST). He also worked as postdoctoral researcher at Nanyang Technological University Singapore. Currently, he is working as Assistant Research Professor at the department of chemical and biological engineering at Drexel University. His research interests include bio-based epoxy and polyimide thermosets and carbon nanomaterials (CNT & graphene) based composites.



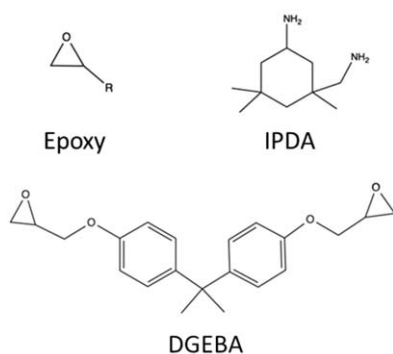
**Giuseppe R. Palmese** is Professor and Head of the Department of Chemical and Biological Engineering at Drexel University where he is also Professor of Materials Science and Engineering. He holds a BSE ('86) in chemical engineering from Princeton University and a Ph.D. ('92) in chemical engineering from the University of Delaware. Dr. Palmese's research focuses on processing-structure-property relationships of thermosetting polymer systems. His current research thrusts include: multifunctional polymer systems, polymer composites, and materials from renewable sources.



**Joseph Stanzone, III** received his B.S. and M.S. degrees at Drexel University and his Ph.D. at the University of Delaware, all in chemical engineering. He then joined the chemical engineering faculty at Rowan University in 2013. His teaching interests include thermodynamics; polymer science and engineering; green chemistry and engineering; and bio-based materials. His research program focuses on the utilization of woody biomass as an alternative chemicals feedstock, the development of next-generation lignocellulosic biorefineries, and bio-based polymers and composites.



1). DGEBA itself is formed from the reaction of BPA and epichlorohydrin in the presence of a basic catalyst.<sup>8</sup> Epichlorohydrin has historically been synthesized from propylene.<sup>16</sup>



**Figure 1.** Structures of a typical epoxy, top left, IPDA, top right, and DGEBA, bottom.

However, newer, more environmental friendly methods of epichlorohydrin production have been recently implemented<sup>16,17</sup> lending some sustainability toward DGEBA production, though more action must be taken by choosing safer monomer and curing agent alternatives to chemicals such as BPA and IPDA.

Therefore, it has been the subject of much research worldwide to develop safer epoxy resins and curing agents from bio-based, sustainable alternative sources. This review covers recent advances in the utilization of renewable resources to produce industrially viable bio-based epoxy resins and epoxy resin curing agents. The renewable resources covered include plant oils, saccharides, catechins, tannins, cardanols, terpenes, rosins, and lignin. Table I serves as an illustrative summary and a guide of the bio-based sources covered and their potential applications. It is with hope that utilizing these bio-based sources will decrease the global dependence on petroleum, thereby, creating a more sustainable production future, but also leads to the creation of

**Table I.** An Illustrative Guide to Bio-Based Epoxy Resins and Epoxy Curing Agents Covered along with Highlighted Properties and Potential Applications of the Cured Epoxy Resins

Review section	Epoxy resin	Curing agents, initiators and accelerators	Properties <sup>a</sup>	Potential applications	References
2.A.	Epoxidized soybean oil	<ul style="list-style-type: none"> <li>• Benzylsulfonium hexafluoroantimonate derivative cationic catalyst</li> </ul>	<ul style="list-style-type: none"> <li>• Max stress of 12.3 MPa</li> <li>• Recovery % at fifth cycle &gt; 90%</li> </ul>	Shape memory polymers	18
	Epoxidized soybean oil	<ul style="list-style-type: none"> <li>• Boron trifluoride diethyl etherate catalyst</li> </ul>	<ul style="list-style-type: none"> <li>• Water vapor permeabilities of <math>4.5 \times 10^{-8} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}</math></li> </ul>	Water resistant paper composites	19
	Epoxidized linseed oil	<ul style="list-style-type: none"> <li>• Methylhexahydrophthalic anhydride</li> <li>• Benzophenone-3,3',4,4'-tetracarboxylic dianhydride</li> </ul>	<ul style="list-style-type: none"> <li>• <math>68^\circ\text{C} &lt; T_g</math> (based on <math>E''</math> peaks) <math>&lt; 134^\circ\text{C}</math></li> </ul>	Composites, adhesives, and laminates	20
	Epoxidized canola oil	<ul style="list-style-type: none"> <li>• Phthalic anhydride</li> </ul>	<ul style="list-style-type: none"> <li>• <math>13 \text{ min} &lt; \text{Gelation time at } 155^\circ\text{C} &lt; 28 \text{ min}</math></li> <li>• <math>-3.6^\circ\text{C} &lt; T_g</math> (based on <math>\tan \delta</math> peaks) <math>&lt; 37.8^\circ\text{C}</math></li> </ul>	Cellulosic particle and fiberboards	21
	Epoxidized karanja oil	<ul style="list-style-type: none"> <li>• Citric acid</li> <li>• Tartaric acid</li> </ul>	<ul style="list-style-type: none"> <li>• <math>280^\circ\text{C} &lt; T_{d5\%}</math> (TGA in <math>\text{N}_2</math>) <math>&lt; 295^\circ\text{C}</math></li> <li>• <math>109^\circ\text{C} &lt; T_g</math> (based on DSC thermograms) <math>&lt; 112.7^\circ\text{C}</math></li> <li>• <math>4.5 \text{ MPA} &lt; TS &lt; 10.6 \text{ MPA}</math></li> </ul>	Paper coating/lamination and mosquito deterrents	22
2.B.	Isosorbide diepoxy (DGEDAS)	<ul style="list-style-type: none"> <li>• Diaryl iodonium salt (I250)</li> </ul>	<ul style="list-style-type: none"> <li>• <math>210^\circ\text{C} &lt; T_{d5\%}</math> (TGA in argon) <math>&lt; 300^\circ\text{C}</math></li> <li>• <math>81^\circ\text{C} &lt; T_g</math> (based on <math>\tan \delta</math> peaks) <math>&lt; 125^\circ\text{C}</math></li> </ul>	Coatings	23
	Diglycidyl ethers of isosorbide (DGEI)	<ul style="list-style-type: none"> <li>• Isosorbide diamine (ISODA) hardeners</li> </ul>	<ul style="list-style-type: none"> <li>• <math>34^\circ\text{C} &lt; T_g</math> (based on <math>E''</math> peaks) <math>&lt; 79^\circ\text{C}</math></li> <li>• <math>41 \text{ MPA} &lt; TS &lt; 62 \text{ MPA}</math></li> <li>• <math>1168 \text{ MPA} &lt; E_{\text{bend}} &lt; 4027 \text{ MPA}</math></li> </ul>	Epoxy resins in food industry	24
	Furan diepoxy of 2,5-bis(hydroxymethyl)furan (BHMF)	<ul style="list-style-type: none"> <li>• IRGACURE 250</li> <li>• Triphenylsulfonium hexafluoroantimonate salt initiators</li> </ul>	<ul style="list-style-type: none"> <li>• Joint tensile shear strength of 3.5 MPa</li> </ul>	Adhesives	25
	Furan diepoxy of 2,5-bis[[2-oxiranylmethoxy)methyl]furan (BOF)	<ul style="list-style-type: none"> <li>• 4, 4'-methylene bis-cyclohexanamine (PACM)</li> <li>• Diethyl toluene diamine (EPIKURE W)</li> </ul>	<ul style="list-style-type: none"> <li>• <math>71^\circ\text{C} &lt; T_g</math> (based on <math>E''</math> peaks) <math>&lt; 133^\circ\text{C}</math></li> </ul>	Polymer composites, insulation materials, coatings and adhesives	26
	diglycidyl ester of 2,5-furandicarboxylic acid (DGF)	<ul style="list-style-type: none"> <li>• Methylhexahydrophthalic anhydride (MHHPA)</li> </ul>	<ul style="list-style-type: none"> <li>• <math>101^\circ\text{C} &lt; T_g</math> (based on <math>\tan \delta</math> peaks) <math>&lt; 152^\circ\text{C}</math></li> </ul>	Resins in aerospace, coatings, adhesives and composites	27

Table I. Continued

Review section	Epoxy resin	Curing agents, initiators and accelerators	Properties <sup>a</sup>	Potential applications	References
		<ul style="list-style-type: none"> <li>• Poly(propylene glycol)bis(2-aminopropyl ether)</li> </ul>	<ul style="list-style-type: none"> <li>• 68 MPa &lt; <math>TS</math> &lt; 84 MPa</li> <li>• 75 MPa &lt; <math>FS</math> &lt; 96 Mpa</li> </ul>		
2.C.	Epoxidized catechin	<ul style="list-style-type: none"> <li>• Methanol soluble lignin</li> <li>• Isophorone diamine (IPD)</li> </ul>	<ul style="list-style-type: none"> <li>• <math>T_g</math> (based on DSC thermograms) of 178 °C</li> <li>• 1500 MPa &lt; <math>E'</math> at 30 °C &lt; 2340 MPa</li> <li>• 142 °C &lt; <math>T_g</math> (based on <math>\tan \delta</math> peaks) &lt; 179 °C</li> </ul>	DGEBA replacements in coatings, laminates, adhesives, floorings, pavings, composites, and electronics	28,29
	Epoxidized cardanol	<ul style="list-style-type: none"> <li>• IPD</li> <li>• Jeffamine D400 diamine</li> <li>• Jeffamine T403</li> </ul>	<ul style="list-style-type: none"> <li>• 15 °C &lt; <math>T_g</math> (based on <math>E''</math> peaks) &lt; 50 °C</li> <li>• 37 °C &lt; <math>T_g</math> (based on DSC thermograms) &lt; 60 °C</li> <li>• 7 MPa &lt; <math>E'</math> at 20 °C &lt; 1218 MPa</li> <li>• 294 °C &lt; <math>T_{d30\%}</math> (TGA in <math>N_2</math>) &lt; 366 °C</li> </ul>	Coatings	30,31
2.D.	Terpene-maleic ester-type epoxy (TME)	<ul style="list-style-type: none"> <li>• Hexamethylene diisocyanate (HDI) tripolymer</li> </ul>	<ul style="list-style-type: none"> <li>• <math>T_g</math>s (based on DSC thermograms) of ~400–420 °C</li> </ul>	Waterborne polyurethane/epoxy resin composite coatings	32
	Glycidyl ether of limonene alkylated naphthol-formaldehyde	<ul style="list-style-type: none"> <li>• Dicyanodiamide</li> <li>• Bisphenol A-formaldehyde novolac resin</li> </ul>	<ul style="list-style-type: none"> <li>• 171 °C &lt; <math>T_g</math> (based on DSC thermograms) &lt; 182 °C</li> <li>• 332 °C &lt; <math>T_{d10\%}</math> (TGA in air) &lt; 343 °C</li> </ul>	DGEBA replacements in electronics	33
	Epoxidized rosin derivatives (tetraglycidyl dimaleopimaric ketone) (TGK)	<ul style="list-style-type: none"> <li>• Rosin-based cross-linker</li> <li>• Dirosin-maleic anhydride imidodicarboxylic acid</li> <li>• <i>p</i>-phenylene diamine</li> </ul>	<ul style="list-style-type: none"> <li>• 0.71 GPa &lt; <math>E'</math> at 25 °C &lt; 1.71 GPa</li> <li>• 122 °C &lt; <math>T_g</math> (based on <math>\tan \delta</math> peaks) &lt; 140 °C</li> </ul>	Replacements for BPA in coatings	34
	Liquid epoxidized natural rubber (LENR)	<ul style="list-style-type: none"> <li>• Epikure d230</li> </ul>	<ul style="list-style-type: none"> <li>• Impact strength of 7.6 kJ m<sup>-2</sup></li> <li>• <math>FS</math> of 58 MPa</li> <li>• <math>E_{bend}</math> of 3.25 GPa</li> </ul>	Fiber-reinforced epoxy composites in the automotive industry	35
2.E.	Cedar, eucalyptus and bamboo-derived epoxies	<ul style="list-style-type: none"> <li>• Lignin-based curing agent</li> <li>• Commercial curing agent TD2131</li> </ul>	<ul style="list-style-type: none"> <li>• 259 °C &lt; <math>T_{d5\%}</math> (TGA in <math>N_2</math>) &lt; 296 °C</li> </ul>	Electronics	36
	Epoxidized versions of de-polymerized organosolv lignin (DOL) and de-polymerized Kraft lignin (DKL)	<ul style="list-style-type: none"> <li>• 4,4-diaminodiphenyl methane (DDM)</li> <li>• Diethylenetriamine (DETA)</li> </ul>	<ul style="list-style-type: none"> <li>• 376 °C &lt; <math>T_{max}</math> (TGA in <math>N_2</math>) &lt; 416 °C</li> </ul>	Adhesives, composites, coatings and electronics	37

