Outlook

15 Biobased Thermosets

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<table>
<thead>
<tr>
<th>OUTLINE</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers from Renewable Sources</td>
<td>577</td>
</tr>
<tr>
<td>Determination of Bio-Based Content in Polymers</td>
<td>578</td>
</tr>
<tr>
<td>Raw Materials for Renewable Sources Polymers</td>
<td>579</td>
</tr>
<tr>
<td>Thermoset from Renewable Sources</td>
<td>594</td>
</tr>
<tr>
<td>References</td>
<td>615</td>
</tr>
</tbody>
</table>

Polymers from Renewable Sources

In the past few decades concern about the environment, climate changes, and limited fossil resources has led to an intensive research of alternatives to fossil-based polymers. From a historical point of view, the first polymers used by mankind were from renewable sources, bio-based polymers, long before the birth of synthetic polymers. Celluloid, a bio-based man-made polymer was invented in the 1860s, and since then, many other bio-based polymers have been developed. However, the development of the crude oil industry in the 20th century transformed the world of polymers, leading to the use of synthetic polymers as a replacement for bio-based polymers. The increasing use of synthetic polymers as a result of the growing human population and standard of living in the next decades will result in higher demands on oil production and will contribute to a possible depletion of crude oil before the end of the 21st century. It is estimated that by 2015 the worldwide annual production of plastics is very likely to reach 300 million tons (14–18% are thermosets), which will require large amounts of petroleum and will result in the emissions of hundreds of millions of tons of CO₂ to the atmosphere [1]. A return to bio-based polymers will reduce the dependency of the polymers and plastics industry on petroleum, thus creating more sustainable alternatives.

Bio-based polymers are derived from renewable resources such as plant and animal mass from CO₂ recently fixed via photosynthesis [2]. Bio-based polymers can be natural or synthetic. Natural bio-based polymers are polymers synthesized by living organisms such as animals, plants, algae, and microorganisms. The most abundant bio-based polymers in nature are polysaccharides [3]. Cellulose and starch are natural polymers based on polysaccharides, and are abundant in nature. Proteins and bacterial polyhydroxyalkanoates are also natural bio-based polymers [4]. Bio-based polymers are not necessarily sustainable; this depends on a variety of issues, including the source material, production process, and how the material is managed at the end of its useful life. Sustainable produced bio-based polymers are those grown without genetically modified organisms (GMOs), hazardous pesticides, certified as sustainable for the soil and ecosystems, and compostable. Sustainability also depends on the reduction of impacts to occupational and public health as well as the environment throughout their life cycles [2]. Bio-based materials are important candidates for sustainable development since they present the potential to reduce greenhouse emissions by sequestering CO₂, to reduce raw material costs, and to create opportunities for growth and employment in agriculture [5].

Life cycle assessment (LCA) is the most widely applied and accepted method to quantitatively assess the environmental impact of a given material.
throughout its life cycle; its principles and framework are described in ISO 14040 [6]. Usually the impact categories considered in LCA are global warming, acidification of soil, ozone layer depletion, aquatic eutrophication, respiratory organics, respiratory inorganics, land occupation, non-renewable energy, and aquatic ecotoxicity [7]. Additional environmental indicators are resource depletion and human toxicity [5].

Global warming impact is measured by the amount of CO$_2$ that is liberated from the material throughout its life cycle. CO$_2$ is the principal anthropogenic gas that is thought to affect the Earth’s radiative balance. For this reason it is believed that there is a close correlation between CO$_2$ and the change of the Earth’s temperature [8]. The CO$_2$ footprint of a material is assessed by the carbon emissions consequent on the creation of a unit mass of material, including those associated with transport, generation of the electric power used by the plant, and that of feedstocks and hydrocarbon fuels. The CO$_2$ footprint, which is measured in units of kg of CO$_2$/kg material, is the sum of all contributions per unit mass of material. Renewable resource polymers have a low CO$_2$ footprint since plants grow by absorbing CO$_2$ from the atmosphere and thus sequester carbon [9].

**Determination of Bio-Based Content in Polymers**

Bio-based polymers can be made totally or partially from renewable source raw materials, produced from photosynthesis and CO$_2$. In order to determine the bio-based content of the polymer, the “new” carbon content must be measured. A renewable source is replenished by natural processes at a rate comparable to its exploitation rate. The carbon content of such polymers is derived from the so-called short carbon cycle within an expected time frame between 1 to 10 years. Most industrial polymers and plastics are presently produced from fossil resources that are non-renewable as they cannot be replenished at a rate comparable to the exploitation rate. Fossil resources have a long carbon cycle, with an expected time frame to convert biomass to petroleum, gas, and coal of greater than 10$^6$ years [10]. The accepted measure of bio-based content is the level of $^{14}$C isotope in the feedstock (basically, carbon dating), because ancient petroleum has lost its $^{14}$C through radioactive decay whereas feedstock derived from recently living organisms have a $^{14}$C content related to the current equilibrium concentration in the atmosphere.

ASTM D6866-11 has developed a protocol to quantify the bio-based content in materials by comparing the $^{14}$C/$^{12}$C ratio to that of a standard specimen typical of living organisms [11]. CEN/TS 16137 is the equivalent European for the ASTM standard test [3]. ASTM D6866-11 is the Standard Test Methods for Determining the Bio-based Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis. It defines bio-based content as the amount of bio-based carbon in the material or product as a percent of the weight (mass) of the total organic carbon in the product. This standard utilizes two methods to quantify the bio-based content of a given product: (a) Accelerator Mass Spectrometry (AMS) along with Isotope Ratio Mass Spectrometry (IRMS); or (b) Liquid Scintillation Counters (LSC) using sample carbon that has been converted to benzene. Those methods directly discriminate between product carbon resulting from new carbon input and that derived from fossil-based input. A measurement of the $^{14}$C/$^{12}$C ratio is determined relative to the modern carbon-based oxalic acid radiocarbon Standard Reference Material (SRM) 4990c (referred to as HOxII), as the oxalic acid standard is 100% bio-based. The percent new carbon can be slightly greater than 100% due to the continuing (but diminishing) effects of the 1950s nuclear testing programs. Because all sample $^{14}$C activities are referenced to a “pre-bomb” standard, all modern carbon values must be multiplied by 0.95 to correct for the bomb carbon and to subsequently obtain the true bio-based content of the sample [11].

CEN/TS 16137 specifies the calculation method for the determination of bio-based carbon content in monomers, polymers, plastics materials and products using the $^{14}$C method based on three test methods: (a) Proportional scintillation-counter method (PSM); (b) Beta-ionization (BI); and (c) Accelerator mass spectrometry (AMS). The analytical test methods specified in this Technical Specification are compatible with those described in ASTM D6866-11. The bio-based carbon content is expressed by a fraction of sample mass, as a fraction of the total carbon content, or as a fraction of
the total organic carbon content. This calculation method is applicable to any polymers containing organic carbon, including bio-composites [3]. Calculation of percentage of bio-based content according to CN/TS 16137:2011 is based on the calculation of carbon content as a fraction of the total organic carbon content (TOC) expressed as a percentage, using Equation (15.1):

\[ X_{B,TOC} = \frac{X_B}{X_{TOC}} \]  (15.1)

Here, \( X_B \) = is the bio-based carbon content by mass, expressed as a percentage; and \( X_{TOC} \) = is the total organic carbon content, expressed as a percentage, of the sample.

### Raw Materials for Renewable Sources Polymers

#### Natural Oils

Natural oils, which can be derived from both plant and animal sources, are considered to be one of the most important classes of renewable sources because of the wide variety of possibilities for chemical transformations, worldwide availability, and relatively low price [12]. Vegetable oils, fish oils, and oils from algae can be transformed in raw materials for polymers. Vegetable oils are inexpensive and offer different degrees of unsaturation while fish oils have a high degree of unsaturation [13]. Plant oil is a type of lipid, stored in an organelle in the form of triglycerides, during the oilseed development. Lipids may be defined as hydrophobic or amphiphilic (both hydrophilic and lipophilic) small molecules. Different plant species contain lipids with different fatty acid compositions and distributions. Lipids help form a hydrophobic biological membrane that separates cells from their surroundings and keeps chloroplasts, mitochondria, and cytoplasm apart, thus preventing or regulating diffusion of chemicals [14].

Plant oil is a mixture of various triglycerides (also called triacylglycerol). One glycerol is attached to three different fatty acids to form a triglyceride. Glycerolipid and fatty acids are synthesized in the oilseed simultaneously during seed development, before forming diacylglycerol and subsequently triacylglycerols. Triglycerides are composed of three fatty acids joined at a glycerol juncture, as can be seen in Figure 15.1. Fatty acids account for approximately 95% of the total weight of triglycerides and their content and chemistry are characteristics of each plant oil and geographical conditions [15]. The most common oils contain fatty acids that vary from 14 to 22 carbons in length with 0 to 3 double bonds per fatty acid. Fatty acids derived from nature have even an number of carbons due to their biosynthesis (acetyl coenzyme A, two carbon carrier). Some of the fatty acids may have additional functional groups like hydroxyl (castor oil), epoxide (vernonia oil), or ketone (licania oil), as well as triple bonds [14,16]. Although fatty acid pattern varies between crops, growth conditions, seasons, and purification methods, each of the triglyceride oils has a unique fatty acid distribution, as can be seen in Table 15.1 [17].

Hydrolysis of vegetable oils provides about 15 different fatty acids (some of them can be seen in

![Figure 15.1](image-url)  
**Figure 15.1** A triglyceride molecule (from top to bottom: saturated palmitic acid and unsaturated oleic acid and alpha-linolenic acid), glycerol linkage (1), ester group (2), \( \alpha \)-position of ester group (3), double bonds (4), monoallylic position (5), and bisallylic position (6).
<table>
<thead>
<tr>
<th>Oil</th>
<th>Palmitic 16:0</th>
<th>Stearic 18:0</th>
<th>Oleic 18:1</th>
<th>Linoleic 18:2</th>
<th>Linolenic 18:3</th>
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<th>Erucic 22:1</th>
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<tr>
<td>Linseed</td>
<td>5.5</td>
<td>3.5</td>
<td>19.1</td>
<td>15.3</td>
<td>56.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Soybean</td>
<td>11</td>
<td>4</td>
<td>23.4</td>
<td>53.2</td>
<td>7.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Palm</td>
<td>44.4</td>
<td>4.1</td>
<td>39.3</td>
<td>10</td>
<td>0.4</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>3</td>
<td>1</td>
<td>13.2</td>
<td>13.2</td>
<td>9</td>
<td>9</td>
<td>49.2</td>
<td>–</td>
</tr>
<tr>
<td>Castor</td>
<td>1.5</td>
<td>0.5</td>
<td>5</td>
<td>4</td>
<td>0.5</td>
<td>–</td>
<td>–</td>
<td>87.5</td>
</tr>
<tr>
<td>Sunflower</td>
<td>6</td>
<td>4</td>
<td>42</td>
<td>47</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>–</td>
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Table 15.1. Triglyceride oils have been used extensively to produce coatings, inks, plasticizers, lubricants, and agrochemicals.

The stereochemistry of the double bonds, the degree of unsaturation, and the length of the carbon chain are important parameters affecting physical and chemical properties. The degree of unsaturation can be expressed by the iodine value (the amount of iodine in grams that can react with double bonds present in 100 grams of sample). According to iodine value, oils can be divided into three categories: (1) drying oils (iodine value above 130, e.g. linseed oil), (2) semi-drying oils (iodine value between 90 and 130, e.g. sunflower or soybean oil), and (3) non-drying oils (iodine value below 90, e.g. palm kernel oil) [17]. Triglycerides contain active sites amenable to chemical reaction: the double bond, the allylic carbons, the ester group, and the carbons alpha to the ester group. These active sites can be used to introduce polymerizable groups on the triglyceride using similar techniques applied in the synthesis of petrochemical-based polymers. The key step is to reach a higher level of MW and cross-link density, as well as to incorporate chemical functionalities known to impart stiffness in a polymer network (e.g. aromatic or cyclic structures) [14].

There are three main routes to obtain polymers from plant oils: (1) direct polymerization through the double bonds, or through other reactive functional group present in the fatty acid chain, (2) chemical modification of the double bonds, which introduces functional groups to facilitate the polymerization, and (3) chemical transformation of plant oils to produce platform chemicals that can be used to produce monomers for the polymer synthesis, usually through the conversion of the triglycerides into mono/diglycerides or into simple fatty acids [12].

**Direct Polymerization of Natural Oils**

Double bonds present in fatty acids can be polymerized through a free radical or cationic mechanism. Drying oils, such as linseed or tung oil, are vegetable oils which polymerize through a free-radical mechanism [18]. The double bonds react with atmospheric oxygen, which leads to the formation of a network in a reaction called oxopolymerization, as can be seen in Figure 15.2. These oils are film-formers and are mostly used in paints, coatings, inks, and resins. The reaction mechanism can be summarized as follows: an initial hydrogen abstraction on the methylene group between two double bonds that leads to the formation of conjugated peroxides, and then, radical recombination that produces cross-linking (alkyl, ether, or peroxy bridges [19–21]. Oils with high iodine value can also be polymerized directly via cationic polymerization using boron trifluoride diethyl etherate as initiator [20].