Table I. Continued

Review section	Epoxy resin	Curing agents, initiators and accelerators	Properties <sup>a</sup>	Potential applications	References
3.A.	Epoxidized cardanol	<ul style="list-style-type: none"> <li>• Cardanol-based amine</li> </ul>	<ul style="list-style-type: none"> <li>• <math>19\text{ }^{\circ}\text{C} &lt; T_g</math> (based on DSC thermograms) <math>&lt; 30\text{ }^{\circ}\text{C}</math></li> <li>• <math>1.4\text{ MPa} &lt; E'</math> at <math>20\text{ }^{\circ}\text{C} &lt; 350\text{ MPa}</math></li> </ul>	Coatings	38
	Furan-based epoxy 2,5-bis[[2-oxiranyl-methoxy)methyl]-furan (BOF)	<ul style="list-style-type: none"> <li>• 5,5'-methylene difurfurylamine (DFDA)</li> <li>• 5,5'-ethylidene difurfurylamine (<math>\text{CH}_3</math>-DFDA)</li> </ul>	<ul style="list-style-type: none"> <li>• <math>62\text{ }^{\circ}\text{C} &lt; T_g</math> (based on <math>\tan \delta</math> peaks) <math>&lt; 142\text{ }^{\circ}\text{C}</math></li> </ul>	Coatings, adhesives, and composites	39
	Vanillin-based diglycidyl ether of methoxyhydroquinone (DGMHQ)	<ul style="list-style-type: none"> <li>• bis(furfurylamine)-A</li> </ul>	<ul style="list-style-type: none"> <li>• <math>74\text{ }^{\circ}\text{C} &lt; T_g</math> (based on DSC thermograms) <math>&lt; 98\text{ }^{\circ}\text{C}</math></li> </ul>	Marine, automobile, or food industries	40
3.B.	Epoxidized sucrose soyate (ESS)	<ul style="list-style-type: none"> <li>• Water-soluble natural acids (citric acid, malic acid, tartaric acid, malonic acid, oxalic and glutaric acid)</li> </ul>	<ul style="list-style-type: none"> <li>• <math>17\text{ }^{\circ}\text{C} &lt; T_g</math> (based on <math>\tan \delta</math> peaks) <math>&lt; 96\text{ }^{\circ}\text{C}</math></li> <li>• <math>1.82\text{ MPa} &lt; E'</math> at <math>25\text{ }^{\circ}\text{C} &lt; 944\text{ MPa}</math></li> </ul>	Coatings and films	41
	DGEBA	<ul style="list-style-type: none"> <li>• Soybean oil derived polyacid hardener</li> </ul>	<ul style="list-style-type: none"> <li>• <math>T_g</math> (based on DSC thermogram) of <math>-3\text{ }^{\circ}\text{C}</math></li> <li>• <math>E'</math> at <math>\sim 20\text{ }^{\circ}\text{C}</math> of <math>0.59\text{ MPa}</math></li> </ul>	Coatings and bindings	42
3.C.	Epoxidized soybean oil	<ul style="list-style-type: none"> <li>• Terpene-based anhydrides (TPAn)</li> </ul>	<ul style="list-style-type: none"> <li>• <math>59\text{ }^{\circ}\text{C} &lt; T_g</math> (based on DSC thermograms) <math>&lt; 67\text{ }^{\circ}\text{C}</math></li> </ul>	Biocomposites	43
3.D.	Epoxidized soybean oil	<ul style="list-style-type: none"> <li>• Tannic acid</li> </ul>	<ul style="list-style-type: none"> <li>• <math>15\text{ MPa} &lt; TS &lt; 26\text{ MPa}</math></li> <li>• <math>58\text{ }^{\circ}\text{C} &lt; T_g</math> (based on <math>\tan \delta</math> peaks) <math>&lt; 61\text{ }^{\circ}\text{C}</math></li> </ul>	Biocomposites	44
	DGEBA	<ul style="list-style-type: none"> <li>• Cardanol-derived phenalkamine (PKA)</li> </ul>	<ul style="list-style-type: none"> <li>• <math>TS</math> of <math>56\text{ MPa}</math></li> <li>• <math>8.88\%</math> elongation</li> <li>• Impact strength of <math>13.92\text{ kJ m}^{-2}</math></li> </ul>	Binders, coatings and paints	45

<sup>a</sup>Property Symbols:  $T_g$ , glass transition temperature;  $T_{d5\%}$ , temperature of 5% weight loss;  $TS$ , tensile strength;  $E_{\text{bend}}$ , flexural modulus;  $E'$  loss modulus;  $FS$ , flexural strength;  $E'$ , storage modulus;  $T_{d30\%}$ , temperature of 30% weight loss;  $T_{d10\%}$ , temperature of 10% weight loss;  $T_{\text{max}}$ , maximum rate decomposition temperature.

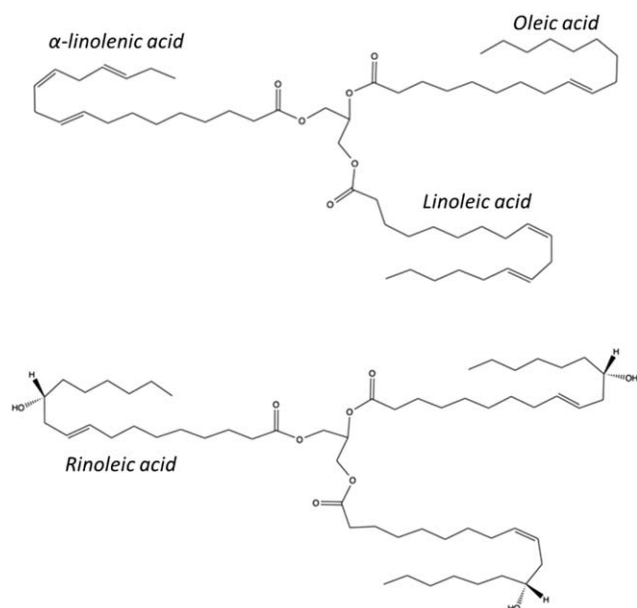
safer chemicals and superior performing polymers than those currently used in industry.

### BIO-BASED EPOXY RESINS

Commercial epoxy resins are usually synthesized from DGEBA, cycloaliphatic epoxies, or diglycidyl ethers of Novolac resins.<sup>8</sup> Renewable natural resources, such as plant oils and starches, have attracted interest as building blocks for polymers because of their low cost, environment-friendly nature and ability to be epoxidized facilely, yielding bio-based epoxy resins.<sup>8</sup> The following section highlights the major recent advances of using renewable resources to create epoxy resins.

### Plant Oils

Plant oils are triglycerides with compositions that depend on the type of plant and growing conditions.<sup>46</sup> The oils can be divided into three classes depending on degree of unsaturation: drying, semi-drying, and nondrying. The degree of unsaturation is typically expressed as an iodine value. Drying oils have high levels of unsaturated fatty acids and iodine values above 150.<sup>47</sup> Drying oils, such as linseed and tung oils, form a tough, elastic film and are used in paints and enamels.<sup>1</sup> Semi-drying oils, such as soybean, sunflower, and corn oils, have iodine values between 100–150 and are used in foods.<sup>1,47</sup> Nondrying oils, such as castor, palm, and rapeseed oils, have iodine values under 100 and are greasy and can rot.<sup>1,47</sup> About 75% of global



**Figure 2.** Representative structures of linseed oil and castor oil, both of which consist of a triglyceride group connected to fatty acid chains. Linseed oil (top) contains many of the following fatty acid chains: oleic acid, linoleic acid, and  $\alpha$ -linolenic acid. Castor oil (bottom) contains many of the fatty acid chains rinoleic acid. The oleic acid on linseed oil and the rinoleic acid on castor oil differ by one additional hydroxyl group.

seed oil production is for food use with the remaining 25% used for industrial applications, such as coatings, adhesives, cosmetics, inks, and plasticizers.<sup>1</sup>

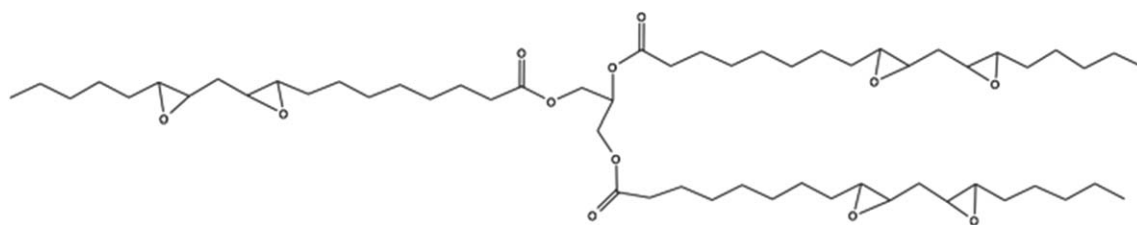
The alkenyl unsaturation and fatty acid compositions of the triglycerides determine the exact physical and chemical properties and the use of the plant oils.<sup>1,46,48</sup> A triglyceride consists of a glycerol attached to three fatty acids (Figure 2). The fatty acids vary with oil and there may be additional functional groups present on the fatty acids.<sup>49</sup> For example, linseed oil contains large amounts of linoleic acid,  $\alpha$ -linolenic acid, and oleic acid attached to a glycerol (Figure 2).<sup>49</sup> Additionally, ricinoleic acid, from castor oil, is almost identical to oleic acid, except for an additional hydroxyl group (Figure 2).<sup>50</sup> The additional hydroxyl increases the viscosity of ricinoleic acid as compared to oleic acid and makes it more suitable for use in lubricating oils and grease applications.<sup>1,50</sup>

The abundance of carbon-carbon double bonds makes plant oils a popular choice for use in thermoset resins, as the double bonds provide useful handles through which polymerizations can occur.<sup>51,52</sup> For use in bio-based polymers, plant oils must

be transformed in one of three ways: (i) through direct polymerization of the double bonds present in the fatty acid; (ii) through transformation of the double bonds into functional groups that can then be polymerized; and (iii) through transformation of the oils into simple fatty acids or diglycerides that can then be used as base monomers for polymer syntheses.<sup>50</sup>

**Soybean Oil.** Epoxidized soybean oil (ESO) (Figure 3) is a commercially available product that shows much promise in the replacement of petroleum-based polymers; the market for ESO is projected to reach 300 million USD by 2020.<sup>50,53</sup> In the past year alone, the use of ESO in a multitude of applications has been extensively researched around the globe. Much focus has been on tailoring specific properties of the resulting polymers by combining the ESO resins with materials, such as, plasticizers, hardeners, and diluents. For brevity yet inclusiveness, the wealth of ESO studies will not be explored in its entirety; instead, select recent papers will be highlighted. For a comprehensive look at advances in bio-based polymers created from ESO, readers are directed to additional studies by: Sahoo *et al.*,<sup>54</sup> Li and Sun,<sup>55</sup> He *et al.*,<sup>56</sup> Sung *et al.*,<sup>57</sup> and Li *et al.*,<sup>58</sup>

To improve the mechanical properties of ESO-based polymers, ESO has been mixed with petroleum-based resins to create thermosetting polymers with minimal petroleum-based content.<sup>59</sup> Such is the case in a 2015 study by Cavusoglu and Çayli where ESO was polymerized with maleate half-esters of oil-soluble resins, *p*-tertiary butyl phenol (*p*-TBP) and *p*-nonyl phenol (*p*-NP), to yield tough, thermosetting polymers.<sup>59</sup> The maleate half-esters were mixed with ESO and heated under nitrogen for a total of 6 h, allowing the maleic acids to react with ESO through a ring-opening reaction.<sup>59</sup> Dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and tensile strength testing were used to quantify the thermal and mechanical properties of the polymers. Storage modulus at 30 °C was determined to be 40 MPa for ESO cured with maleate half-ester of *p*-TBP at 150 °C (ESO-*p*-TBPMA-150), 10 MPa for ESO cured with maleate half-ester of *p*-NP at 150 °C (ESO-*p*-NPMA-150), 1088 MPa for ESO-*p*-TBP cured at 190 °C (ESO-*p*-TBPMA-190), and 180 MPa for ESO-*p*-NPMA cured at 190 °C (ESO-*p*-NPMA-190).<sup>59</sup> The glass transition temperatures ( $T_g$ s) (based on  $\tan \delta$  peak) were determined to be 33 °C, 25 °C, 65 °C, and 45 °C, respectively, and the tensile strength at break values were 4 MPa, 1.5 MPa, 12 MPa, and 13 MPa, respectively.<sup>59</sup> These mechanical results indicate that the resins cured at lower temperatures produced softer, more rubbery polymers. Thermal resistance was determined by TGA by the temperature at 5% weight loss. ESO-*p*-TBPMA-190 had the highest thermal



**Figure 3.** Structure of epoxidized linolein, a major component of ESO. Since this is epoxidized, there are epoxy functional groups in place of double bonds on the fatty acid chains.



resistance (247 °C), whereas ESO-*p*-TBPMA-150 had the lowest at 164 °C.<sup>59</sup> The aim of the study was to produce cheap, partially bio-based, industrially viable thermosetting polymers, an aim that was achieved.

Advanced applications of ESO have also appeared in the past year as researchers across the globe attempt to extend bio-based, renewable sources to every industry. In a 2015 study by Tsujimoto *et al.*,<sup>18</sup> ESO and the biodegradable polymer polycaprolactone (PCL) were crosslinked in an acid-catalyzed cure to create shape memory polymers. Shape memory polymers are advanced smart materials that can return to their original shape when induced by an external trigger, such as a change in temperature or pH.<sup>60</sup> Adding PCL to ESO helped to improve maximum stress, which increased from 1.0 to 12.3 MPa with the addition of 75 wt % of PCL. Additionally, the ESO/PCL networks showed excellent shape memory recovery characteristics when deformed with heat addition, making the bio-based and biodegradable polymer blend a novel path forward for designing smart materials.

Another advanced application of ESO was presented by Miao *et al.*<sup>19</sup> in a 2015 study where ESO was diffused into paper and polymerized *in situ* with a boron trifluoride diethyl etherate catalyst. Paper with ESO weight content of 40% and 50% yielded low water vapor permeabilities of  $4.5 \times 10^{-8}$  and  $3.5 \times 10^{-8}$  g m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup> as compared to  $1.17 \times 10^{-10}$  g m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup> of regular paper. Thus, thermally stable materials with lower water vapor permeability than that of other bio-based polymers were created, indicating that ESO could be used in future applications for water-resistant materials.

**Linseed Oil.** Linseed oil is the most commonly epoxidized oil because of the surplus of double bonds available in its linolenic acid chains (Figure 2).<sup>50</sup> As a drying oil, it is often used as a paint binder or wood finish. Epoxidized linseed oil (ELO) has become popular in thermoset applications as a result of the global effort to create bio-based polymers and to provide desired flexibility to petroleum-based epoxy resins for coatings and adhesive applications.<sup>52,61</sup> ELO is commercially available, though research is still focused on developing ELO as a matrix for composite materials with various reinforcements.<sup>50,62</sup>

To create thermally and mechanically stable materials, it was found that combining ELO with hardeners/curing agents, such as dicarboxylic acids<sup>61</sup> or anhydrides,<sup>20</sup> yielded highly cross-linked networks favorable for use in industrial applications. An industrially viable manufacturing process, resin transfer molding, for ELO-based resins crosslinked by methyl nadic anhydride was also evaluated and deemed an attractive method for production of bio-based epoxy resins.<sup>62</sup> The study, conducted by Samper *et al.*,<sup>62</sup> used ELO-based resins combined with reinforcing fibers from slate waste to create ELO-slate composites that could compete with traditional glass fiber reinforced composite laminates. The ELO-slate composites had tensile strengths between 328.2 and 359.1 MPa<sup>62</sup> and flexural strengths between 299.2 and 402.1 MPa,<sup>62</sup> whereas comparable glass composites in previous studies had tensile strengths of 186 MPa<sup>63</sup> and flexural strengths of 240 MPa.<sup>63</sup> However, the ELO-slate composites still could not compare with high performance fiber-based

composites, such as those based on carbon and aramids, which display tensile and flexural strengths of 242–312 MPa<sup>63</sup> and 600 MPa,<sup>63</sup> respectively. Still, the high cost and unsustainable nature of glass, carbon, and aramid fibers is causing the composites industry to turn to natural fibers in conjunction with bio-based composites, such as ELO-based resins.<sup>64</sup>

**Canola Oil.** The progress of canola oil as a base chemical for bio-based epoxy resins is not as far along as that of soybean or linseed oil. Studies over the past couple of years explored the ability to epoxidize canola oil with various catalysts.<sup>65,66</sup> For example, in a 2014 study aiming to find renewable, bio-based sources for lubricant applications, Somidi *et al.*, found sulfated SnO<sub>2</sub> to be the most selective and stable catalyst for epoxidation of canola oil.<sup>66</sup> Some work has also been done using canola oil to create bio-based polymers with improved physical properties.<sup>21,67</sup>

Omonov and Curtis created ECO-based thermosets with phthalic anhydride (PA) as the curing agent at various temperatures, 155 °C, 170 °C, 185 °C, and 200 °C, and with various molar ratios of ECO to PA, 1:1, 1:1.5, and 1:2.<sup>21</sup> The  $T_g$ s (based on peak of tan  $\delta$ ) of the cured resins do not vary much with curing temperature, 37.8 °C to 39.1 °C for 1:2 ECO:PA cured at 155 °C and 200 °C, respectively, but, do increase with increasing amount of PA, -3.6 °C to 37.8 °C when the molar ratio of PA is doubled at a cure temperature of 155 °C.<sup>21</sup> For all the polymers, the storage moduli below the  $T_g$ s were inversely proportional to the amount of PA used while the storage moduli above the  $T_g$ s increased with increasing amount of PA.<sup>21</sup> Using a higher amount of curing agent lead to enhanced crosslinking which in turn, decreased segmental mobility resulting in higher energy storage in the rubbery region.<sup>21</sup> In the glassy region below  $T_g$ , the authors suggest that higher energy storage was exhibited with lower PA contents due to the local relaxation of the unbounded/unreacted epoxy monomer, a monomer that contains significant side chains available for enhanced energy storage in the glassy region.<sup>21</sup> Though the thermo-mechanical properties were more influenced by molar ratio of ECO:PA than temperature, the reaction rate was influenced by both increasing temperature and increasing molar ratio of PA, both leading to increased reaction rates.<sup>21</sup> The study concluded that ECO-PA based thermosets could prove industrially viable with specific thermal and mechanical properties tailored by curing temperature and amount of PA curing agent. Thus, ECO provides an avenue of future research in the development of cost-effective, bio-based resins.