Direct cationic homogenous copolymerization of some vegetable oils with olefinic copolymers such as styrene, divinylbenzene, norbornadiene, or dicyclopentadiene can be achieved using BF$_3$OEt$_2$ modified with methyl oleate or Norway fish oil ethyl ester as initiator [12]. Ronda et al. [12] has shown that a cationic polymerization of soybean oil with styrene, divinylbenzene, and trimethylsilylstyrene can lead to flame retardant bio-based thermosets. In order to accelerate the reaction that usually proceeds for long periods of time due to low reactivity of the internal double bonds, microwave irradiation was used as an alternative to a heat source.

**Chemical Modification of the Double Bonds of Natural Oils**

There are two different sites in triglycerides available to chemical modification: ester groups, which can be readily hydrolyzed or trans-esterified,
double bonds along the aliphatic chains, and hydroxyl groups [22]. Some of the important chemical pathways of functionalization are described in the following sections.

**Epoxidation of Triglycerides**

Epoxidized triglycerides can be found in natural oils, such as vernonia (see vernolic acid, Figure 15.3), or can be obtained from unsaturated oils by a standard epoxidation reaction. Different pathways of epoxidation can be found in the literature. Epoxides of fat and oils and their ester derivatives are usually used as plasticizers, toughening agents, and stabilizers in plastics industry, especially as alternative plasticizers for the polyvinyl chloride (PVC) industry. Linseed oil is the most epoxidized oil due to the high content of double bonds (linolenic acid), and is commercially available. Epoxidized soybean oil is also commercially available, usually with a functionality of 4.1—4.6 epoxy rings per triglyceride [14]. The oxirane ring is useful for further chemical modifications and for the synthesis of thermosetting resins by cross-linking with anhydride or amine compounds or by homopolymerization of the oxirane rings initiated by catalysts [23]. Epoxidation can be done using organic and inorganic peroxides together with a metal catalyst; it can also be obtained using halohydrins (haloalcohols), molecular oxygen, and by in situ epoxidation with percarboxylic acid. A suitable technique for clean and efficient epoxidation of vegetable oils is the epoxidation in situ with percarboxylic acid using Acidic Ion Exchange Resin (AIER) as the catalyst [24]. It is possible to use either acetic acid or formic acid as the carboxylic acid in the epoxidation process. Peroxy-acid is created by the reaction between hydrogen peroxide and the carboxylic acid. The process can be controlled by the quantitative analysis of oxirane rings and iodine number [25]. Different catalysts have been studied, including ion-exchange resins, phosphotungstic acids, rhenium catalysts, titanium catalysts, and enzyme catalysts [26,27]. A schematic example of a triglyceride epoxidation process can be seen in Figure 15.4. Chemo-enzymatic epoxidation is a relatively new process and has the advantage of suppressing undesirable ring opening of the epoxide. In this method, unsaturated fatty acid or ester is initially converted into unsaturated percarboxylic acid by a lipase-catalyzed reaction with hydrogen peroxide and is then self-epoxidized via an intermolecular reaction [28,29]. The epoxidation of triglycerides makes them capable of reacting via ring opening [30]. Arkema is already commercializing a line of epoxy plasticizers from renewable sources under the trade name of Vokoflex® based on epoxidized linseed oil, soybeans, and tall oil of fatty acids [31]. The preparation of bio-based epoxy resins from epoxidized vegetable oils will be discussed later.

**Acrylation of Epoxidized Oils**

Acrylation of epoxidized oil can be achieved from the synthesis reaction of acrylic acid with epoxidized triglycerides [14,32]. Acrylated triglycerides can react via additional polymerization. Acrylated epoxidized soybean oil is commercially available for the surface coatings industry. The reaction of acrylic acid with epoxidized soybean oil occurs through a standard substitution, as can be seen schematically in Figure 15.5. Although the reaction of epoxidized soybean oil with acrylic acid is partially catalyzed by the acrylic acid, the use of additional catalysts such as tertiary amines or

![Figure 15.3 Vernolic acid.](image)

![Figure 15.4 Epoxidation process.](image)
organometallic catalysts is common. The resulting polymer properties can be controlled by changing the molecular weight of the monomer or the functionality of the acrylated triglyceride, residual amounts of unreacted epoxy rings, as well as newly formed hydroxyl groups, both of which can be used to further modify the triglyceride by reaction with a number of chemical species (such as diacids, diamines, anhydrides, and isocyanates). The polymer can be stiffened by the introduction of cyclic or aromatic groups.[14]

Maleinization of Acrylated Epoxidized Oils

According to Wool[14], oligomers of maleinized acrylated epoxidized oils can be obtained by reacting the acrylated epoxidized oil with maleic anhydride (Figure 15.6). The maleinization reaction introduces more double bonds in the triglycerides. The reaction, if not controlled, can lead to an increase in the viscosity, which leads to gelation of the oligomer. After maleinization the oligomer can be cured with styrene.

Hydroxylation of Triglycerides

The introduction of hydroxyl groups at the position of double bonds creates polyols that can be used in the polyurethane and polyester industry, as well as for creating new pathways for triglyceride functionalization[33]. Natural occurring hydroxyl groups can be found in ricinoleic acid (castor oil). The hydroxylation can be done by reacting an epoxidized triglyceride with an acid, or alternatively by the hydroxylation of the double bonds. Ring opening of epoxidized triglycerides can be obtained by reacting with hydrochloric or hydrobromic acid or by an acid-catalyzed ring-opening reaction with methanol (yielding methoxylated polyol), or reacting with water forming vicinal hydroxyl groups, or even through a catalytic hydrogenation[30]. The cross-linking density of thermoset polymers obtained from hydroxylated oils depends on the number of hydroxyl groups in the oil and the position in the fatty acid (end or middle of the fatty acid chain)[33]. The hydroxylation process can be controlled, measuring the hydroxyl values according to the ASTM titration method (D 1957-86). The reactivity of the polyol obtained is relatively low due to the nature of the secondary alcohol. Furthermore, multiple numbers of hydroxyl groups with varied reactivity are also obtained, which leads to premature gelation[34].

Hydroformylation is another method for preparing polyols; hydrogenation of the formyl group produces hydroxyl, using cobalt or rhodium as catalysts, at high temperatures[35]. In this process aldehydes are formed and an extra carbon is introduced per double bond. Hydroformylation creates primary hydroxyl groups which are more reactive than the secondary polyols created via epoxidation (Figure 15.7)[13].

Ozonolysis is another alternative chemical process utilized to synthesize polyols with terminal hydroxyl groups from vegetable oils. Ozone, a very powerful oxidation agent, is used to cleave and oxidize the double bonds in the vegetable oil and then the ozonides formed are reduced to alcohols using $\text{NABH}_4$ or similar catalysts. Tran et al. [34] developed a method to synthesize vegetable oil-based primary polyol (soybean oil) in a single-step ozonolysis procedure. When the oil is exposed to ozone in the presence of ethylene glycol and an alkaline catalyst, double bonds are cleaved, yielding a mixture of polyols that is dependent on the relative concentration of the unsaturated fatty acids present (Figure 15.8). In this type of ozonolysis, the ozonides produced react with the hydroxyl group of the glycol to form an ester linkage with a terminal hydroxyl group.
Figure 15.6 Maleinization of acrylated epoxidized triglyceride oil (soybean oil).

Figure 15.7 Hydroformylation process [13].
Maleinization of Hydroxylated Oils
The synthesis of maleinized hydroxylated oil is similar to that used to obtain acrylated epoxidized oil. After the hydroxylation, the oil is reacted with maleic anhydride in order to functionalize the triglyceride with maleate half-ester, as can be seen in Figure 15.9. The reaction can be catalyzed with N,N-dimethylbenzylamine [14].

Enone-Containing Triglycerides
According to Ronda et al. [12], allylic hydroperoxides can be readily prepared by reacting alkenes with photochemically generated singlet oxygen, which results in a mixture of enones (Figure 15.10). The researchers utilized this process to obtain enone-containing triglycerides from high oleic sunflower oil. Enone-containing triglycerides are interesting alternatives to epoxidized oils for the production of thermosets by cross-linking with amines via aza-Michael addition [12].

Conversion of Triglycerides into Mono/Diglycerides/Simple Fatty Acids
The conversion of the triglycerides into mono/diglycerides or into simple fatty acids can produce platform chemicals for producing monomers toward polymer synthesis. Mono or diglycerides can be obtained using a transesterification reaction with glycerol (glycerolysis). Standard glycerolysis
**Figure 15.9** Maleinization of hydroxylated triglycerides.

**Figure 15.10** Synthesis of enone-containing triglycerides from high oleic sunflower oil, cross-linked with 4,4'-diaminodiphenylmethane [12].
requires high temperatures and the use of an inorganic homogeneous catalyst such as sodium, potassium, or calcium hydroxide. Although this process is energy consuming it has high conversion rates and relatively short reaction times [36]. Enzymatic glycerolysis of fats and oils at atmospheric pressure at nearly ambient temperatures has been investigated in the last decade and has been found to be an attractive and advantageous route compared to the chemical process [37,38]. Usually the product of glycerolysis is a mixture of monoglycerides, diglycerides, and glycerol. According to Can et al. [39] maleinization of soybean oil and castor oil monoglycerides can produce maleate half-esters which in turn can react via addition polymerization. Maleates are relatively unreactive with each other and the addition of styrene increases the polymerization conversion rate and the stiffness of the resultant polymer.

**Methacrylation of Monoglycerides**

Methacrylation of monoglycerides can be performed after the glycerolysis of the triglyceride (soybean oil). The glycerolysis product can be reacted with methacrylic anhydride to form the methacrylic ester of the glycerides and methacrylic acid using pyridine as catalyst and hydroquinone as inhibitor of the radical polymerization of the methacrylic esters (Figure 15.11).
**Glycerol**

Glycerol is a non-toxic, edible, biodegradable compound. It is an extremely versatile building block. Glycerol is usually found in pharmaceuticals, cosmetics and personal care products, alkyd resins, etc. Glycerol is produced in two forms: natural glycerol, as a by-product of the oleochemical and biodiesel industries, and as synthetic glycerol, from propylene. Glycerol forms the backbone of triglycerides and is mainly produced by saponification of oils as a by-product of the soap industry. Around 75% of the glycerol produced in the United States is derived from natural sources [40]. Glycerol can be used as oligomers or co-monomers in copolymers. Catalyzed self-condensation of glycerol yields a mixture of linear and branched oligomers. Linear growth involves only the primary hydroxyl groups while the secondary ones can have consequences. The preparation of hydroxyesters or hydroxyacids from glycerol and their polycondensation by transesterification can lead to exquisite polymers such as hyperbranched polycarbonates and polyesters [41]. In recent years the amount of natural glycerol-based monomers increased considerably, and includes diols, diacids, hydroxyacids, oxiranes, acrolein, and acrylic acid, among others. Ethylene and propylene glycol are particularly relevant for the polyester market (polyethylene terephthalate and polytrimethylene terephthalate).

**Saccharides**

Carbohydrates are considered a very important renewable source of monomers for the preparation of a variety of polymers since they are the most abundant class of organic compounds found in living organisms. Sugars and starches are carbohydrates used as sources of metabolic energy in plants and animals, while cellulose, also a carbohydrate, serves as structural material. Carbohydrates are also called saccharides, and small molecules of saccharides are called sugars. They can be divided into three categories: (1) monosaccharides (glucose, galactose, and fructose); (2) oligosaccharides, a combination of two to ten monosaccharides; and (3) polysaccharides such as cellulose, starch, glycogen, and hemicellulose [42]. The most abundant oligosaccharide is sucrose, a disaccharide of glucose and fructose. The vast majority of carbohydrates present in nature are polysaccharides, with starch and cellulose being the most abundant. Starch is a branched polymer while cellulose is a long, rigid molecule. Sugar-based monomers can be introduced into polymer architecture as follows: (1) Addition reactions involving vinyl-type saccharides; (2) functionalization based on appending the carbohydrate to a reactive backbone; and (3) polycondensation reactions of sugar-based monomers [41]. Sugars are basically polyols with a high number of hydroxyl groups along the chain. In order to control the reactivity of the many different hydroxyl groups on carbohydrates, simple molecules with two hydroxyl groups are desired. Dianhydrohexitols, such as isosorbide, isomannide, and isoidide (Figure 15.12), are a result of intramolecular dehydratation; having two reactive hydroxyl groups, they can be used as raw material for polycondensation, which leads to polyester, polyether, or polyurethane chiral polymers. Isosorbide is prepared from starch, isomannide from D-mannose, and isoidide from isosorbide [41]. Isosorbide, or 1,2,3,6-dianhydrosorbitol, is the product of a multi-step process, starting with starch, and passing through D-glucose and sorbitol. It is produced from biomass in a combination of enzymatic and chemical technologies [44]. Due to steric effects and hydrogen bonding, isomannide with two endo hydroxyl groups is the least reactive compound compared with isoidide, which has two exo hydroxyl groups. However, isoidide is rare in nature while isosorbide is widely available [45]. Isosorbide, which is water soluble and non-toxic, can be a substitute for bisphenol A in different polymers, especially in epoxy polymers. It can be attached to glycidyl ether or allyl ether to make cross-linkable epoxy monomer with similar properties to bisphenol A-diglycidyl ether [46]. According to Feng et al. [45] the bisisosorbide diglycidyl ether can be prepared by heating isosorbide with sodium hydroxide solution with a large excess of epichlorohydrin. Two equivalents isosorbide are linked to sugars.
three molecules of epichlorohydrin to form the epoxide dimer (Figure 15.13).