**Karanja Oil.** Karanja oil is a nonedible oil derived from the seeds of the Karanja tree that grows wildly across the coasts and river banks of India, Sri Lanka, and Japan.<sup>22</sup> Karanja oil is plentiful across those regions and poses a highly abundant, renewable resource. Like canola oil, the progress of industrial uses for karanja oil is not as advanced as that of soybean oil or linseed oil. Karanja oil was successfully epoxidized with sulfuric acid using acetic acid and hydrogen peroxide in 2006, but, recently, a more beneficial method of epoxidation involving a Prilezhaev peracid reaction was accomplished using peroxy formic acid.<sup>68</sup> This peracid method is advantageous because the reaction

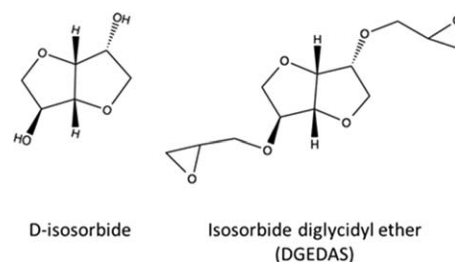
conditions can be optimized to yield maximum conversion to the epoxy groups. The epoxidized karanja oil could be used for metal working, hydraulic fluid applications or for developing other bio-based materials. Within the past year, thermosetting epoxy resins derived from epoxidized karanja oil were synthesized.<sup>22</sup> The cured karanja-based epoxy resins showed good thermal stability with statistic heat resistant index temperatures (determined by TGA results) of 170 and 175 °C, higher than that of the comparable DGEBA resins (158 °C). The karanja-based cured epoxy resins were concluded to be potential bio-based replacements for paper laminates and coatings. The resins were also shown to be a deterrent to mosquito larvicidal activity, implying potential use as a way to manage the mosquito populations in areas such as India where mosquitos pose health hazards by transmitting diseases like Dengue.<sup>22</sup>

### Saccharides

Saccharides, also known as carbohydrates, are compounds containing solely oxygen, hydrogen, and carbon and are the most common source of energy in most plants and animals.<sup>69</sup> Saccharides can be categorized depending on the amount of sugar molecules they contain: monosaccharides are single sugars, such as glucose or fructose, disaccharides are comprised of two sugars, such as sucrose or lactose, oligosaccharides are combinations of up to 10 sugars and, polysaccharides are long, complex chains of carbohydrates, such as, cellulose, starch, and hemicellulose.<sup>50</sup> Saccharide derivatives have found use in a variety of research areas including biopolymer adsorbents in wastewater treatment and hydrogels.<sup>70,71</sup> Saccharide-based epoxy resins are also well-explored materials in the adhesives, coatings, and composites industries where epoxy resins with more efficient curing and better physical properties are required.<sup>72</sup> Recent work has used isosorbides and furans derived from sugars to create desirable epoxy resins. Thus, the next subsections focus on these advancements.

**Isosorbides.** Isosorbide (Figure 4) is a sugar-derived molecule that is widely available, water soluble and nontoxic, making it a great alternative to and a proven replacement for BPA in epoxy polymers.<sup>73</sup> Isosorbide is prepared initially from starch in a multi-step process that involves hydrogenation of glucose and dehydration of sorbitol.<sup>50,74</sup> From a high performance polymer properties standpoint, advantages of isosorbide are linked to its rigidity and chirality, both of which can provide stiffness and thermal stability to a thermosetting polymer network.<sup>23,73</sup>

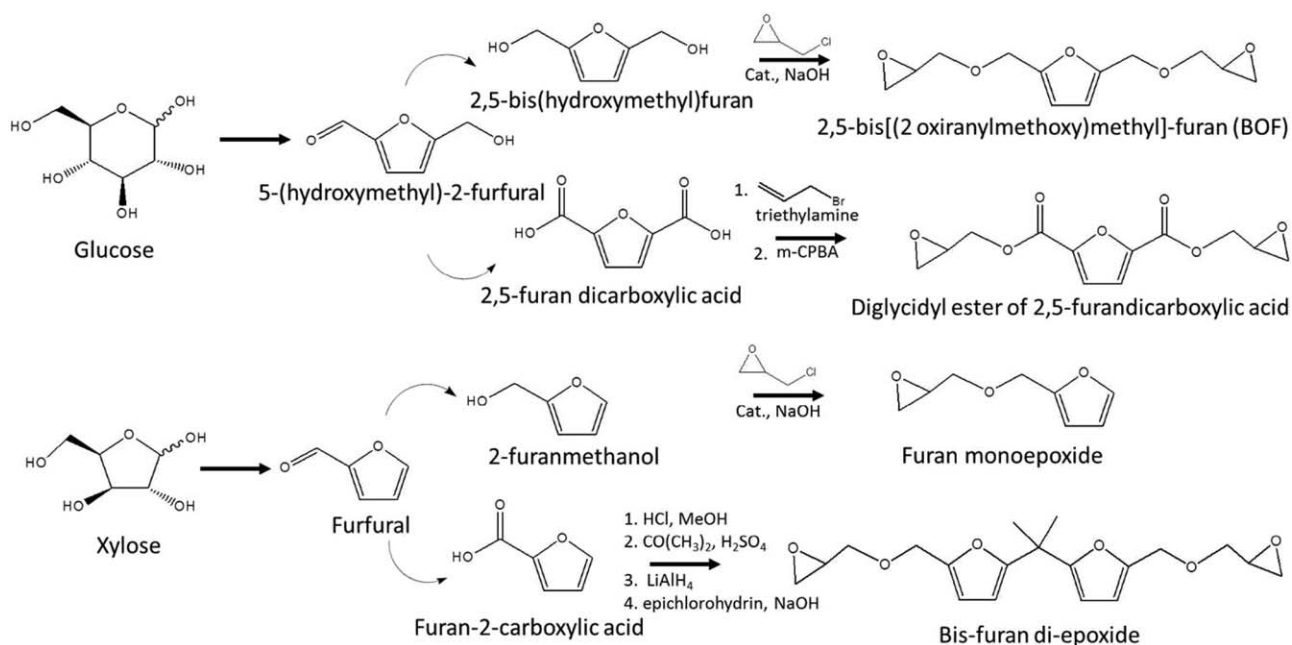
Much work is still being done to incorporate isosorbide into commercially viable polymers. For example, in a 2015 study, isosorbide diglycidyl ether (DGEDAS) was copolymerized with poly(3-hydroxyalkanoate)-diepoxy (PHA-diepoxy) in the presence of diaryl iodonium salt (I 250) to create a bio-based epoxy network in a simple photo-polymerization technique.<sup>23</sup> The resulting networks showed enhanced flexibility as demonstrated by a decrease in  $T_g$  (based on peak of  $\tan \delta$ ) from 125 to 81 °C.<sup>23</sup> Higher degradability was also demonstrated with an increase in weight loss during hydrolytic degradation from 9.2% to 21.6% with the natural PHA content increasing from 0% to 25%, indicating a potential replacement as a biodegradable thermosetting polymer.<sup>23</sup> Additionally, a 2014 study used



**Figure 4.** Structures of D-isosorbide (left) and its epoxidized form DGEDAS (right).

isosorbide-based epoxy resins in combination with isosorbide diamine hardeners to create fully bio-based, isosorbide-derived cured resins.<sup>23</sup> The combination of isosorbide epoxies with isosorbide diamine hardeners created cured resins with low  $T_g$ s (based on DSC thermogram) of about 43 °C; however, the combination of DGEBA with isosorbide diamine hardeners yielded better cured resins with higher  $T_g$ s of about 79 °C (based on DSC thermogram).<sup>23</sup> The fully isosorbide epoxy resins had good tensile and impact strengths, 52 and 57 MPa, respectively, as compared to 26 and 60 MPa of the DGEBA and diamine hardener system.<sup>23</sup> Completely isosorbide-based epoxy resins disintegrated into pieces during water swelling tests. Therefore, the authors concluded further research must be pursued if such isosorbide epoxy resins are to be used in wet conditions. Still, the good mechanical properties of the isosorbide epoxy resins and the excellent curing of the isosorbide-based hardeners demonstrated potential for future isosorbide polymer applications.

**Furans.** Furan building blocks are favorable bio-based alternatives to petroleum-based phenyl building blocks in commercial thermoset resins due to their aromaticity and availability. Furan chemicals derived from existing biomass sources include furfural (F) and 5-(hydroxymethyl)-2-furfural (HMF), which are readily prepared from pentose and hexose sugars or polysaccharides (Figure 5).<sup>75</sup> These two furanic chemical building blocks can be transformed into the well-known precursors of furan-based green polymers 2,5-furandicarboxylic acid (FDCA) and furfuryl alcohol (FA), respectively.<sup>20,75</sup> However, these precursors do not have the ability to develop networks via cross-linking. Therefore, the two are generally used as network modifiers where furan rings become pending groups of the polymer network. There are several works reported on multifunctional furanyl based epoxy resins, which have the ability to develop full thermosets networks for various applications. Cho *et al.*<sup>25</sup> recently reported the preparation of two furan based epoxy monomers, a monofuran diepoxide (2,5-bis[(2-oxiranylmethoxy)methyl]-furan (BOF)), and bis-furan diepoxide, using 2,5-bis(hydroxymethyl)furan (BHMF). These epoxies were photocured cationically using IRGACURE 250 and triphenylsulfonium hexafluoroantimonate salt initiators and their applications to the adhesive industry was investigated. Palmese *et al.*,<sup>26</sup> cured monofuran epoxy 2,5-bis[(2 oxiranylmethoxy)methyl]-furan (BOF) with alicyclic and aromatic curing agents 4,4'-methylene biscyclohexanamine (PACM) and diethyl toluene diamine (EPIKURE W), respectively. Furan-based thermosets cured with PACM and EPIKURE W showed promising  $T_g$ s (71 and 88 °C,



**Figure 5.** Synthetic pathways of furanic based epoxy monomer prepared from biomass-based polymeric carbohydrates.

respectively) and room temperature storage moduli ( $\approx 3.5$  GPa). However, furan-based polymers possessed lower  $T_g$ s (29 °C lower when cured with PACM and 44 °C lower when cured with EPIKURE W) but improved glassy moduli as compared to their phenylic analogues. Deng *et al.*,<sup>27</sup> prepared the diglycidyl ester of 2,5-furandicarboxylic and compared the properties of furanyl-based epoxies and their phenyl-based counterparts after being cured with the same amine curing agents. The results showed that the furan-based epoxy resins possessed higher  $T_g$ s, strength and moduli, contrary to the BHMf based diepoxide (BOF) system. This may be due to the presence of carboxylic groups adjacent to the furan ring in diglycidyl ester of 2,5-furandicarboxylic, which hindered the rotation of furan ring in the polymer networks system.