Xylitol, sorbitol, mannitol, and maltitol (Figure 15.14) are additional naturally occurring sugar alcohols; polyols that can be polycondensated with dicarboxylic acids such as sebacic acid, citric acid, glutaric acid, and others [47]. The polymer obtained can be made photo-cross-linkable by adding methacrylate units to the polymer.

**Polyphenols**

Naturally occurring polyphenols are characterized by the presence of multiple phenol structural units. *Tannins* are a naturally occurring broad class of polyphenols present in trees and shrubs. Tannins can appear in nature as condensed tannins (polyflavonoids) or hydrolyzable tannins [41]. Condensed tannins are oligomeric in nature while hydrolyzable tannins are non-polymeric. Tannin has been used for centuries in leather treatment. Tanning leather involves a process which permanently alters the protein structure of leather, thus increasing its durability. Condensed tannin constitutes more that 90% of the total world production of commercial tannins (Figure 15.15). Hydrolyzable tannins are a mixture of phenols based on complex substances built with simple molecules such as gallic acid, ellagic acid, flavogallonic acid, valoneic acid, etc. Hydrolyzable tannins have relatively low reactivity. In condensed tannins the main polyphenolic pattern is represented by flavonoid moieties based on resorcinol A-rings and pyrogallol B-rings. A-rings contain one highly reactive nucleophilic center while the other reactive centers accommodate the inter-flavonoid bonds. A-rings in tannins are highly reactive to aldehydes (formaldehyde) in wood adhesive compositions and the reaction kinetics can be controlled by the addition of alcohols to the system. Self-condensation reactions of polyflavonoid tannins are used to prepare adhesives in the absence of aldehydes. The reaction is based on the opening under alkaline or acid conditions of the flavonoid repeating unit and the subsequent condensation of the reactive center with free sites of a flavonoid unit on another tannin chain [48].

![Figure 15.13 Bisisosorbide diglycidyl ether preparation](image)

**Figure 15.13** Bisisosorbide diglycidyl ether preparation [45].

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<th>xylitol</th>
<th><img src="image" alt="Figure 15.14" /> Naturally occurring polyols</th>
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Lignin is the second most abundant organic polymer on Earth, after cellulose, and the most abundant polyphenol in nature. It is most commonly derived from wood. Lignin is an integral part of the secondary cell wall of plants and some algae and has the function of bonding cells together in the woody stems, giving the stem rigidity and impact resistance [14]. Lignin accounts for 24 to 33% of the dry matter of softwood and 16 to 24% of the hardwood [49]. Lignin chemical structure is based on syringyl, guaiacyl, and $p$-hydroxyphenol, bonded together by a set of linkages to form a complex matrix [50], as can be seen by the schematic structure in Figure 15.16. Lignin is a complex, three-dimensional, amorphous, cross-linked phenolic-based polymer. It is a by-product of paper pulping and biorefineries, and is considered a waste product. Lignin is separated from wood during pulping and papermaking operations where it serves as fuel for the process. Major differences exist between lignin derived from different pulping processes [51]. Sulfite processes generate water-soluble sulfonate lignin while kraft processes generate alkaline soluble lignin. Hydrolysis lignin is produced by strong hydrolysis, organosolv lignins are produced from different organic solvent-based systems, and steam-explosion lignin is obtained through high temperature/pressure treatment with steam [42]. Recent pulping trends involving organic solvents (organosolv) produce less-modified, sulfur-free lignins, which simplifies the pyrolysis process for obtaining low-molecular-weight lignin sub-products [52]. All chemical pulping processes are associated with the chemical splicing of natural lignin producing fragments with high molecular weights [41].

Polymeric lignins can be used in thermosetting resins and as additives in thermoplastic polymers. Lignin can be chemically modified to improve polymer-lignin compatibility and to introduce reactive sites. The phenyl propane units in lignin are generally bonded through carbon and ether bonds, where only ether bonds can be easily disrupted. The methoxy group substituted at the ortho positions also influences the reactivity and solubility of the lignin [49]. Lignin and its degradation products can originate various polymers such as phenol–formaldehyde, poly(azophenylene)s, polyamides, polyurethanes, polyesters, polyamides, polyphenylene oxides, polyphenylene sulfide, and others. Due to the high number of reactive hydroxyl groups present, esterification and etherification are the most common reactions used for chemical modification of the lignin. According to Lora et al. [51], etherification with alkylene oxides (ethylene oxide, propylene oxide, and butylene oxide [53,54]) results in hydroxyalkyl lignin derivatives with aliphatic hydroxyl groups. Nonphenolic hydroxypropyl lignins are already commercially available in the market. Extended alkyl ether chain lignins can be also prepared, although propylation through heterogeneous reaction of lignin with propylene oxide can lead to unpredictable and even dangerous reactions [51]. Etherification and acetylation of lignin provide solubility in a variety of organic solvents such as acetone, tetrahydrofurane, and chloroform. Lignin can also be sulfonated, sulphonated, aminated, halogenated, and nitrated.

According to Wool et al. [14], grafting of lignin is another possible chemical modification, despite the inhibiting effect of the phenolic hydroxyl groups, which reduces the efficiency of the process. The addition of polar solvents, such as alcohols, can increase the efficiency though swelling the lignin molecules improves the accessibility of the reagents. Lignin has reportedly been grafted with methyl methacrylate, vinyl acetate, styrene, acrylonitrile, acrylic acid, acrylamide, maleic anhydride, and others. Methacrylated lignin can form cross-linked networks when copolymerized with methyl methacrylate. Other grafting techniques such as ionic chain polymerization and chemo-enzymatic grafting have also been reported [14]. A great deal

![Figure 15.15 Condensed tannin.](image)

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of effort and research has been done to determine the possible effects of lignin addition to polymers, introducing functional groups to increase chemical interactions. Lignin can be used as a co-monomer in phenolic thermosetting polymers in wood adhesive applications. Lignin can also be co-reacted with epoxy resins and polyurethane precursors [14]. Star-like macromers from lignin were obtained by Oliveira et al. [55] through a combination of chain extension and etherification reaction, synthesizing lignin with propylene oxide following capping of OH functional groups with aliphatic ethers. Polyurethane films were prepared by Kelley et al. [56] based on hydroxypropyl lignin. In order to reduce rigidity of the network polyethylene glycol and polybutadiene glycol extended lignin-based polyurethanes were prepared mixing two polyol components prior to cross-linking. Feldman et al. [50] modified a bisphenol A-based epoxy adhesive poly-blending with Kraft lignin.

Figure 15.16 Generic structure of lignin.
Cardanol is the main constituent (97%) of thermally treated cashew nut shell liquid and is based on phenolic compounds (Figure 15.17). In the last few decades several new methodologies were developed for the preparation of polymers using cardanol [16]. Cardanol is a phenol derivative with a meta-substituent of a C15 unsaturated hydrocarbon chain with one to three double bonds; it has potential applications in surface coatings and resins. Cardanol is used to industrially produce phenolic resins with formaldehyde (novolac) for coatings applications, generating high-gloss films for indoor use [57]. Ikeda et al. [57,58] studied oxidative polymerization of cashew nut shell liquid using iron-N, N'-ethylenebis(salicylideneamine) (Fe-salen) as catalyst, in bulk and at room temperature. A soluble cross-linkable polymer was obtained. The polymer was cross-linked using heat and a hard, glossy film was obtained. Gopalakrishnan et al. [59] developed a novel polyurethane based on cardanol, condensing cardanol with formaldehyde using sebacic acid as catalyst. The resulting resin (novolac phenol—formaldehyde resin) was epoxidized, followed by hydrolysis in order to obtain a hydroxyl alkylated derivative, a polyol. The resulting polyol was reacted with hexamethylene diisocyanates, generating rigid polyurethanes. Benedetti et al. [60] developed cardanol-based polyurethanes by reacting cardanol derivatives with diisocyanates or polyisocyanates and blowing agents in order to obtain foamed polyurethanes. Cardanol was derivatized by condensing cardanol with alkylic aldehydes or acrylic aldehydes with an acid catalyst. The product was epoxidized and hydrolyzed to obtain polyols, which in turn were reacted with isocyanates using blowing agents. Cardanyl acrylate prepolymer with controlled molecular weight and polydispersity can be used in the formulations of inks, coatings, and adhesives with good adhesion and gloss [16]. Campaner et al. [61] investigated the use of cardanol-based novolac resins as curing agents of commercial epoxy resins. The novolacs were prepared by the condensation reaction of cardanol and paraformaldehyde using oxalic acid as catalyst.

**Proteins**

Proteins are readily available raw materials from plants (wheat gluten, soy, sunflower, and zein) and animals (collagen, keratin, casein, and whey) [62]. Proteins are macromolecules consisting of one or more polypeptides, based on amino acids (up to 19 different amino acids) bonded together by peptide bonds. Polypeptides are usually folded into globular or fibrous form according to their biological function [63]. Proteins hold together, protect, and provide structure to the body of living organisms in the form of skin, hair, calluses, cartilage, muscles, tendons, and ligaments. Proteins can catalyze, regulate, and protect the body chemistry as enzymes, hormones, antibodies, and globulins [64]. Most proteins fold into 3-dimensional structures. The primary structure of proteins is defined by the sequence of amino acids in the chain; the folding pattern defines the secondary structure, resulting from the rigidity of the amide bond and from intramolecular hydrogen bonding. Coiling and aggregation of polypeptides creates the tertiary structure. The quaternary structure refers to the spatial arrangement of a protein, as an oligomeric structure containing several subunits [42]. Covalent disulfide cross-linking bonds stabilize the tertiary and quaternary structures. The shape into which a protein naturally folds is known as its native conformation.

Denaturation is the breakdown of the tertiary structure of a protein, and involves structural or conformational changes to native structure, such as unfolding of the protein molecule [14]. These changes can be induced by pH, detergents, heat, etc., and are accompanied by irreversible enthalpy changes [63]. Plasticization of proteins can be obtained by the interaction between molecules of plasticizer and protein macromolecules via polar interactions (with hydroxyl groups) that increase, as a result, the free volume. Through plasticization, proteins can be transformed using various
processing methods [42]. According to Verbeek [62], melt extrusion of proteins can occur through denaturation, dissociation, unraveling, and alignment of polymer chains. The presence of disulfide cross-links in this case is unfavorable, and decreases chain mobility, increases viscosity, and prevents homogenization. Proteins usually decompose at temperatures below the softening temperatures, and the introduction of plasticizers helps to avoid degradation. Animal and vegetable proteins can be cross-linked by the reaction of tannic acid, chromic acid, or formaldehyde. The use of proteins as raw materials for polymers is not new. Some of the earliest plastics were based on casein, phosphoproteins found in abundance in cow milk. Casein-based paints were used until the late 1960s, when they were replaced by acrylic-based paints.

Another important cow milk protein is the whey protein, isolated from the whey, a liquid by-product of cheese production. The protein in cow’s milk is 20% whey protein and 80% casein protein. Whey protein films and coatings have been the focus of recent research as potential materials for high oxygen barrier packaging [65,66]. Whey protein can be plasticized using glycerol and sorbitol [66]. Gao et al. developed whey protein-based aqueous polymer-isocyanate adhesives. The adhesive properties improved cross-linking of the resulting polymer with methylene bisphenyl diisocyanate [67].

Zein, a class of prolamine protein found in corn, was historically used as polymeric resins and coatings in a variety of applications such as fibers and tough, glossy, and grease-resistant coatings. Zein has also antimicrobial resistance and can be cured with formaldehyde. Zein has regained interest in the last few years, and the water resistance was improved by chemical modification where hydrophylic groups such as −NH₂, −OH, −COOH, and −SH were modified by hydrophobic groups or polymer segments. Plasticizers can be introduced in order to flexibilize zein films. Wu et al. [68] introduced dibutyl L-tartarate (DBT), which contains ester and hydroxyl moieties to form potential hydrogen bonds with zein. Sessa et al. [69] introduced isocyanates and diisocyanates to reduce the hydrophilicity of zein and, as a consequence, decrease the water moisture uptake. Cross-linking through isocyanate moieties should improve dimensional stability. Lai et al. [70] used oleic acid to plasticize zein, thus creating more flexible and tough films.

Collagen, a triple helical, self-organizing protein, is the main component of connective tissue and is the most abundant protein in mammals. Mano et al. [71] has shown that collagen can be effectively cross-linked with glutaraldehyde in order to overcome the drawbacks of fast biodegradation and lack of mechanical properties.

Albumin usually refers to any protein that is water soluble and denatures by heat. Oss-Ronen et al. [72] conjugated serum albumin to polyethylene glycol (PEG) and cross-linked it to form PEGylated albumin hydrogels. The main application is as scaffolds for controlled drug release.

Gluten is a protein composite based on gliadin and glutenin, forming, together with starch, the endosperm of grass-related grains. The term gluten comes from Latin, meaning “glue,” due to its adhesive properties. Gliadin and glutenin comprise around 80% of the overall protein in wheat grains. Wheat gluten is an important resource for bio-based polymers due to its viscoelastic properties, mechanical strength, excellent gas barrier properties, low price, and large-scale availability [73]. Gliadin and glutenin form a cross-linked network that contributes to the extensibility of mixed dough. In order to reduce the strong intramolecular interactions, plasticizers are usually required, which leads to an undesired reduction in mechanical properties. Gluten has found applications in the pressure-sensitive adhesives field [74]. A gluten-based PSA, with internal plasticizer, was developed by Aranyi et al. [75]. An acetic acid soluble hydrolysate was obtained using a hydrochloric and acetic acid mixture. The gluten hydrolysate was then epoxidized using ethylene oxide, and generated a water soluble, epoxidized gluten hydrolysate. This hydrolysate was then reacted with hydroxyethyl methacrylate giving rise to an acrylic copolymer of gluten with PSA properties. A reduction in water vapor transmission of gluten coatings was obtained by Cho et al. [76] using glycerol as plasticizer and oleic acid as a hydrophobic component. Kim et al. [77] developed a gluten/zein composite with flexural properties similar to those of polypropylene.

Soy protein is the major co-product of soybean oil extraction comprising around 50% of the defatted soy flour [42]. Soy protein is a storage protein held in discrete particles called protein bodies which provide amino acids during soybean seed germination. Soy protein comprises a high percentage of water soluble albumins and salt solution soluble globulins. Water is considered a major
plasticizer in the processing of soy proteins. High quantities of water content reduce the denaturation temperature of soy proteins. Soybean protein plastics can be prepared using a variety of different processes: compression molding, injection molding, and lamination [78]. According to Sun [14], smooth surface soy protein plastics can be prepared by hot pressing soy protein at 150°C, the temperature at which soy protein molecules melt and unfold, leading to a homogeneous distribution. A posterior interaction between the molecules leads to entanglement upon curing.

Plastics based exclusively on soy protein are rigid and brittle and plasticizers are usually introduced in order to increase the flexibility and toughness. Polyols have often been used as plasticizers. Plasticizers disrupt molecular interactions, decreasing the forces holding the chains. According to Sun [14], polypropylene glycol and glycerol appear to be more compatible with soybean protein and easier to introduce between protein chains. Mo et al. [78] studied the effect on soy protein properties of different plasticizers, such as glycerol, polyethylene glycol, and butanediols (1,2- and 1,3-substituted). Ethylene glycerol, propylene glycerol, sorghum wax, and sorbitol have also been studied for this purpose [42,79]. Addition of cross-linking agents such as formaldehyde, glutaraldehyde, and adipic/ acetic anhydride improve mechanical properties as well as the water resistance of the resulting soy protein plastic [80]. Gonzalez et al. [81] used the naturally occurring cross-linker genipin, a chemical compound found in gardenia fruit extract, in order to tailor mechanical properties and biodegradability. Denaturants such as sodium dodecyl sulfate and urea also act as plasticizers, reducing the glass transition temperature and increasing tensile strength, elongation, and water resistance. A high degree of entanglements and cross-links is expected when a high degree of denaturation is obtained, leading to an increase in stiffness and strength. Su et al. [82] investigated the moisture barrier properties of blends of soy protein with polyvinyl alcohol using glycerol as plasticizer. Water vapor transmission was significantly affected by the PVA content. Studies on chemical modification of soy proteins with monomers or oligomers have been done based on functional groups able to react with hydroxyl or amino groups in the protein. Acetylation and esterification are known pathways for chemical modification [80].

Soy protein can be modified using polycaprolactone/hexamethylene diisocyanate prepolymer [68]. It was found that HDI-modified PCL forms urea—urethane linkages with the amino acids in the protein, increasing substantially the water resistance and the elongation. Grafting can be obtained with acrylate-based polymers via free radical reaction, although branching is created, disrupting the strong inter and intramolecular interactions [80]. Grafting with polyurethane pre-polymer has been proved to enhance toughness and water resistance [42].

Soy can be used as an adhesive and the performance can be controlled depending on the particle size and structure of the protein, viscosity, and pH [83]. In order to enhance the adhesion strength of soy protein, a chemical modification is needed to break the internal bonds and uncoil or disperse the polar molecules. Dispersion and unfolding of protein is obtained by hydrolysis or by an alkali environment.

**Thermoset from Renewable Sources**

**Epoxy**

Approximately 90% of all non-bio-based epoxy in the market is based on diglycidyl ether of bisphenol A (DGEBA) derived from epichlorohydrin and bisphenol A. Epichlorohydrin is an epoxide. The conventional, petrochemical process of producing epichlorohydrin is the chlorohydration of allyl chloride, which in turn is made by chlorination of propylene. Until recently, epichlorohydrin has also been used to produce glycerol (glycerine). The large availability of bio-based glycerol, obtained as a by-product of biodiesel production, has made the production of glycerol using epichlorohydrin superfluous [4]. Epichlorohydrin can be produced using glycerol from renewable feedstock. The glycerin-to-epichlorohydrin (GTE) is a process based on two chemical steps: (1) hydrochlorination of glycerin with hydrogen chloride gas at elevated temperature and pressure using a carboxylic acid as catalyst, and (2) conversion of the dichlorohydrin formed in the first step to epichlorohydrin with a base [84]. This new glycerin-to-epichlorohydrin process reduces energy consumption by about one-third, generates less than one-tenth the waste water, and produces less chlorinated organics, when
compared to conventional processes [85]. Solvay Chemicals produces epichlorohydrin from bio-based glycerol, a by-product of biodiesel production using rapeseed, according to EPICEROL® technology [86]. The Dow Chemical Company, currently the world’s largest producer of epichlorohydrin, also announced its intent to manufacture epichlorohydrin via a novel, acid-catalyzed hydrochlorination process using bio-based glycerin [4].

Krafft et al. [87] developed a process from glycerol via 1,3-dichloropropanol. Bio-based DGEBA is chemically identical to the fossil one, and the bio-based epichlorohydrin accounts for approximately 20% of the molecular weight of DEGABA. Glycerol-based epoxy resins such as glycerol polyglycidyl ether and polyglycerol polyglycidyl ether are industrially available, and have been used in the textile and paper industry as processing agents, tackifiers, coatings, etc. Shibata et al. [88] developed a bio-based epoxy system based on a mixture of commercially available sorbitol polyglycidyl ether (SPE, DENACOL EX-614B) [89] and glycerol polyglycidyl ether (GPE, DENACOL EX-313) [89] cured with e-poly(L-lysine) as the bio-based curing agent. Sorbitol polyglycidyl ether is a multifunctional epoxy resin obtained by the reaction of epichlorohydrin and sorbitol, which in turn is obtained by the reduction of glucose. Tannic acid was used as the bio-based curing agent.

Bio-based epoxy can also be obtained using plant oils and fatty acids. Unsaturated vegetable oils can be converted into epoxidized oils using peracetic acid and peroxide (see the section on natural oils) or through enzymatic processes [90]. Natural epoxidized oil can be found in vernolic acid, present in Vernonia species. Epoxidized UV-curable resins can be synthesized via transesterification of vernonia fatty acids with hyperbranched hydroxyl functional polyether. The resin can then be cationically polymerized in the presence of vernolic acid and methyl ester as diluents [17].

Epoxidized vegetable oils (castor oil, soybean oil, linseed oil, etc.) are currently used in epoxy compositions [91]. Epoxidized oils can be polymerized in the presence of latent catalysts or in the presence of curing agents, such as anhydrides. The low reactivity of the epoxy groups together with a tendency for intramolecular bonding lead to a low degree of cross-linking. As a result, poor mechanical and thermal properties are obtained with higher water uptakes, compared to fossil epoxy systems. On the other hand, the polymer obtained is potentially biodegradable via hydrolytic cleavage of glycerol ester bonds present in the triglyceride oils. Blends of epoxidized oils and fossil epoxy resins have also been studied. Epoxidized soybean oil (EBSO) is considered to be the second largest epoxide following epichlorohydrin, and it is prepared commercially by epoxidation with percarboxylic acids. Epoxidized linseed oil (ELSO) can be produced by epoxidation with formic acid and hydrogen peroxide [4].

Tan et al. [92] added epoxidized palm oil to a fossil-based epoxy blend of diglycidyl ether of bisphenol A/cycloaliphatic epoxy resin/epoxy novolac resin in order to obtain a thermal curable partially bio-based epoxy system. The epoxidized palm oil acts as plasticizer, thus reducing the glass transition temperature of the system. In order to overcome those limitations, Tan et al. [93] synthesized a thermally curable epoxidized soybean oil in the presence of tetraethylammonium bromide catalyst. Increasing catalyst concentrations led to a reduction of curing cycles and temperatures, and to higher degrees of conversion and cross-linking density. As a result, higher storage modulus and glass transition temperatures were obtained.

Chemical modification of the epoxidized oils is another method used to improve final properties. Transesterification of soybean oil with allyl alcohol followed by epoxidation in the presence of benzoyl peroxide, and cured with anhydride, resulted in highly cross-linked polymers with better mechanical properties. cis-9,10-Epoxy-18-hydroxyoctadecanoic acid is a naturally occurring epoxidized monomer present in birch tree. Lipase-catalyzed condensation polymerization of this naturally occurring epoxidized acid creates epoxidized oligomers [91]. Lu et al. [94] synthesized high stiffness polymers from epoxidized linseed oils as a result of the high degree of unsaturation of the linseed oil. Chandrashekhara et al. [95] developed a soy-based epoxy resin consisting of mixtures of epoxidized fatty acid esters, specifically, epoxidized allyl soyaate. Epon 9500 and Epicure 9550 from Shell Chemical Company were used as base epoxy resin. Epoxidized allyl soyaate (EAS) was synthesized through a lab-scale process from food grade soybean oil. The epoxidized allyl soyaate was prepared by transesterification of triglycerides, and yielded fatty acid methyl ester and allyl ester using methyl alcohol and allyl alcohol, respectively. The fatty acid
esters were then epoxidized and yielded soyate epoxy resins. The resin formulations were prepared by directly mixing the epoxidized soyate resins into base Epon resin and curing in one step. The following ratios of Epon/epoxidized soyate resins were used: 100% Epon resin, 90/10%, 80/20%, and 70/30%. Tensile tests results can be seen in Figure 15.18. An increase in the ductility could be noticed with the increase of the epoxidized soyate resin content, accompanied by a corresponding decrease in the ultimate strength and modulus. The increase in the ductility was related to the higher molecular weight of the soybean oil. It could be concluded that epoxidized allyl soyate provided better intermolecular cross-linking, yielding tougher materials as compared to commercially available epoxidized soybean oil. The addition of epoxidized allyl soyate to a commercial epoxy resin led to a viable low-cost, high-performance thermostet product with improved properties when used with glass fibers in the pultrusion process. The pultruded composites, based on soy-based resin systems, have shown comparable mechanical properties compared to neat resin. The presence of soybean oil increased the lubricity, thus reducing the pull force during the pultrusion process, an additional bonus.

Espana et al. [96] cured epoxidized soybean oil of commercial grade (Traquisa S.A.—Barcelona, Spain, EEW of 238 g/equivalent) with maleic anhydride (AEW index of 98.06 g/equivalent) with the aid of a mixture of catalysts (1,3-butanediol anhydrous and benzyldimethylamine). The mixture was cured at various temperatures for 5 hours using different epoxidized soybean oil (EBSO):anhydride (AEW) ratios. The best-balanced mechanical and thermal properties were obtained for a ratio of 1:1, representing a high level of cross-linking. Maximum values of flexural modulus (432 MPa) and Shore D (70) were obtained for an EBSO:AEW ratio of 1:1, while maximum glass transition temperature (42.6°C) was obtained for a ratio of 1:0.9. Lignin can be used as the hard segment in epoxy resin networks, increasing the glass transition of the resultant polymer. Hirose et al. [97] investigated the properties of ester-type epoxy resins derived from lignin. An ester-carboxylic acid derivative of lignin was previously obtained from the alcoholysis of lignin with succinic acid anhydride. The ester-carboxylic acid obtained can be reacted with ethylene glycol diglycidyl ether to form epoxy resins. Glass transition temperature increased with increasing ester-carboxylic acid derivative content, suggesting that lignin indeed acts as the hard segment (reaching a maximum value of −11°C).