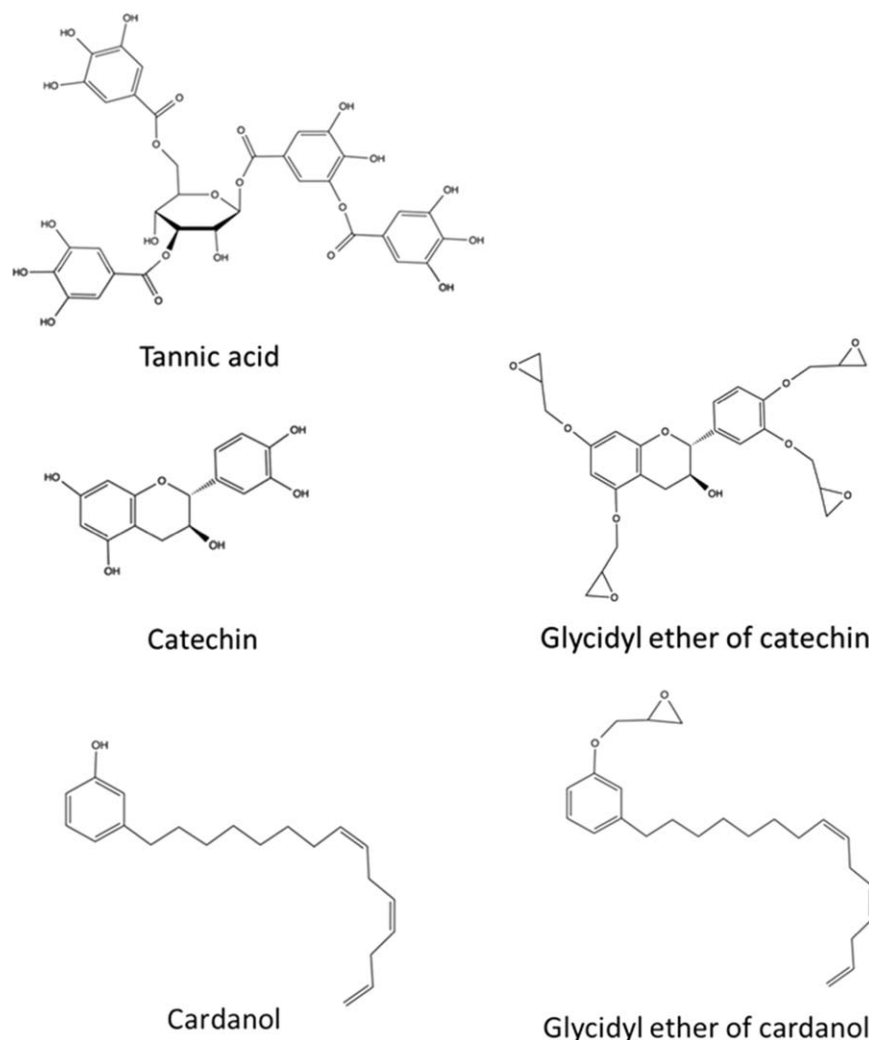
### Polyphenols and Phenols

Natural polyphenols are usually large molecules containing multiple phenol structures. Polyphenol is a large group of compounds that can be classified based on origin, biological function or chemical structure.<sup>1</sup> Polyphenols can be broadly organized into two groups: flavonoids and nonflavonoids.<sup>76</sup> Flavonoids are compounds synthesized by plants that consist of two phenyl rings and a heterocyclic ring.<sup>76</sup> Nonflavonoids do not have this structure and can be subdivided into groups such as simple phenols, phenolic acids, hydrolysable tannins, and benzophenones.<sup>76</sup> Phenolic compounds are of interest in the development of better epoxy resins because they impart chemical and temperature resistance as well as structural stability to the polymer network.<sup>77</sup> This section focuses on epoxy resins developed from tannins and cardanol, a phenol derivative and the main constituent of cashew nut shell liquid (Figure 6).

**Tannins.** Tannins are phenolic compounds derived from plants that can be divided into two categories: hydrolyzable and condensed.<sup>78</sup> Hydrolyzable tannins have low reactivity while condensed tannins are more reactive, though both are used for the preparation of epoxy monomers.<sup>78,79</sup> Tannins are usually obtained from the barks of trees, but can be extracted from other biomass as well, such as, nuts and leaves.<sup>80</sup> Tannins have been long investigated for use in composite applications. For example, in 2006, Ndazi *et al.* produced composite panel boards from rice husks and mimosa tannins.<sup>81</sup>

Catechin is one of the most commonly studied tannin-derivative for use in epoxy resins.<sup>79</sup> Catechin was extracted from green tea and used for the synthesis of an epoxy resin in a 2015 study by Basnet *et al.*<sup>28</sup> The catechin was epoxidized and cured with methanol soluble lignin extracted from eucalyptus as a natural curing agent. The resulting cured resins showed good thermal stability with heat resistant temperatures ( $T_s$ ) of about 169 °C, identical to that of the BPA-based resins cured with lignin.<sup>28</sup> Additionally,  $T_g$ s (based on DSC thermogram) of the catechin epoxy resins cured with lignin were desirably high, 178 °C, showing potential for use in advanced applications.<sup>28</sup> This study also investigated the two types of evaporation techniques to extract catechin from green tea: heat drying and freeze drying. The heat-dried catechin epoxy resin exhibited lower thermal stability with a  $T_g$  of 148 °C as compared to 168 °C of freeze-dried catechin, indicating that the extraction method is an important aspect for further investigation of advanced catechin-based polymers.<sup>28</sup>

Prior to that, in 2013, a study by Benyaha *et al.*<sup>29</sup> compared the polymer formation of epoxidized catechin, green tea extract, and bisphenol-A based resin systems. Green tea extract has multiple catechin-based phenolic compounds and possibly dimers and gallate functional groups. The results showed that the



**Figure 6.** Structures of tannic acid and catechin, two main components of tannins. Also pictured is cardanol, which is a derivative of cashew nut shell liquid. Glycidyl ether of catechin and cardanol with their epoxy group functionalities are also shown.

catechin and green tea extract based resins exhibited higher storage moduli at 30 °C as compared to the bisphenol-A based system, 2340 and 1500 MPa versus 1290 MPa, respectively, indicating improved mechanical properties.<sup>29</sup> However, the green tea extract system, with the various other functionalities present, displayed a reduced  $T_g$  (based on the peak of the  $\tan \delta$ ), 142 °C versus 179 °C, as compared to the straight catechin-based resins.<sup>29</sup> Still, the cured resins based on epoxidized green tea extract showed promising results for future use of direct natural tannin by creating viable, bio-based epoxy resins.

**Cardanol.** Cardanol is a nonedible byproduct extracted from cashew nut shell liquid (CNSL).<sup>30</sup> Because of the large production of cashew crop, 2.7 million tons/year,<sup>82</sup> cardanol is a highly abundant, renewable source that has already been studied in a variety of polymers applications, such as, in polyurethanes, as Novolac resins and in epoxy resins, including bio-based epoxy resins.<sup>30,83</sup> Cardanol is a yellow liquid that is a mixture of alkylphenols with varying degrees of unsaturation.<sup>84</sup> In 2014, Jaillet *et al.* cured epoxidized cardanol resins and obtained polymers with  $T_g$ s (based on DSC thermogram) less than 50 °C and crosslinking

densities approximately five times lower than comparable DGEBA resins.<sup>31</sup> To replace bisphenol A-based materials, the cardanol-based materials would require higher thermomechanical properties. Thus, in a 2015 study, Darrroman *et al.*,<sup>30</sup> investigated using sorbitol and isosorbide (bio-based saccharides) as epoxidized reactants in epoxidized cardanol-based resins in an attempt to create more durable cardanol-based materials. The  $T_g$  (based on DSC thermogram) and hardness of epoxidized sorbitol at a 1:1 weight ratio to cardanol were higher than that of the same ratio of epoxidized isosorbide: 60 °C and 93 as compared to 48 °C and 91.<sup>30</sup> Resins with a 3:1 weight ratio of epoxidized isosorbide to cardanol exhibited  $T_g$ s of 83 °C for those with isosorbide 100 (EEW = 155 g/eq) and 62 °C for those with isosorbide 102 (EEW = 158 g/eq).<sup>30</sup> This emphasizes that combinations of bio-based epoxy reactants can alter the thermomechanical properties of blended cardanol resins to produce resins comparable to bisphenol A-based materials.

#### Natural Resins

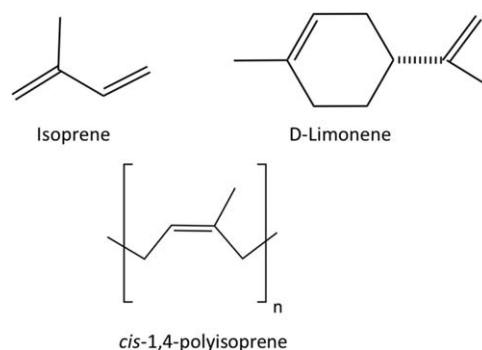
Natural plant resins are usually viscous liquids that are produced by plants in special resin cells and can be excreted

through the bark, the flowers or the buds.<sup>85</sup> Resins are composed mainly of terpenes, strong, pleasant-smelling compounds built upon isoprene subunits, and sometimes resinic acids.<sup>86</sup> Rosin is a solid resin that is made by heating and evaporating the volatile, terpene-based compounds in fresh resin.<sup>86</sup> Natural rubber (*cis*-1,4-polyisoprene) (Figure 7) is also composed of polyisoprene chains, obtained from latex from the Brazilian rubber tree.<sup>87</sup> Terpenes, rosin, and natural rubber are explored for use in bio-based epoxy resins below.

**Terpenes.** The term terpene generally refers to the natural isoprene-based compounds obtained from plant seeds, flowers, leaves, stems, and roots.<sup>86</sup> Various terpenes are used in the flavors and fragrances industries due to their strong taste and odor.<sup>86</sup> Terpene compounds are usually classified by the number of isoprene units (Figure 7): hemiterpenes (a single isoprene), monoterpenes (two isoprenes), sesquiterpenes (three isoprenes), diterpenes (four isoprenes), etc.<sup>88</sup> Terpenes are also divided based on various structures: acyclic monoterpenes, monocyclic monoterpenes, bicyclic monoterpenes, etc. There are many terpene derivatives that are employed in various applications.<sup>86</sup> The following paragraphs will review a general terpene-based epoxy resin and the more specific limonene building block.

Terpene-maleic ester-type epoxy resin (TME) was synthesized from turpentine and used to prepare a crosslinked polyurethane/epoxy resin composite coating in a 2014 study by Wu *et al.*<sup>32</sup> The resulting film was transparent and flexible, had good thermal stability with temperatures at 50% weight loss all above 400 °C and good antifouling properties, making the terpene epoxy/polyurethane resin composite a potential alternative for current coatings.<sup>32</sup> Additionally, TME and a waterborne dispersion of TME (WTME) were cured and investigated in 2007 as bio-based alternatives to BPA-based epoxy resins.<sup>89</sup> However, the resulting networks did not have suitably comparable mechanical properties to that of the BPA-based epoxy resins. In 2015, the same group published a study with more successful results. Cellulose nanowhiskers (CNWs) were incorporated with the WTMEs to make thermoset nanocomposites cured with a hydrophilic modified aliphatic amine curing agent.<sup>89</sup> Incorporating the 8 wt % of CNWs in the WTME matrix led to increased storage modulus at 150 °C (from 0.8834 to 4.756 MPa), Young's modulus (from 295.6 to 800.1 MPa), and tensile strength of the networks (from 7.08 to 15.2 MPa).<sup>89</sup> Therefore, stable thermosets derived from renewable sources were successfully created from a combination of the modified terpene-based compound WTME and CNWs.