Sugar-based epoxy systems were also developed. East et al. [98] developed substitutes for bisphenol A based on bisglycidyl ethers of anhydro-sugars, such as isosorbide, isomannide, and isoidide (Figure 15.12). The curing agent used could be either bio-based polyamines or polycarboxylic acids. The novel sugar-based epoxy system developed can be synthesized to be water soluble. Isosorbide epoxy with equivalent weight 230 g/eq was cured with methylenedianiline (MDA, with equivalent weight of 49.6 g/eq) at 80°C for 2 hours and 16 hours at 120°C. The glass transition temperature obtained for the cured epoxy was 89°C.

Boutevin et al. [99] developed epoxy prepolymer 596 HANDBOOK OF THERMOSET PLASTICS
PC 19 system Tg is 47°C. For the ratio of 40:60%, a Tg of 32°C was obtained.

Stemmelen et al. [90] developed cross-linking materials from renewable resources and created fully bio-based epoxy systems. Amines are considered the most popular cross-linking agent due to their nucleophilicity, which makes possible reactivity at room temperature. Functionalization of natural oils, such as grapeseed oil, with amine groups involving the reaction of cysteamine chloride and UV initiated thiol-ene chemistry created bio-based cross-linking agents. The curing reaction with a commercial epoxidized linseed oil can be seen in Figure 15.20. An additional bio-based curing agent was developed by Takahashi et al. [100]. A terpene-derived acid anhydride (TPAn) was synthesized by Diels-Alder reaction of maleic anhydride and allo-octimene obtained by the isomerization of α-pinene, a terpene found in coniferous trees.

The authors compared the thermal and mechanical properties of epoxidized soybean oil (ESO) cured with three different curing agents: terpene-based acid anhydride (TPAn), hexahydrophthalic anhydride (HPAn), and maleinated linseed oil (LOAn). ESO-TPAn showed a higher glass transition temperature (67.2°C) and a higher tensile modulus and strength.

Wang et al. [101] used rosin as a bio-based curing agent. Rosin is a natural and abundant product.
obtained from coniferous trees. The acidic component of rosin is mainly a mixture of isomeric abietic-type acids (Figure 15.21). Rosin and its derivatives have been used as tackifiers for adhesives, varnishes, paints, etc.

The researchers have studied a rosin-based, anhydride-type curing agent and rosin-based glycidyl ether-type epoxies. Glycidyl ether of abietic alcohol was synthesized, reducing first the carboxyl group of rosin acid to a hydroxyl group, and then reacting with epihalohydrin to obtain glycidyl ether.

Cimteclab [102] developed a series of products based on the phenolic structure currently derived from cashew shell oil, a by-product of the cashew nut industry. Novocard™ is a curing agent developed for epoxy systems based on the reaction of cardanol and paraformaldehyde using oxalic acid as catalyst [61]. Using Novocard™ (18%) as a curing agent for a composite matrix based on DGEBA epoxy (EC01, Camattini, Spa, Italy), a Tg of 110°C was obtained, compared to the 122°C obtained using a regular amine hardener. Mechanical properties obtained were similar to the conventional system except for the impact strength. The bio-based hardener increased the impact strength from 9.2 kJ/m² to 24.3 kJ/m² [103].

Wang et al. [104] synthesized rosin-based flexible anhydride-type curing agents based on maleopimarate-terminated polycaprolactone (MPA-terminated PCL). Commercial epoxy resin (DER 332 Epoxy resin, DOW) was cured with (MPA-terminated PCL) in different stoichiometric ratios, using 2-ethyl 4-methylimidazole as accelerator. Epoxide/anhydride ratio affects the mechanical properties. At a ratio of 3:2, the cured resin exhibited clear stress yield. As the ratio increased to 5:2, the cured resin became less ductile, stronger, and stiffer. These changes can be attributed to an increase in the amounts of rigid polyether segments formed. The length of the soft segment in the curing agent affected the cross-linking density. As the molecular weight of the PCL segment increased, the corresponding cured epoxy became more ductile and less strong.

It can be concluded that the obstacles to replace petroleum-based epoxy resins with bio-based polymers in commercial applications are mainly due to inferior mechanical and thermo-physical properties. In the meantime, bio-based epoxy systems can be used to partially replace conventional epoxy systems.

**Bio-Based Unsaturated Polyester**

Unsaturated polyester resins are widely used as the matrix in commodity composite materials, usually reinforced with fiber glass. Unsaturated polyesters are produced by polycondensation of unsaturated and saturated dicarboxylic acids with diols. Curing reactions are usually performed through radical or thermal processes in the presence of vinyl monomers, such as styrene. Polyester resins are usually classified as: (1) Ortho resins, (2) Isoresins, (3) Bisphenol A-Fumarates, (4) Chlorenics, and (5) Vinyl ester [105]. The most widely used diol for standard unsaturated polyester is propylene glycol (1,2-propanediol). Additional polyols are dipentaerythritol, glycerol, ethylene glycol, trimethylpropane, and neopentylglycol [91]. Maleic anhydride and fumaric acid are among the most common unsaturated acid monomers used. Phthalic acid (iso or ortho acid) is the saturated dicarboxylic acid used in all standard unsaturated polyester resins [4]. Ortho resin is the least expensive among all polyester resins. Monomers of styrene are usually used as cross-linking agents, and solutions of unsaturated polyesters and styrene vinyl monomers (reactive diluents) are known as unsaturated polyester resins (UPR). The curing reaction of UPR is a free-radical chain growth polymerization between reactive diluent (styrene) and the resin. Curing procedures are considered versatile, from room temperature to elevated temperature, according to the catalyst used [105].
These building blocks can be substituted by bio-based analogs, either partially or even totally, in some cases. Bio-based propylene glycol (1,2-propanediol) and 1,3-propanediol (PDO) are currently being commercially produced from glycerol. In the presence of metallic catalysts and hydrogen, glycerol can be hydrogenated to propylene glycol (1,2-propanediol), 1,3-propanediol, or ethylene glycol. 1,3-Propanediol (PDO) is also being used for production of bio-based unsaturated polyesters [86]. Several entities are working to develop and/or commercialize glycerin-to-propylene glycol technology: Senergy/Suppes (University of Missouri), Cargill/Ashland, Archer Daniels Midland (ADM), UOP/Pacific Northwest National Laboratory (PNNL), Virent Technologies (University of Wisconsin), Huntsman, and Dow Chemical. The cost of production for propylene glycol made from crude biodiesel-based glycerin is compared to conventional propylene oxide-based propylene glycol [106]. Page et al. [107] detailed the polymerization of unsaturated polyester resins based on biologically derived 1,3-propanediol. PDO monomers can be obtained via a fermentation process of corn feed stocks, using bacterial strains able to convert glycerol into 1,3-propanediol (Susterra™, DuPont). Maleic anhydride was chosen as the unsaturated diacid, and anhydride was added in order to increase the solubility in styrene since aromatic diacids increase the solubility of unsaturated polyesters in vinyl monomers (Figure 15.22). Solubility in styrene enables storage, handling, and processing of the unsaturated polyester/vinyl monomer solution. The solubility is dependent on the ratio between the saturated and unsaturated diacids, e.g. the ratio between phthalic anhydride (PA) and maleic anhydride (MA). Compositions containing orthophthalic acid, maleic anhydride, and Susterra™ 1,3-PDO were compared to compositions containing ortho-phthalic acid, maleic anhydride, and 1,2-propylene glycol (instead of 1,3-PDO) using the same ratio between the components. The curing was obtained using styrene (60%). The bio-based composition has shown higher tensile strength (70 MPa compared to 44 MPa), higher flexural strength (112 MPa compared to 67 MPa), but slightly lower HDT (67°C compared to 75°C) [107].

Szkudlarek et al. [108] synthesized low-viscosity unsaturated polyester resins based on bio-based 1,3-propanediol and C5-C10 unsaturated dicarboxylic building blocks, such as bio-based itaconic acid or anhydride. Maleic anhydride was added as the unsaturated diacid and ortho/isoanhydride was added as the aromatic saturated diacid building block. A styrene or methacrylate-containing compound was used as reactive diluent. Radical inhibitors based on phenolic groups such as hydroquinones, catechols, or phenothiazines may be added. A tertiary aromatic amine was used as co-initiator for the free radical polymerization. The composition containing bio-based itaconic acid and 1,3-propanediol were compared to a fossil-based composition containing maleic anhydride and 1,2-propylene glycol (with similar ratio between the components). The compositions were cured using the same amount of styrene (65%). The bio-based unsaturated polyester compositions showed comparable mechanical properties to similar fossil compositions with higher elongation and slightly lower HDT (105°C compared to 109°C). Fatty acids or oils can be used as polyacids, while rigid carbohydrates, such as isosorbide, can be used as polyols.

\[ \text{Maleic anhydride (MA)} + \text{Phthalic anhydride (PA)} \]

\[ \text{1,3-propanediol (1,3-PDO)} \]

**Figure 15.22** Unsaturated polyesters based on bio-based 1,3-propanediol [107].
Szkudlarek et al. [109] also synthesized unsaturated polyester resins using corn-based isosorbide and 1,3-propanediol, corn-based itaconic acid/anhydride, and maleic anhydride in styrene solution. Isosorbide provides the aromatic building block needed to obtain the solubility in styrene. Low thermal stability obtained by Szkudlarek et al. was improved by introducing bio-based itaconic, citraconic, and mesaconic ester units [110]. The unsaturated polyester described by the researchers can be obtained by polycondensation of a polyol (bio-based 1,3-propanediol or 1,2-propanediol) and itaconic, citraconic, and/or mesaconic acid or anhydride as unsaturated dicarboxylic acids. The heat deflection temperature of this new composition was considerably improved (from 70 to 105°C). Citric acid can also be converted into bio-based polyol. Kraft lignin, esterified with anhydrides, is soluble in styrene, and can be used as an additive in unsaturated polyesters, which improves toughness and connectivity in the polymer network [91].

Epoxidized vegetable oils can be used as a replacement for polyester resins. Robert et al. [111] reported a new strategy, based on tandem (serial) catalysis, to obtain alternating polyesters from renewable sources, using available complexes to catalyze the cyclization of dicarboxylic acids followed by alternating copolymerization of the resulting anhydrides with epoxides. Rosh et al. [112] prepared cross-linked partially bio-based polyesters by curing epoxidized soybean oil with various dicarboxylic acid anhydrides in the presence of cure catalysts such as tertiary amines, imidazoles, or aluminum acetylacetonate. The anhydride dictates the final thermal and mechanical properties. Anhydrides of hexahydrophthalic acid, succinic acid, and norbornene dicarboxylic acid have led to high flexibility with glass transition temperatures below room temperature. Maleic anhydrides gave rise to more rigid, stiff polyesters with higher glass transition temperatures between 43 and 73°C.

Haq et al. [113] replaced partially petroleum-based unsaturated polyester with functionalized vegetable oils such as epoxidized methyl soyate. Ortho-unsaturated polyester resin (UPE, Polylite 32570, Reichhold Inc., USA) containing 33.5 wt.% styrene was used in the research. The bio-resin based on epoxidized methyl soyate (EMS) was obtained from Arkema Inc., USA (Vikotex 7010). The amount of bio-based portion in the resin varied from 0 to 20%. A reduction in the tensile modulus of 28% was observed for polyester resins containing 10% EMS in the blend, and 42% for 20% EMS, relative to neat UPE. The failure strain increased, while the tensile strength decreased, which led to increased toughness with increasing EMS content. The blend containing 10% EMS showed 44% higher toughness relative to neat UPE. The addition of EMS also increased the moisture absorption of the resulting bio-based resin.

Acrylated epoxidized vegetable oils can be cured alone or mixed with unsaturated polyester resins. Grishchuk et al. [114] developed hybrid thermosets with interpenetrating network (IPN) structures based on vinyl ester/acrylated epoxidized soybean oil hybrids with IPN structure, cross-linked with styrene, and anhydride as an additional cross-linker. The styrene diluted (~30 wt%) bisphenol A-type vinyl ester (VE; Daron-XP-45-A2) was obtained from DSM Composite, Nederland, and the acrylated epoxidized soybean oil (AESO) containing monomethyl ether hydroquinone as inhibitor, was obtained from Sigma-Aldrich Chemieg GmbH. The following vinyl ester (VE)/AESO combinations were synthesized: 75/25, 50/50, and 25/75 wt.%. Lower storage moduli were obtained for combinations containing AESO. Two Tg were detected for the polymerized AESO (at −50 and 15°C), probably due to the multi-functionality and high unsaturation level of the AESO generating hard and soft segments. The presence of the acrylated epoxidized soybean oil in the hybrid system led to a reduction of the flexural modulus (around 50% lower for the 50/50 composition) and to an increase in the toughness of the system. The resistance to thermal decomposition of the hybrid resin system was improved due to the interpenetrating network structure created.

Liu et al. [115] obtained unsaturated polyester-like resins from functionalized tung oil. Tung oil is extracted from the seeds of tung trees. The principal compound of this oil is a glyceride based on alpha-elaeoestearic acid (cis-9, trans-11, trans-13-octadecatienoic acid). This compound is a highly unsaturated conjugated system that is used as a drying oil, mostly for coatings, paints, and varnishes, but cannot compete with the properties of a general purpose unsaturated polyester. In order to obtain unsaturated polyester-like resin with enhanced properties, tung oil was functionalized in two steps: (a) alcoholyis with pentaerythritol to produce tung oil pentaeritritol; and (b) maleination to produce...
tung oil pentaerithritol (maleinated). The product was blended with styrene, and cross-linking took place via a free radical polymerization, as can be seen in Figure 15.23. Promising mechanical properties were obtained: tensile strength was 35.9 MPa, tensile modulus was 1.94 GPa, flexural strength was 46.2 MPa, and flexural modulus was 2.08 GPa.

Ashland Performance Materials, a commercial unit of Ashland Inc., developed the first commercially available bio-based unsaturated polyester resin (Envirez™) based on soybean oil triglycerides. Different grades of Envirez™ are available that contain from 8 to 22% bio-based content [116]. Envirez™ is obtained by a process where a carboxylic acid or corresponding anhydride containing an ethylenic unsaturation is first reacted with a saturated, monohydrated alcohol to form the half ester of the acid or anhydride. The half ester is then reacted with a polyol to form the polyester. Soybean oil is introduced in the reaction step of the half ester and the polyol [117]. A comparison between mechanical properties of one of Envirez™ grades and a standard UPR can be seen in Table 15.2.

### Bio-Based Polyurethanes

Polyurethanes are extremely versatile polymers with a great variety of applications: flexible and rigid foams, elastomers, coatings, adhesives, and sealants. Polyurethanes can be thermoplastic or thermoset. Polyurethanes are synthesized by the reaction of a polyol and a diisocyanate. The functionality of the polyol determines the properties of the final polyurethane. Diols lead to linear thermoplastic polyurethane whereas polyols with three or
more hydroxyl groups are required to prepare thermoset, polyurethane networks.

The terminology “bio-based polyurethanes” usually refers to polyurethanes based on renewable source polyols [42]. Bio-based isocyanates have been introduced only recently and the results have not yet been conclusive. Bio-based content of polyols can range from 30 to 100%, and as a result, polyurethane bio-based content varies from 8 to 70%, depending on the building blocks chosen [4]. Bio-based polyols available in the market for polyurethane production are divided into three groups: polyether polyol, polyester polyol, and oleochemical polyols from vegetable oils.

a. Bio-based polyether polyols: Sucrose and sorbitol are short-chain polyether polyols used for rigid foams [4]. Polyether polyols can also be obtained by condensation of 1,3-propanediol synthesized for bio-based glycerol [118]. Bio-based 1,3-propanediol can be used to produce polytrimethylene ether glycol as the soft segment in elastomers and spandex fibers.

b. Bio-based polyester polyols: These can be obtained by polycondensation of bio-based dicarboxylic acids such as adipic or succinic acid with bio-based polyols (1,3-propanediol) [118]. Polyester-based polyurethanes have better mechanical properties and are more resistant to oil, grease, solvents, and oxidation, compared to polyether-based. Polyester-based polyurethanes are more sensitive to hydrolysis and microorganism attack [119]. Longer and hydrophobic chain polyols can result in greater flexibility and hydrolytic stability of the resulting polyurethane.

c. Vegetable oil-based polyols: These can be prepared using distinct methods such as epoxidation of the double bonds with further oxirane ring opening with alcohols or other nucleophiles [120], transesterification with multifunctional alcohols, and the combination of hydroformylation or ozonolysis with subsequent reduction of carbonyl groups (see the section on natural oils for more details). Fatty acids can be easily isolated from triglycerides and can be used to prepare diols and polyols. Triglycerides of castor oil and lesquerella oils are characterized by the presence of ricinoleic and lesquerolic fatty acids, respectively, both presenting hydroxyl groups on their backbones [42]. Both oils are important sources of naturally occurring polyols, however, the number of hydroxyl groups in castor oil are substantially higher compared to lesquerella oil.

### Polyurethanes from Vegetable Oils

Most of the bio-based polyols for polyurethanes are synthetized from vegetable oils. The hydroxyl groups present in oils can react with isocyanates to form branched polyurethanes. Natural oils vary greatly regarding the type, composition, and distribution of fatty acids in the triglycerides molecules. The principal variation in fatty acid composition of the oils results from variations in chain length, degree of unsaturation, and position of the double bond in the fatty acid chains. As a result, there is a great variation in the length of elastically active network chains (related to the double bonds/hydroxyl groups) and dangling chains (the soft segments resulting from the saturated portions) in polyurethane networks obtained from vegetable oil-based polyols [33]. The functionality of the polyol determines the properties of the final polyurethane polymers. Diols lead to linear thermoplastic polyurethanes, whereas polyols with three or more

<table>
<thead>
<tr>
<th>Property</th>
<th>Bio-based Envirez™ 70302*</th>
<th>Aropol S 542 H (Std ref. resin)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>73</td>
<td>75</td>
</tr>
<tr>
<td>Tensile Modulus (MPa)</td>
<td>2500</td>
<td>4300</td>
</tr>
<tr>
<td>Elongation at Break (%)</td>
<td>4.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Heat Deflection Temperature (°C)</td>
<td>90</td>
<td>94</td>
</tr>
</tbody>
</table>

*Envirez™ 7030 (Ashland) is an isophthalic-based resin with 22% bio-content used for pultrusion.

**Aropol S 542 H (Ashland) is a standard reference unsaturated polyester resin used for pultrusion.
hydroxyl groups are required to obtain thermoset polyurethane networks [120]. Petroleum-based polyols usually present hydroxyl groups as primary alcohols while the majority of functional groups in vegetable oils are secondary. The reaction rate of primary alcohols with isocyanate is about 3.3 times faster than that of the secondary ones [121]. Additionally, when polyurethane foams are created from secondary polyols, slower reaction rates during gas expansion might weaken the three-dimensional network of the polyurethane foam, thus creating more open cells with lower carbon dioxide content and reduced thermal isolation properties [121].

Castor oil can be used in the synthesis of crosslinked polyurethanes and interpenetrating networks. Soybean oil, palm oil, and rapeseed oil are more popular and cheaper oils compared to castor and lesquerella oils (natural polyols). In order to obtain polyols from these oils, chemical modifications have to be made (refer to the section on natural oils for more details). Polyurethanes produced from vegetable oil-based polyols include elastomers obtained from oils with low hydroxyl content and rigid foam and plastics from high hydroxyl content. The extent of unsaturation conversion to hydroxyl groups can tailor the final properties of the polyurethane since the hydroxyl content controls the degree of cross-linking and the resulting stiffness of the polymer. The polymer structure must be highly cross-linked when a rigid foam is required, whereas less cross-linking gives rise to flexible foams [115]. The degree of cross-linking is also dependent on the NCO/OH ratio. Highly cross-linked and stiffer polyurethanes are obtained when the ratio is high [122].

Most vegetable oil-based polyols are of relatively low molar mass (around 1000 Da) with a functionality distribution that ranges from 1 to 8 hydroxyl groups per molecule. As a result, the average hydroxyl equivalent (molecular weight divided by the hydroxyl functionality) varies from 200 to 300, making them suitable for rigid and semi-rigid applications, rigid foams, cast resins, coatings, and adhesives [13]. Rigid polyurethane foams can be obtained from 100% vegetable oil-based polyols, while flexible foams are obtained by mixing vegetable oil-based polyols with petroleum-based polyols.

Castor oil, for example, is a naturally occurring polyol with a functionality of 2.7 hydroxyls per molecule. Polyurethane obtained from castor oil with diphenylmethane diisocyanate is a hard elastomer with a glass transition temperature around 7°C. According to Petrovic [13], in order to obtain flexible foams and elastomers, polyols with molecular weight greater than 3000 Da and hydroxyl equivalent weight of 1000 and higher are required. These polyols were synthesized by Petrovic from ricinoleic acid via transesterification, which produced polyricinoleic acids (Figure 15.24). The dangling chains act as plasticizers, and inhibit crystallization. Elastomers with glass transition temperatures ranging from −33°C to −58°C were obtained when polyricinoleic acids were polymerized with diphenylmethane diisocyanate. According to Petrovic, lower glass transition temperatures and higher elongations can be achieved using a triol polyricinoleic acid obtained by introducing a triol during the transesterification step.

Zlatanlic et al. [33] synthesized polyurethanes from different vegetable oils — midoleic sunflower, canola, soybean, sunflower, corn, and linseed oil — with 4,4-diphenylmethane diisocyanate. The functionality of the polyols ranged from 3.0 for the midoleic sunflower polyol to 5.2 for the linseed oil. The conversion of the double bonds to epoxy groups during the epoxidation reaction was relatively high for all the oils, and ranged from 91 to 94%. The polyols were obtained by epoxidation

![Figure 15.24 Polyester diol obtained from ricinoleic acid [13].](image-url)
followed by ring opening. Polyurethanes were obtained by reacting the polyols with MDI. Linseed oil-based polyurethanes presented higher cross-linking density, better mechanical properties, and higher glass transition temperatures. The lowest Tg was obtained for the polyurethane from midoleic sunflower oil (33°C), and the highest was observed for the linseed oil-based polyurethane (77°C). Tensile strengths of all polyurethanes ranged from 15–23 MPa, except for the polyurethane based on linseed oil, which showed tensile strength three times higher than the others (56 MPa). The tensile modulus of linseed oil-based polyurethane was near four times higher (2.0 GPa) compared to other oil-based polyurethanes. The variation in properties resulted primarily from the different cross-linking densities and less from the position of the reactive sites in fatty acids chains.

Dwan’Isa et al. [122] used soy phosphate ester polyol with hydroxyl content ranging from 122 to 145 mg KOH/g and diphenylmethane diisocyanate to prepare highly cross-linked bio-based polyurethanes.

Del Rio et al. [124] obtained polyols with different hydroxyl contents using the synthesis of polyether polyols through the combination of cationic ring-opening polymerization of epoxidized methyl oleate and the reduction of carboxylate groups to hydroxyl groups. Polyurethanes were obtained from the reaction of the polyols with MDI or L-lysine diisocyanate (LDI), a non-toxic diisocyanate. It was observed (as expected) that the higher the functionality of the polyol, the higher the degree of cross-linking that occurred, which in turn led to higher Tg values. Additionally, the aromatic MDI led to higher Tg values compared to the aliphatic LDI.

Lligadas et al. [120] synthesized diols and polyols from oleic acid (C18 fatty acid found mostly in olive oil) and undecylenic acid (C11 fatty acid derivative with a terminal double bond obtained from castor oil) using click chemistry. Click chemistry was tailored to generate substances quickly and reliably, mimicking nature, and was designed to generate substances by joining small units together.

Undecylenic acid was obtained by heating ricinoleic acid under vacuum pyrolysis to create undecylenic acid and heptaldehyde. Using thiol-ene click chemistry, Lligadas et al. [120] applied photo-initiated coupling of 2-mercaptoethanol and methyl esters of oleic and undecylenic acids, followed by reduction (Figure 15.25).

Bio-based triols were also obtained by transition metal-catalyzed cyclotrimerization of methyl 10-undecynoated and methyl 9-octadecynoated compounds that can be synthesized from oleic and undecylenic acid via bromination and further elimination to alkyne functionality, and then subsequent reduction of carboxylate groups to obtain primary hydroxyl groups (Figure 15.26). The resulting polyol was reacted with methylene diphenyl isocyanate (MDI) using 1,4-butanediol as the chain extender.

Desroches et al. [125] synthesized ester-containing diols of fatty acids via transesterification with diol compounds followed by thiol-ene radical coupling. Polyurethanes were prepared from the synthesized oleochemical pseudo-telechelic diols, which were reacted with methylene diphenyl-4,4 diisocyanate (MDI). In Desroches’ study, soybean oil was used as raw material, and contained different fatty acids with 0 to 3 double bonds. The soft segments of vegetable oils were based on ester groups or amide groups with various spacer lengths in between. These were obtained through the transesterification with a diol or amidification with hydroxylamine or through thio-ene radical coupling. Amide groups containing polyurethanes exhibited the highest glass transition temperatures (62°C) due to hydrogen bonding enhancement.

Miao et al. [126] developed a polyol with high hydroxyl value from epoxidized soybean oil and isopropanolamine (Figure 15.27). Both ester groups and epoxide groups in epoxidized soybean oil reacted with amino group generating hydroxyls, leading to a hydroxyl value of 317 mg KOH/g. The resulting polyol was reacted with 1,6-diisocyanato-hexane to obtain polyurethane, and additionally used 1,3-propanediol (PDO) as the chain extender. A single glass transition was noticed (24.4 to 28.7°C).