D-limonene, a stable terpene used in the fragrances and coatings industries (Figure 7) has previously been investigated to synthesize D-limonene/naphthol based epoxy resins as a bio-based replacement for conventional DGEBA resins.<sup>33</sup> Compared to DGEBA resins, the D-limonene/naphthol based epoxy resins, synthesized with a dicyanodiamide curing agent, showed higher  $T_g$  by 75 °C and higher thermal stability with higher temperatures of maximum rate of weight loss in air by about 40 °C.<sup>33</sup> Though this showed promise, more recent research with D-limonene has focused on controlling the crosslinking of



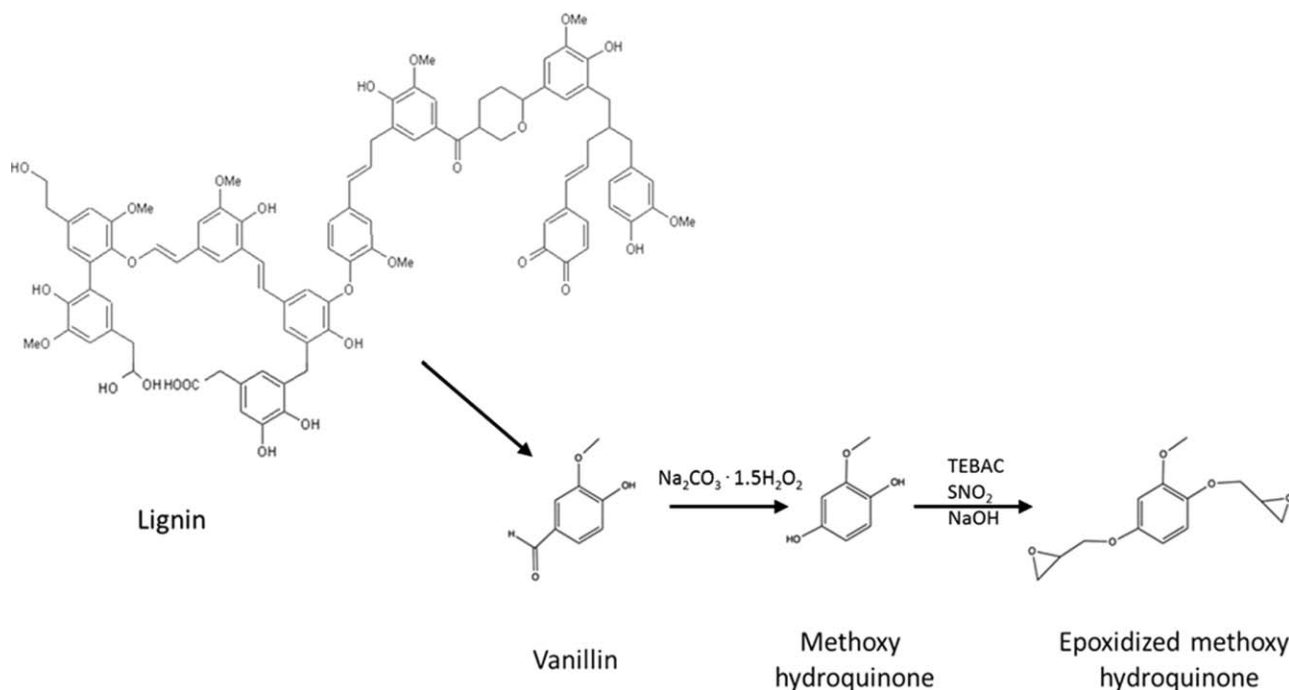
**Figure 7.** Structures of isoprene (left), D-limonene (right) and *cis*-1,4-polyisoprene (bottom). Isoprene is the main repeating unit of terpenes. D-limonene is classified as a cyclic terpene. *Cis*-1,4-polyisoprene is the major constituent of natural rubber.

terpene-based compounds in the production of thermosets for coatings applications.<sup>90,91</sup>

**Rosin.** Rosin is an abundant natural resource derived from pine and conifer trees or obtained from the waste of the pulp and papermaking industries.<sup>92</sup> It is a complex mixture of high molecular weight rosin acids and some neutral materials.<sup>93,94</sup> Historically, rosin has been used in applications such as soaps, inks, coatings, and adhesives; however, due to its abundance and rigid phenanthrene ring, there has been recent interest in using rosin and its derivatives as a feedstock for chemicals and polymers.<sup>95</sup> A few recent key studies are covered below.

In a 2015 study, rosin derivatives were epoxidized and then cured with a rosin-based crosslinker, dirosin-maleic anhydride imidodicarboxylic acid, to yield polymers with properties as comparable to those of commercial DGEBA resins; the rosin-based polymers had comparable storage moduli at 25 °C to those of DGEBA (1.58–1.71 GPa) and had  $T_g$ s (based on peak of  $\tan \delta$ ) about 50 °C higher.<sup>34</sup> In a different study, epoxidized rosinic acid oligomer polygral, consisting mainly of abietic acid, was used as a coreactant with DGEBA and isophorone diamine crosslinking agent to study the feasibility of using renewable rosin as a coadditive to DGEBA.<sup>96</sup> As the addition of the epoxidized polygral (PGrE) increased from 0 to 60 wt %, the  $T_g$  (based on DSC thermogram) decreased from 140 to 114 °C and the storage modulus decreased from  $1.0 \times 10^9$  MPa to  $4.0 \times 10^8$  MPa.<sup>96</sup> However, the authors concluded that the  $T_g$  of the system is still better than those from plant oils previously reported in the literature and still comparable to the  $T_g$ s and storage moduli of DGEBA materials in applications such as liquid-solution epoxy products.<sup>96</sup> Therefore, rosin and its oligomers could have industrial potential to provide a renewable component to epoxy products.

**Natural Rubber.** Natural rubber is collected from the Brazilian rubber tree, which is indigenous to South America but is grown in places like Southeast Asia and Africa now as well.<sup>87</sup> Natural rubber is one of the most important natural polymers because of modern society's great dependence on it in a variety of applications, including cements, adhesives, tires, and insulations.<sup>97</sup> Epoxidized natural rubber is a modified rubber that is commercially sold with varying degrees of epoxidation.<sup>98</sup> The



**Figure 8.** Proposed chemical structure of lignin, top left. Lignin can either be directly epoxidized, or depolymerized into single phenolic compounds via enzymatic oxidation, pyrolysis, hydrodeoxygenation catalysis, Organosolv or Kraft processes. For example, lignin can be depolymerized into vanillin, bottom left. Vanillin can be transformed into methoxy hydroquinone, bottom middle, via a Dakin oxidation reaction involving sodium percarbonate ( $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ ).<sup>103</sup> Methoxy hydroquinone can then be epoxidized, bottom right.<sup>104</sup>

epoxidation of rubber makes it useful in areas like polymer composites, polymer modifications, and advanced green polymers.<sup>98</sup>

Epoxidized natural rubbers have been used as modifiers for epoxy resins and to reinforce epoxy nanocomposites.<sup>99,100</sup> Specifically, in a 2014 study, epoxidized natural rubber (ENR) was explored as a modifier to BPA-based epoxy resins.<sup>89</sup> The addition of ENR decreased the  $T_g$  (based on peak of  $\tan \delta$ ) of the epoxy resin, from 118 °C of the neat polymer to 109 °C with 20 wt % addition of ENR.<sup>100</sup> However, the thermal stability was maintained with temperatures of maximum rate of weight loss consistent at 400 °C for neat DGEBA polymers and those mixed with 5, 10, 15, and 20 wt % ENR.<sup>100</sup> It was determined that an addition of 10 wt % of ENR yielded optimal properties and increased the bio-based content of the resins.

In a 2015 study by Muhammad *et al.*, liquid epoxidized natural rubber (LENR) was used as a matrix toughener to improve the mechanical properties of fiber-reinforced epoxy composites.<sup>35</sup> LENR was added to a hybrid glass/kenaf fiber-reinforced epoxy composite in order to boost the mechanical properties of the hybrid composite closer to that of the solely glass fiber-reinforced epoxy. And, indeed, addition of LENR increased impact strength by 40%, flexural strength by 13%, and flexural modulus by 15%.<sup>35</sup> The success of the LENR showed that a mix of synthetic and natural fibers could be used for commercial applications along with the strengthening addition of LENR.

#### Lignin and Lignin Derivatives

Lignin is a natural polymer found in the cell walls of dry land plants whose main purpose is to provide structural support and

rigidity.<sup>101,102</sup> It has aromatic functionality (Figure 8) and is highly abundant.<sup>105</sup> Lignin comprises anywhere from 15 to 40% of the dry weight of land plants<sup>102</sup> and is removed from plants during processes utilized by the pulp and papermaking industries.<sup>105</sup> In paper mills, wood is separated into lignin, cellulose, and hemicellulose. Lignin is not used in the production of paper because it can cause degradation, discoloration, and generally decreases the quality of the paper.<sup>101</sup> Instead, lignin is separated and primarily used as a low-grade fuel.<sup>101</sup> As of 2010, the pulp and paper-making industries extract roughly 50 million metric tons of lignin per year and burn about 98% of it; only around 2% is used for low-value products, such as dispersing or binding agents.<sup>106</sup> The high abundance of this renewable resource and its aromatic structure afford it great potential for use in the chemicals and polymers industries.<sup>102</sup>

Current research aims to develop bioengineering methods to recover and chemically transform lignin under biorefinery conditions so that the isolated lignin can be used in high-value products, such as polymers and foams.<sup>107</sup> The uses and products that are derived from lignin depend on the methods utilized to separate and process the lignin as well as the natural feedstock.<sup>106</sup> The kraft process involves treating wood chips with sodium hydroxide and sodium sulfide that breaks the bonds between the lignin and cellulose.<sup>108</sup> The resulting lignin is called kraft lignin. The organosolv process uses an organic solvent to separate the lignin and is a more environmental friendly method of separation than the kraft process.<sup>108</sup> Both kraft lignin and organosolv lignin have the potential to serve as the starting materials for high value products such as bitumen, activated carbon, carbon fibers, phenol derivatives, phenolic

resins, and vanillin.<sup>106</sup> The following section focuses on just a few of the numerous advances employing lignin in high-value polymer applications from the past year.

Lignin for polymer applications can be obtained from any number of dry land plants. A study by Asada *et al.*<sup>36</sup> compared the lignin-derived epoxy resins obtained from three different biomass sources, cedar, eucalyptus, and bamboo, to determine if lignin-based polymers could be used in printed circuit boards. The lignin-based resins were cured with biomass-derived lignin as a curing agent to create almost fully lignin-based polymers. The resulting networks were compared with DGEBA cured with the lignin curing agent as well. The thermal decomposition temperatures of the lignin-based epoxy resins were found to be slightly lower than those of the DGEBA-based resin, ranging from 259 to 336 °C for the lignin-based epoxy cured resin and from 315 to 378 °C for the DGEBA-based cured resin.<sup>36</sup> The heat-stability properties of the lignin-based epoxy resins cured with lignin-based curing agents indicated that all three of these mostly lignin-based resins could work well in electronics applications.

Industrially available lignin derivatives, such as vanillin, have been explored recently since they are currently available for commercial production. In a 2015 study, Fache *et al.*<sup>103</sup> developed bio-based epoxy thermosets from vanillin-derived oligomers. Methoxyhydroquinone was synthesized from vanillin, was epoxidized (Figure 7), oligomerized and crosslinked with a diamine agent IPDA to form an epoxy thermoset.<sup>103,104,109</sup> The thermal properties of the resulting networks were high compared to other bio-based thermosets found in literature<sup>103</sup>; the  $T_g$ s (based on DSC thermogram) were between 80 and 110 °C.<sup>103</sup> The study concluded that vanillin-derived bio-based thermosets show much potential, but future work should evaluate other mechanical properties, such as, tensile strength.<sup>103</sup>

The curing agents involved in the curing of lignin-derived epoxy resins have also been investigated. Ferdosian *et al.*<sup>37</sup> investigated the curing behavior and kinetics of lignin-based epoxy resins using two different curing agents, 4,4-diaminodiphenyl methane (DDM) and diethylenetriamine (DETA). The overall activation energies of the systems were determined and it was discovered that the resins cured with DETA had higher energies than those of DDM, implying that the aromatic amine has better activity than the aliphatic amine in these lignin-derived resin systems. It was also found that the thermal stability of the cured lignin-based resins was influenced by the choice of curing agent. The lignin-based resins cured with DDM showed higher maximum rate decomposition temperatures than those cured with DETA, 416 °C compared to 406 °C; however, the thermal stability of all the samples on the whole was comparable to that of petroleum-based epoxy resins.<sup>37</sup>

In another study from 2015, epoxy nanocomposites were synthesized from lignin-derived compounds, yielding another viable production route of lignin-based epoxy thermosets.<sup>110</sup> Dihydroeugenol (DHE) was derived from lignin, modified and epoxidized. The DHE-based epoxy was combined with nanoclay that helped improve the thermal stability of the polymers. This was exemplified by TGA analysis that showed an increase in

temperature at 5% weight loss from 190 °C of the neat polymer to 251 °C of the DHE polymer with 12 wt % nanoclay.<sup>110</sup> Additionally, from DMA analysis, it was shown that the  $T_g$  (based on peak of  $\tan \delta$ ) increased from 40 to 51 °C with the addition of 6 wt % of nanoclay to the DHE resins indicating increased thermomechanical properties of the bio-based epoxy nanocomposites as compared to neat bio-based polymers.<sup>110</sup>

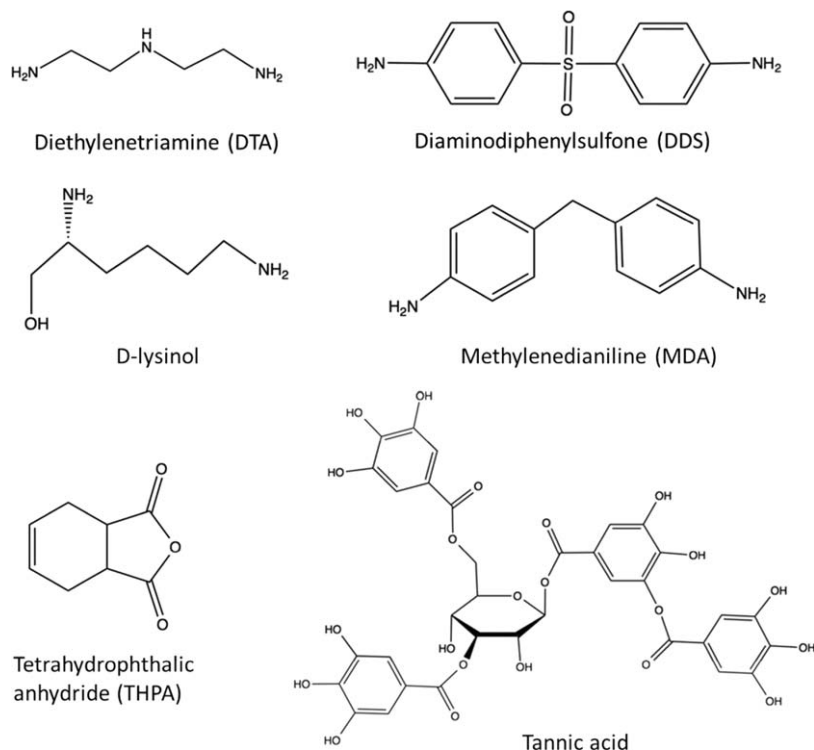
## BIO-BASED EPOXY CURING AGENTS

The process of curing involves changing the properties of the given resin to form a network, by creating crosslinking, thereby hardening the resin.<sup>111</sup> To aid the curing process, additives, called curing agents, are often added to the resin. There are a variety of curing agents commercially available and investigation into the curing kinetics of these resin systems is still ongoing in various areas.<sup>112</sup> Common curing agents include amines, amides, hydroxyls, acid anhydrides, phenols, and polyphenols (Figure 9).<sup>13</sup> Most commonly used commercial curing agents are petroleum-based; however, work is being done to develop alternative curing agents from biomass.<sup>113</sup> The remainder of this article will review the most recent advances in the development of curing agents from renewable resources. As opposed to the previous section on bio-based epoxy resins that was organized by source, the following section on bio-based epoxy curing agents will be organized based on type of curing agent. There exists a plethora of information on bio-based curing agents; only a few recent, novel studies will be covered in the following sections. For further information, readers are directed to works such as Handbook of Thermoset Plastics<sup>114</sup> and Thermoset Nanocomposites.<sup>115</sup>

### Amines and Amine Derivatives

Amine and amine derivatives encompass a wide range of curing agents. Amines are commonly used for curing epoxy resins because their nucleophilicity enable them to be reactive at ambient temperatures.<sup>116</sup> Attempts to transform natural resources into aminated curing agents have been investigated for many years.<sup>117,118</sup>

**Polyamines.** A polyamine developed from grapeseed oil was investigated for use as a curing agent for a bio-based epoxy resin in two studies by Stemmlen *et al.*<sup>116,119</sup> The aminated grapeseed oil (AGSO), successfully created via UV initiated thiol-ene coupling, was used to cure epoxidized linseed oil (ELSO) and was compared to an aminated fatty acid (AFA) curing agent also derived from grapeseed oil in addition to a commercially available curing agent, Priamine.<sup>116,119</sup> The resulting AGSO-cured network, with a  $T_g$  (based on peak of loss modulus) of around -38 °C, is classified to the category of thermoset amorphous polymer.<sup>119</sup> Polymers cured with the Priamine exhibited  $T_g$ s of -31 °C, comparable to the AGSO curing agent.<sup>119</sup> However, the AFA-cured polymer had a higher  $T_g$  of -9 °C.<sup>119</sup> The shear storage modulus at 30 °C followed a similar pattern: 4.2 and 1.6 MPa for AGSO and Priamine curing agents, respectively, and 25 MPa for the AFA curing agent.<sup>119</sup> The authors concluded that the thiol-ene coupling method to produce a fully bio-based thermoset, in both the AGSO and AFA cases, was successful and utilizing alternative oil-based compounds for



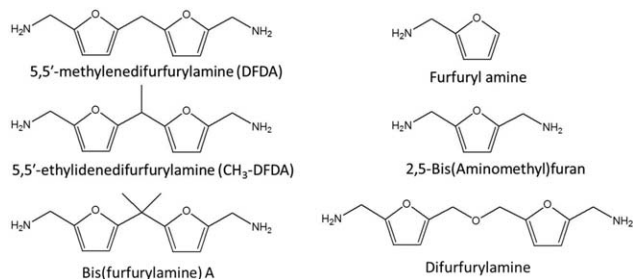
**Figure 9.** Structures of curing agents: diethylenetriamine (DTA) is an aliphatic polyamine curing agent known to be toxic; diaminodiphenylsulfone (DDS) is an aromatic amine curing agent; D-lysine is an amino acid that has been used as a curing agent; methylenedianiline is another toxic, aromatic amine curing agent; tetrahydrophthalic anhydride (THPA) is an anhydride curing agent; and tannic acid is a natural polyphenol that has been used as a curing agent.

both the resin and the curing agent could yield polymers of various thermomechanical properties.

**Aromatic Amines.** Aromatic bio-based amines can impart thermomechanical stability to cured epoxy resins. Cardanol was functionalized in a 2015 study by Darroman *et al.* to create a bio-based aromatic amine.<sup>38</sup> Cardanol is already a commercially viable feedstock for the production of amine-based epoxy resin hardeners; however, the current methods of production are not very “green” as they involve formaldehyde and create limited amines.<sup>120</sup> In the 2015 study, more mild reaction conditions to aminate cardanol were achieved through use of thiol-ene coupling chemistry.<sup>38</sup> Resins cured with the new cardanol-based amines demonstrated thermal and mechanical properties comparable to resins cured with commercially available cardanol-based amine agents. For example, as far as thermal stability, TGA analysis under nitrogen yielded degradation temperatures at 10% weight loss of 325 °C for commercially available cardanol-based amine agents and 328 °C for the new cardanol-based amines.<sup>38</sup> The  $T_g$ s (based on DSC thermogram) for the commercial and the new curing agents were different, 30 °C as compared to 19 °C, respectively; however, the thiol-ene method of creating aminated cardanol agents shows promise as an environmental-friendly production technique.