Natural oil polyols are produced commercially by several companies — Agribusiness Cargill (BiOH, soybean-based polyol), Dow Chemical (Renuva soybean-based polyols), Urethane Soy Systems Company, and BioBased Technologies (Agrol) BASF (BALANCE, castor oil-based polyol), Bayer (BAYDUR, castor oil-based polyol) and Mitsui Chemicals (castor oil-based polyols) — for making polyurethane foams for the automotive, furniture, spray insulation, and other industries. Polyurethane rigid foams are widely used as insulation and structural materials for construction, transportation, decoration, and appliances, which accounts for approximately one-third of the
polyurethane market. Flexible polyurethane foams are used in automobile seating, upholstered furniture, carpet backing, and bedding (mattresses and pillows). Bayer recently developed a visco-elastic polyurethane foam based on castor oil polyol for application in cushioning and vibration-damping materials [127]. The visco-elastic effect is obtained due to small open cells (with little opening, which delays the air re-entrance after compression and leads to a slow-down recovery). A summary of bio-

![Figure 15.25 Preparation of undecylenic and oleic acid-derived diols using thiol-ene click chemistry [120].](image-url)
based polyols, raw materials, and producers can be seen in Table 15.3.

Polyols from Lignocellulosic Materials

Lignocellulosic materials including wood, agricultural, or forestry wastes are a mixture of natural polymers based on lignin, cellulose, and hemicellulose, and tannins with more than two hydroxyl groups per molecule, and can be used as polyols for polyurethane preparation [137]. In order to obtain polyols from lignocellulosic materials, they must first be liquefied by chemical or thermochemical treatments at high temperatures and high pressure [42,138,139]. In the presence of alcohols such as ethylene glycol, liquefied wood with hydroxyl content suitable to reaction with isocyanate is obtained. Foam with varied densities can be obtained with properties similar to conventional rigid polyurethane foams.

Figure 15.26 Preparation of undecylenic aromatic triol (UDT) and oleic aromatic triol (OLT) using cyclotrimerization process [120].
Polyols from Carbohydrates

Sugars and starches are carbohydrates that are considered a very important renewable resource for polyols (see the saccharides section for more details). Sugars are basically polyols with a high number of hydroxyl groups along the chain, and therefore are potential raw materials for polyurethanes [22,41]. Starches and cellulose can be liquefied in the presence of alcohols in order to obtain polyols to be used in the preparation of polyurethanes. The process includes the use of liquefaction solvents based on polyethylene glycol, glycerol, and sulfuric acid. The solution obtained is then neutralized with caustic soda [122].

Polyols from Natural Polyphenols

As detailed in the section on polyphenols, naturally occurring polyphenols such as tannins and lignins are characterized by the presence of multiple phenol structural units. Polyurethanes having mechanical properties ranging from soft to hard were synthesized by varying the kraft lignin content. High content (30–35%) of kraft lignin results in rigid and brittle materials, while lower amounts provide soft polyurethanes [122]. Kelley et al. [140] synthesized polyurethanes from kraft hydroxypropyl lignin with varied molecular weights and hexamethylene diisocyanate. The mechanical properties of the polyurethane obtained improved as the molecular weight of the hydroxypropyl lignin increased. Kelley et al. [56] tried to increase the elongation and toughness of polyurethanes based on lignins by introducing chain extenders to the lignin. Polyethylene glycol and polybutadiene glycol were used as chain extenders. In order to eliminate phase separation, a polyether soft segment was attached to the lignin derivative by propylene oxide chain extension, which created a star-like copolymer with rigid aromatic core and flexible polyether arms. Saraf et al. [141] compared the properties of polyurethanes synthesized from two types of lignin: kraft and steam explosion lignin. Kraft lignin showed inferior mechanical properties.

Cashew nut-based phenols, especially cardanol, are considered an attractive raw material for polyurethanes. Cardanol can be recovered from cashew nut shell liquid by double vacuum distillation and can be converted into a diol to be reacted with a diisocyanate [60]. According to Mohanty et al. [123], cardanol can be reacted with glycol in the presence of phosphoric acid as catalyst. The resulting mixture can be reacted with aromatic diisocyanate to obtain films of polyurethane. Mixtures of cardanol, formaldehyde, and diethanolamine, blended first with polyethylene glycol and then with methylene diphenyl diisocyanates; MDI and hexamethylene diisocyanate led to rigid polyurethane foams [59].

Isocyanate-Free Polyurethanes and Bio-Based Isocyanates

Isocyanates are the derivatives of isocyanic acid (H-N=C=O). The functionality of the isocyanate (R-N=C=O) group is highly reactive toward
Table 15.3 Summary of Bio-Based Polyols for Polyurethanes [4]

<table>
<thead>
<tr>
<th>Source Material</th>
<th>Trade Name</th>
<th>Producer</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean oil</td>
<td>BiOH</td>
<td>Cargill</td>
<td>Flexible foams</td>
<td>[128]</td>
</tr>
<tr>
<td></td>
<td>Renuva</td>
<td>Dow</td>
<td>Flexible foams and CASE*</td>
<td>[129]</td>
</tr>
<tr>
<td></td>
<td>SoyOil</td>
<td>Urethane Soy Systems</td>
<td>Flexible and rigid foams, spray foams, elastomers</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td>Baydur</td>
<td>BAYER</td>
<td>Rigid and flexible foams</td>
<td>[130]</td>
</tr>
<tr>
<td></td>
<td>Agrol</td>
<td>BioBased Technologies</td>
<td>CASE*, molded foams</td>
<td>[131]</td>
</tr>
<tr>
<td>Castor oil</td>
<td>Lupranol BALANCE</td>
<td>BASF</td>
<td>Rigid foams, mattresses</td>
<td>[132]</td>
</tr>
<tr>
<td></td>
<td>Polycin</td>
<td>Vertellus</td>
<td>Coatings</td>
<td>[133]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mistui Chemicals</td>
<td>Rigid and flexible foams</td>
<td>[134]</td>
</tr>
<tr>
<td>Renewable and recycled oil</td>
<td>Enviropol</td>
<td>IFL Chemicals</td>
<td>Rigid foams for insulation and refrigeration</td>
<td>[135]</td>
</tr>
<tr>
<td>Rapeseed/ Sunflower oil</td>
<td>Metzeler-Schaum GmbH</td>
<td></td>
<td>Flexible foam</td>
<td>[136]</td>
</tr>
</tbody>
</table>

*CASE: Coatings, Adhesives, Sealants, and Elastomers.

proton-bearing nucleophiles, and the reaction of isocyanate proceeds with addition to the carbon-nitrogen bond [142]. Important isocyanates used in polyurethane manufacturing include 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 1,6-hexamethylene diisocyanate, and 1,5-naphthalene diisocyanate, among others (all petroleum-derived). The reactivity of isocyanates depends on their chemical structures. Aromatic isocyanates are usually more reactive than their aliphatic counterparts. The presence of electron-withdrawing substituents on isocyanates increases the partial positive charge on the carbon atom and moves the negative charge further away from the reaction site, which results in a fast reaction. Isocyanate is obtained from the reaction between amines and phosgene, a hazardous chemical that requires special precautions, is toxic, and is an irritant to mucous membranes. Polyurethanes are currently being produced from bio-based polyols with toxic isocyanate. Environmental and public health concerns motivate the research for alternative routes to create bio-based, non-toxic isocyanates. Isocyanate-free, environmentally friendly polyurethane systems can be obtained from vegetable oils. Mahendran et al. [143] developed a new bio-based non-isocyanate urethane by the reaction of a cyclic carbonate synthesized from a modified linseed oil and an alkylated phenolic polyamine from cashew nut shell liquid (Figure 15.28). Cyclic carbonates can be synthesized from any epoxy monomers. The cyclic carbonate groups were added to the triglyceride by reacting epoxidized linseed oil with carbon dioxide in the presence of a catalyst.

Çayli et al. [144] synthesized isocyanate derivatives from unsaturated plant oil triglycerides. The triglyceride was first brominated at the allylic positions by a reaction with N-bromosuccinimide, and then, the brominated species were reacted with AgNCO to convert them to isocyanate-derivative triglycerides (Figure 15.29).

Polyurethanes and polyureas were synthesized curing the fatty isocyanates obtained with alcohol and amines, respectively. Glycerin polyurethane exhibited a glass transition temperature of 19°C, castor oil polyurethane showed two glass transition temperatures at 24 and 36°C, and triethylene tetramine polyurea showed a glass transition
temperature of 31°C. The polyurethanes synthesized demonstrated similar mechanical properties (tensile modulus around 50 kPa and tensile strength around 100 kPa). Despite the low tensile strength and modulus, castor oil polyurethane and glycerin polyurethane showed excellent elongation, 410% and 353%, respectively.

Hojabri et al. [145] described the synthesis of linear saturated terminal aliphatic diisocyanates from fatty acids via Curtis rearrangement, a thermal
decomposition of acyl azide. Diacids such as azea-
llic acid, can be produced from oleic acid, as in
Figure 15.30.
Saturated diacids can be prepared by ozonolysis
of oleic acid to the corresponding aldehyde fol-
lowed by purification and oxidation of the aldehyde
to obtain the diacid. Hojabri et al. compared physi-
cal properties of polyurethanes obtained using the
same polyol with fatty acid-derived diisocyanate
(1,7-heptamethylene diisocyanate, HPMDI) and a
similar but petroleum-derived commercially avail-
able diisocyanate: 1,6-hexamethylene diisocyanate
(HDI). Canola polyols were synthesized using ozo-
nolysis and hydrogenation. Desmophen 800 (Bayer)
was used as the commercial polyol. The polyur-
ethanes obtained had comparable properties to
fossil-based diisocyanates.

**Bio-Based Alkyd Resins**

Alkyds are polyesters obtained by polycondensa-
tion of three monomers: polyols, dicarboxylic acids,
or anhydrides, and natural fatty acids or triglycer-
ides. The term alkyd is a modification of the origi-
nal name “alcid” coined by R. H. Kienle, meaning
from alcohol and organic acids [146]. Since alkyd
resins emerged in the market in the late 1920s, they
have always had a substantial bio-based content
[4]. These resins are used in paints and coatings. In
1927 Kienle combined fatty acids with unsaturated
esters while searching for a better insulating resin
for General Electric [146]. Double bonds present in
the fatty acids are capable of oxidative coupling
reactions that lead to “air drying” of plant oils, thus
creating film coatings. This is the chemistry behind
the alkyd resins [14]. When the resin is applied to a
substrate, heat or oxidizing agents are achieved by
changing the oil length or chemical modification,
such as introducing chain stopping agents, phenolic
resins, acrylic monomers, styrene, vinyl toluene,
silicones, isocyanates, etc. Alkyd resins are compat-
ible with a vast number of polymers, making them
very versatile to produce coatings, binders, paints,
lacquers, and varnishes, both transparent and semi-
transparent [147]. Fatty acids are produced from
vegetable oil. The common polyols are synthetic
glycol or glycerol, although bio-based glycerol can
be used instead, which increases the bio-based con-
tent of the final polymer [4] and extends up to 70%
of the bio-based content [147]. Fossil-based phtha-
lic acid and maleic acid (and anhydrides) are the
most commonly used organic acids; glutaric and
succinic anhydrides can also be used in alkyd for-
mulations [17]. Drying times can be controlled by
the type and amount of anhydride, with drying
times increasing with the amount of anhydride. An
illustrative reaction between glycerol and phthalic
anhydride is shown in Figure 15.31.

Alkyd resins can be classified according to oil
length, which refers to the oil percentage in the
alkyd. Short oil alkyds contain below 40% oil;
between 40 and 60% they are called medium, and
above 60%, long oil alkyds [17]. The oil length
affects the properties of the final product. A typical
long oil alkyd is made of 60% soybean fatty acids,
21.5% polyol (pentaerythritol), and 25.4% phthalic
anhydride [4]. Most alkyd-based coatings are used
for industrial goods (vehicles, wood products, etc.)
and infrastructure (traffic control striping, bridges,
etc.). Alkyd coatings are inexpensive, durable, and
heat resistant. Durability and abrasion resistance
can be increased by modifying alkyd with rosin
(pine resin) [146]. Phenolic and epoxy resins
improve hardness and resistance to chemicals and
water. Styrene extends flexibility of coatings and
can be used to cross-link alkyd resins (using

![Figure 15.30](image_url) Synthesis of bio-based isocyanate from oleic acid [145].
peroxides as initiators). Thermoset alkyds can be used to produce billiard balls, appliance housings, motor cases, switches, electronic encapsulations, etc. More ecological friendly versions of alkyds were produced based on the synthesis of alkyd resins with relatively high acid value, and neutralized using amines to form colloidal solutions in a mixture of water and water miscible solvents such as glycol ether [147]. Nevertheless, solvents present in alkyd formulations at an amount of 20 to 30% present an environmental problem. High-quality alkyd coatings with low solvent amounts are an important target in the coating industry. High solid content alkyd resins can be obtained by reducing polymer viscosities using lower-molecular-weight polymers, thus enabling a reduction in the solvent content [17]. The same effect can be obtained by synthesizing highly branched and star-structured resins [148]. Hyperbranched alkyd resins can be obtained using trimethylpropane and dimethylolpropionic acid. Saturated polyesters with hydroxyl end groups are first obtained. The alkyd resin is obtained by the esterification of the polyester obtained in the first step, with unsaturated fatty acids. According to Gruner [17], star-like resins with three or four arms can be formed by the esterification of dipentaerythritol with fatty acids.

In the 1980s and 1990s, environmentally friendly, zero VOC (Volatile Organic Contents) versions of alkyd waterborne resins were developed. In order to obtain water-based resins, alkyd resins with high acid numbers were prepared and neutralized by amines. Amines were avoided by using suitable surfactants. According to Hofland [147], surfactants can also be eliminated by in situ polymerization of hydrophilic monomers within solvent-less alkyd resin, followed by inverse-phase emulsification. Water-soluble alkyd resins were synthesized by the copolymerization of acrylic acid, glycidyl methacrylate esterified with unsaturated fatty acid, styrene, and methyl methacrylate [17]. Kuhneweg [149] developed a waterborne acrylic-modified alkyd resin based on the polymerization of a sulfonated alkyd resin with an acrylated fatty acid. After polymerization, the polymer could be dissolved in water.

Hofland [147] described an ultimate low carbon footprint alkyd resin that had not only a low content of fossil carbon, but also low energy content (i.e. low energy bio-based raw materials such as succinic acid, colophonium (rosin), glycerol, and isosorbide). Water-based alkyd and high-solid alkyd resins can be ecological friendly solutions. High-solid alkyd solvents can be replaced by bio-based ones like ethanol, methyl ester of soybean fatty acids, or methyl lactate.

Kemwerke (Philippines) developed eco-friendly short oil coconut alkyd resins for paint formulations. Coconut alkyds are a range of tough resinous products formed by reacting polybasic organic acids or anhydrides with polyhydric alcohols in the presence of coconut fatty acid or the monoglyceride state of the refined coconut oil [150]. Soy Technologies LCC (KY, EUA) produces soy-based alkyd emulsions for coating formulations (Soyanol) [151]. Perstop (Sweden) produces bio-based glycerol in medium oil-length, soybean oil-based, air-drying alkyd resin formulations [103].

Bio-Based Phenolic Resins

Phenol—formaldehyde is one of the oldest commercial synthetic polymers, first introduced by Leo Hendrik Bakeland in 1907 [152]. The polymer is the result of a step-growth polymerization of two simple chemicals: phenol or a mixture of phenols and formaldehyde using an acidic or basic catalyst [153]. Phenol is reactive towards formaldehyde at the ortho and para sites, allowing up to three units of formaldehyde to attach to the aromatic ring. The main product of the reaction between them is the production of methylene bridges between aromatic rings, as can be seen in Figure 15.32.
The ratio between formaldehyde and phenol determines the degree of cross-linking. When the molar ratio is one, theoretically, every phenol can be linked together via methylene bridges, enabling total cross-linking. Novolacs (novolaks originally) are phenol–formaldehyde resins where the molar ratio of formaldehyde to phenol is less than one. The polymerization is catalyzed by acids such as oxalic acid, hydrochloric acid, or sulfonate acids; the reaction is slow and relatively low molecular weights are obtained [153]. In a second step, a hardener such as hexamethylenetetramine can be added to cross-link the resin. The hexamine forms methylene and dimethylene amino bridges between the aromatic phenol rings at high temperatures. Resoles are one-stage phenol–formaldehyde resins obtained with formaldehyde/phenol ratios greater than one (~1.5) using a basic catalyst. Hydroxymethyl phenols and benzylic ether groups are formed in the first step of the reaction, at around 70°C. Cross-linking occurs when the temperature reaches around 120°C to form methylene and methyl ester bridges through the elimination of water molecules. A three-dimensional, cross-linked network is formed. Resole-type phenol–formaldehyde resin becomes hard, and heat and chemically stable, after curing. Resoles are used as adhesives (plywood, oriented strand boards, laminated composite lumber, etc.) and in composite materials (glass and carbon composites). Resole and novolac are soluble and fusible low-molecular-weight products at A-stage, rubbery at B-stage, and rigid, hard, and insoluble at C-stage [153]. One of the most common applications of novolac phenol resins is as photoresists.

Since phenol–formaldehyde is one of the major adhesive resins in the manufacture of plywood, and the raw materials are petroleum-based, their replacement by bio-based, non-toxic substitutes has become a necessity. In the polyphenols section, bio-based polyphenols were presented as well as the chemical pathways used to transform them into raw materials for polymers. Lignin, a renewable, non-toxic, widely available, low-cost raw material was presented as having a high potential to be used as a phenol substitute in phenol–formaldehyde resins; it is a relatively expensive petroleum-based chemical [154].

Lignin is highly cross-linked; three-dimensional aromatic polymers with phenyl–propane units are linked together by carbon-carbon or ether bonds with phenolic and hydroxyl groups (Figure 15.16). Lignin is the second most abundant polymer in
nature, after cellulose, and it is produced as a by-product of the paper industry. One of the functions of lignin in plants, together with hemicellulose, is to bind cellulose fibers, although isolated lignins have proven to be poor adhesives for wood composites [155]. Lignin is not structurally equivalent to phenol. Phenol has five free sites on the aromatic ring and no ortho and para substituents around the hydroxyl group. In lignin, the aromatic ring is para-substituted by the propyl chain of the propylphen-4-ol(coumaryl) structural unit, which affects lignin reactivity during cross-linking with formaldehyde [155]. Lignin presents most ortho and para sites as blocked by functional groups, which leads to slower reaction with formaldehyde when compared to phenol. For this reason, lignin is used to replace phenol in a limited amount, between 40 to 70% in adhesives formulations. Brosse et al. [156] added lignin to phenol-formaldehyde resins without deteriorating the mechanical and adhesion properties, and observed that an additional environmental benefit was obtained: the presence of lignin reduced the formaldehyde emissions for both the resin and the finished products.

Phenolic precursors can also be prepared by liquefying wood, bark, and forest and wood industry residues using a fast pyrolysis process. Monomeric phenols can be produced by thermochemical conversion of biomass using fast and vacuum pyrolysis [51,147]. Liquefication, phenolysis, and fractionation methods can be also used. Fast pyrolysis is based on fast heating rates using temperatures between 400 and 600°C. Chum et al. [157] synthesized novolac and resole resins using phenol derivatives obtained by fast pyrolysis from softwood, hardwood, and bark residue. Reactive components for resin synthesis were obtained by fractioning the pyrolysis oils and isolating phenolic and neutral fractions, which were directly polymerized [154,157]. These pyrolytic oils contained a complex mixture of compounds including phenolics, guaiacol, syringol and para-substituted derivatives, carbohydrate fragments, polyols, organic acids, formaldehyde, acetaldehyde, furfuraldehyde, and other oligomeric products. The fraction containing phenolic and neutral components substituted for not only the phenol, but also some of the formaldehyde present in the fraction.

Giroux et al. [158] developed a technology called Rapid Thermal Processing [159] based on fast pyrolysis or rapid destructive distillation that enables one to obtain natural resins from a ligninic fraction of the liquid pitch produced, all without having to extract the phenol fraction using solvents. The total phenolic content obtained ranged from 30 to 80 wt.% and was considered highly reactive and suitable for use within resin formulations without requiring any further fractionation procedure. Resole-type resins were used in the production of oriented strand board and plywood, with similar results compared to fossil-based resins [154].

Vergopoulo-Markessini et al. [160] used a mixture of phenol compounds obtained from pyrolysis and cashew nut shell liquid. A synergistic effect between phenolic-based pyrolysis products and cashew nut shell liquid was noticed, which enabled the substitution of up to 80 wt.% of the phenolic component of a standard formaldehyde-based resin. Cashew nut shell liquid contains cardanol, a phenolic compound (Figure 15.17) that can be used to substitute phenol in novolac or resole resins. Cardanol—formaldehyde resins have shown improved flexibility due to an internal plasticization effect of the long chain and better processability. Additionally, hydrophobic behavior was noticed due to side chains, making the resin water-repellent and resistant to weathering [91].

Tannins are also polyphenolic compounds (Figure 15.15), with good reactivity towards formaldehyde. Tannins are composed mostly of flavan-3-ol units, for which two phenolic rings are joined together by a heterocyclic ring, as can be seen in Figure 15.33 [91]. The high reactivity of the tannin towards formaldehyde is due to the A-ring. In novolac resins, the presence of tannins enable
reactions with hexamine at lower temperatures, compared to fossil-based phenol formulations. However, the high reactivity and the large molecules of tannin can result in premature gelation, which leads to brittleness [91]. Pizzi et al. [161] developed polymers derived from the cross-linking of condensed tannins by polycondensation reactions with furfuryl alcohol and small amounts of formaldehyde. The addition of blowing agents created tannin-based rigid foams with fire resistance similar to synthetic phenolic foams.

Lignin has fewer reactive sites compared to petroleum-based phenol. More than half of the potentially reactive aromatic hydroxyl groups in kraft lignin, for example, are blocked by methyl groups, which hinders the aromatic hydroxyl group [162]. Sulfur-mediated demethylation can be used to remove methyl groups on the aromatic ring, thus increasing the reactivity. Methylolation or hydroxymethylolation can be used to introduce hydroxymethyl groups (—CH₂OH) to lignin molecules using formaldehyde in an alkaline medium. Methylolated lignin can be directly incorporated in phenol—formaldehyde resin, replacing part of the phenol, in wood adhesives compositions [155,162]. El-Mansouri et al. [163] replaced the formaldehyde in the methylolation process by glyoxal, a bio-based, non-toxic dialdehyde. The process was called glyoxalation.

Lignin can be treated with phenol in the presence of organic solvents such as methanol or ethanol in a process called phenolation or phenolysis [154]. The phenolation process is based on a thermal treatment of lignin with phenol in an acidic medium, which leads to the condensation of phenol with the aromatic ring of the lignin and side chains. A reduction of the molecular weight of the lignin is also observed, as a result of ester bond cleavage [162]. Cetin et al. [164,165] utilized phenolated-lignin (20—30% of overall phenol) instead of unmodified lignin in phenol—formaldehyde resins to achieve an improvement in mechanical and physical properties when utilized as wood adhesive in particleboard. Hu et al. [166] modified a foamed resole resin using phenolated lignosulfonate (lignin from the sulfite process) to achieve mechanical and physical properties similar to fossil-based phenol-formaldehyde foams. Perez et al. [167] synthesized two types of novolac resins based on lignin: (a) ammonium lignosulfonate, which was used directly, as filler, and (b) ammonium lignosulfonate modified by methylolation. Cheng et al. [168] obtained bio-oil from hydrothermal liquefaction of pine sawdust. The bio-oil obtained was methylolated with formaldehyde (Figure 15.34) in the presence of sodium hydroxide. The methylolated bio-oil was polymerized with formaldehyde, replacing up to 75 wt.% of phenol in the resin for the production of plywood. The methylolation treatment improved the thermal stability of the bio-based phenolic resin. Phenolation and methylolation have shown the best results in terms of number of reactive sites created. The origin of the lignin may affect the reactivity. Softwoods may yield more reactive phenolics than hardwoods due to the

![Figure 15.34 Methylolation reaction of bio-oil with formaldehyde [167].](image)

![Figure 15.35 Guaiacol and syringol chemical structures (in lignin) [154].](image)
relatively high presence of guaiacol with one methoxy group (Figure 15.35) [154].

Formaldehyde-containing resins (urea—formaldehyde, melamine—formaldehyde, and phenol—formaldehyde) for applications as wood adhesives and mineral fiber binders for thermal insulation are under intense pressure to reduce or eliminate formaldehyde content due to ecological concerns and toxicity issues [152]. There is a need to develop non-toxic, bio-based formaldehyde substitutes. Ramires et al. [169,170] utilized glyoxal (OCH$_2$CHO), a bio-based chemical obtained by the oxidation of lipids, a non-toxic and non-volatile dialdehyde that can be used as a substitute for formaldehyde in phenolic resins. Both resole and novolac resins based on glyoxal-phenol resins were developed for application in composite materials using sisal fibers as reinforcement, and showed improved results for novolac-type resins in terms of mechanical and physical properties. The novolac glyoxal-phenol composite showed higher impact strength (237 J m$^{-1}$) than the resole glyoxal-phenol composite (118 J m$^{-1}$), indicating a better fiber/matrix interaction. The novolac glyoxal-phenol composite exhibited a higher storage modulus (E’), and consequently was more rigid than the resole composite. In addition to glyoxal, oxazolidine, solid resole, epoxy, resorcinol, and tannins are being examined to substitute formaldehyde in phenolic resins [152].

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