**Furanic Amines.** Furan building blocks are primarily derived from polysaccharides and sugars and have been used for preparing not only epoxy resins but also amine hardeners. Several furan-based amines have been prepared and investigated

including the basic diamine 2,5-bis(aminomethyl) furan (Figure 10).<sup>121,122</sup> In this preparation, the corresponding aldoxime and nitrile resist reduction, often causing low yields.<sup>121,122</sup> Additionally, Hu *et al.*<sup>39</sup> reported the synthesis of two furanyl amine hardeners, 5,5'-methylene difurfurylamine (DFDA) and 5,5'-ethylenedifurfurylamine (CH<sub>2</sub>-DFDA) that were used to cure furan-based epoxy 2,5-bis[(2-oxiranylmethoxy)methyl]-furan (BOF) creating a fully furan-based thermoset. These furan-based thermosets showed encouraging  $T_g$ s (62 and 69 °C, respectively, using  $\tan \delta$ ) and room temperature storage moduli ( $\approx 3.5$  GPa). The CH<sub>3</sub>-DFDA cured epoxy sample exhibited higher  $T_g$  than the DFDA cured epoxy system due to the presence of the additional methyl group. Onset degradation temperature of the fully furan-based samples is observed around 270 °C with 40 wt % char yields. Further, diglycidyl ether of bisphenol A (DGEBA) was cured using the furan-based amines.



**Figure 10.** Chemical structures of furanyl amines.



The samples DGEBA/DFDA and DGEBA/CH<sub>3</sub>-DFDA displayed  $T_g$ s (tan  $\delta$  peak temperatures) of 128 and 142 °C, respectively.

Cache *et al.*<sup>40</sup> prepared a furan-based amine, bis(furfurylamine)-A, using furfural amine as the starting material. To investigate the properties of the furan-based amine hardener, DGEBA and vanillin-based epoxy, diglycidyl ether of methoxyhydroquinone (DGMHQ), were cured with bis(furfurylamine) A and the  $T_g$ s were observed using DSC. The bis(furfurylamine) A cured with DGEBA and DGMHQ displayed  $T_g$ s of 98 and 74 °C, respectively, which are lower than those cured with IPDA (166 °C for IPDA/DGEBA and 132 °C for IPDA/DGMHQ). Bis(furfurylamine) A bears aromatic cycles that confer rigidity to the network. However,  $T_g$  reduction was attributed to the (bis)furfurylic structure where the amine groups are separated from the furan ring by a CH<sub>2</sub> group bringing flexibility to the network and lowering the  $T_g$ . However, in the IPDA epoxy, the amine group is directly linked to the ring, which limits its mobility.

**Amino Acids.** Amino acids are important bio-based amines and are commercially manufactured either by fermentation or enzymatic methods.<sup>93</sup> For example, the hydrogenation of lysine, a product of sugar fermentation, produces the amino acid lysinol (Figure 9) that can act as a great epoxy resin curing agent.<sup>123</sup> The preparation and use of lysinol was explored in a 2014 study where it was used to cure DGEBA epoxy resins and was compared to a petroleum-based hardener, diethylenetriamine (DETA).<sup>123</sup> The resulting polymers had similar tensile strengths, 4.6 MPa for the lysinol hardener and 4.7 MPa for the DETA, and thermal stability, with initial degradation temperatures of 300 °C for lysine and 350 °C for DETA, providing a bio-based replacement for the petroleum-based hardener. Another commonly studied amino acid is tryptophan. For example, in 2015, tryptophan was used as a curing agent for DGEBA in the presence of silica nanoparticles to create thermally stable epoxy nanocomposites potentially for use in the electronics industry.<sup>14</sup> It was determined that a 2 : 1 molar ratio of DGEBA to tryptophan with 5 parts per hundred of silica nanoparticles (SiNP) yielded the best thermo-mechanical results with a  $T_g$  (based on DSC thermogram) of 101.9 °C.<sup>14</sup> An additional kinetics analysis revealed that the degradation rate of the nanocomposite was lower than that of the neat DGEBA and the thermal degradation time of the nanocomposite was higher than that of the neat DGEBA (9.07 × 10<sup>16</sup> min as compared to 8.05 × 10<sup>14</sup> min at 0.8 conversion, respectively) for all conversions at 298 K in a nitrogen atmosphere.<sup>14</sup> Therefore, the study concluded, adding SiNP to the DGEBA and tryptophan can improve the thermal stability of the cured resins.<sup>14</sup>

### Acids

Carboxylic acids are common epoxy resin curing agents that are usually derived from petrochemical feedstocks.<sup>93</sup> However, carboxylic acids can be derived from natural sources, such as, fruit juices or fatty acids.<sup>93</sup> Using carboxylic acid curing agents from natural sources can help increase the bio-based content of cured epoxy resins. A comprehensive 2015 study by Ma and Webster investigated using water-soluble natural acids, citric acid, malic acid, tartaric acid, malonic acid, oxalic and glutaric acid, as

crosslinkers for an epoxidized sucrose soyate system.<sup>41</sup> The natural acids all crosslinked rapidly to create thermosets with excellent thermal and mechanical properties ( $T_g$ s (based on peak of tan  $\delta$ ) in the 90 °C range and initial degradation temperatures in the 240–250 °C range) that also were degradable, a promising result as far as green polymer engineering is concerned.<sup>41</sup>

Vegetable oils can be used as acid curing agents for epoxy resins. Soybean oil was modified into a polyacid hardener by Jaillet *et al.* in order to cure a DGEBA system.<sup>42</sup> The reactivity of the soybean oil acid derivative was very high and its use as a curing agent yielded high conversions in short times (almost 100% in 20 min at 120 °C).<sup>42</sup> This makes it viable for use in coatings and bindings applications as a bio-based curing agent. Another interesting bio-based source for curing agents is lignin. In a 2014 study by Qin *et al.*, lignin was depolymerized and subsequently reacted with succinic anhydride to yield lignin-based polycarboxylic acid (LPCA).<sup>124</sup> It was concluded that LPCA provided comparable thermomechanical properties to that of anhydride curing agents ( $T_g$ s (based on peak of tan  $\delta$ ) in the upper 70 °C range, storage moduli at room temperature between 2.4 and 2.7 GPa) and therefore LPCA could be a commercially viable bio-based curing or cocuring agent for epoxy resins.<sup>124</sup>

### Anhydrides

Anhydride curing agents generally require more severe conditions than amine-based agents for curing, but, are great for electrical applications.<sup>125</sup> There exists several bio-based sources for the production of anhydride curing agents. Terpene-based anhydrides are a feasible curing agent developed from renewable resources. Terpene-based anhydrides have been used to cure epoxidized soybean oil to form a completely bio-based network.<sup>43</sup> The ESO resins cured with terpene-based curing agents had higher  $T_g$ s (based on DSC thermogram) than those cured with a more common hexahydrophthalic anhydride (HPA) (67.2 as compared to 59.0 °C) and also displayed higher storage moduli at 20 °C.<sup>43</sup> Rosin-based curing agents have also been well explored.<sup>113,126,127</sup> Through a series of esterification and Diels-Alder reactions, rosin-based anhydride can be formed, as shown by Wang *et al.*<sup>126</sup> Qin *et al.*,<sup>128</sup> used such a rosin-based anhydride to cure an epoxidized eugenol network, creating a fully bio-based polymer. The rosin-based systems were compared to those cured with commercially available, petroleum-based curing agents, such as HHPA. It was discovered that the rosin-based networks yielded higher  $T_g$ s (based on peak of tan  $\delta$ ) than the networks created with HHPA, 155.3 °C as compared to 114.2 °C, and had similar storage moduli at room temperature, 2.9 as compared to 2.8 GPa.<sup>128</sup> The good mechanical properties and thermal stability of the resulting polymers indicates that rosin-based anhydrides could act as viable, bio-based alternatives to current industrially used curing agents.

### Phenols and Polyphenols

Phenolic epoxy curing agents are commonly used with polyfunctional epoxy resins and enable the formation of crosslinked networks that are commercially used for pipeline coatings.<sup>93</sup> Bio-based polyphenols are highly abundant in nature and can be recovered from various plants and food through commercial

processing techniques.<sup>93</sup> Natural sources of polyphenols include tannic acid and cardanol.

Tannic acid (Figure 8) has been investigated for use as a bio-based curing agent with epoxy resins based upon the natural aliphatic polyols glycerol and sorbitol.<sup>129</sup> Tannins are composed mostly of phenolic structures and prove a viable bio-based replacement for petroleum-derived curing agents.<sup>129</sup> Recently, Shibata and Nakai successfully used tannic acid as a curing agent with epoxidized soybean oil, creating a fully bio-based epoxy resin.<sup>44</sup> The ESO and tannic acid created cured resins with tensile strength and  $T_g$  (based on peak of  $\tan \delta$ ) of 15.1 MPa and 58 °C, respectively.<sup>44</sup> To increase the mechanical properties, microfibrillated cellulose (MFC) was added. The new ESO, tannic acid, MFC biocomposite demonstrated tensile strength of 26.3 MPa and  $T_g$  of 61 °C, creating a bio-based polymer with much potential for future application.<sup>44</sup>

Cardanol is another phenolic compound that can be used as a curing agent.<sup>93</sup> This may involve transforming cardanol into phenalkamine in a Mannich reaction.<sup>45</sup> In a 2015 study, a phenalkamine curing agent derived from cardanol was compared to a traditional polyamine hardener, triethylenetetramine (TETA), in the curing of DGEBA resins.<sup>45</sup> The authors concluded that mechanical properties of epoxy composites could be greatly improved with the addition of cardanol-based hardeners based on the results of the study.<sup>45</sup>

## CONCLUSIONS

There are several characteristics that classify chemicals and polymers as environmental friendly; to name a few, materials must be created from bio-based sources and produced sustainably.<sup>130</sup> As described in this review, much research is being conducted worldwide to develop advanced polymers from bio-based resources. Currently, petroleum-based compounds are widely used in the production of epoxy resins for plastics and food container linings.<sup>131</sup> However, commonly used bisphenol analogs, such as BPA and bisphenol S (BPS), are associated with environmental and health concerns prompting researchers to replace the building blocks for epoxy resins as well as the curing agents for such resins with compounds derived from natural sources.<sup>131</sup> The most explored bio-sources at the moment seem to be plant oils, lignin, and furanols. When epoxidized, plant oils, specifically soybean and linseed oil, prove excellent green monomers that yield polymers with desirable thermomechanical properties. Lignin is another important renewable resource that provides phenols and phenolic derivatives useful for the chemicals and polymers industries.

The biggest hurdle for commercial advancement of many bio-based polymers is the isolation and synthesis of the natural monomers.<sup>79</sup> For example, lignin is a complex compound with a multifunctional nature that makes it challenging to commercially process. However, work has already been done to this effect and further strides are continually being made by improving processing techniques and technology.<sup>133,134</sup> As biorefineries that produce and process biomass advance, more and more useful and economically feasible bio-based building blocks will become commercially available. Thus, it is important that

research into the strategic utilization of such building blocks to produce economically viable and environmental friendly polymers, including bio-based epoxy resins, be conducted now.

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