Bio-based Thermosetting Polymers from Vegetable Oils

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ABSTRACT: Vegetable oils are promising renewable resources for polymers, due to their low cost, ready availability, and versatile applications. Recently, increasing attention has been paid to vegetable oil-based polymeric materials due to both economic and environmental concerns. This review focuses on the latest developments in vegetable oil-based thermosets prepared by a variety of polymerization methods. The thermosets obtained exhibit a wide range of thermomechanical properties from soft and flexible rubbers to rigid and hard plastics. Some of the thermosets have properties comparable to petroleum-based analogs and show promise as replacements, providing possible solutions to environmental and energy concerns.

1 INTRODUCTION

Plastics are divided into thermoplastics and thermosets according to their response to heat [1]. Compared to thermoplastics, thermosetting polymers are infusible and insoluble materials, because of the formation of a three-dimensional (3D) network during curing [2,3]. The main advantage of a thermoset over a thermoplastic is the variety of properties that can be easily tuned by simply adjusting the crosslink density of the thermoset network, without changing the polymers' chemical structure [2]. Nowadays, most commercially-available thermosets, such as phenolic resins and epoxies, are produced from petroleum sources, and the utilization of fossil fuels in the manufacture of plastics accounts for approximately 7% of worldwide oil and gas consumption [4]. The use of petroleum sources for plastics is limited by the continuous depletion of fossil oils, the increasing price of the oils, and environmental concerns [5]. Therefore, increasing efforts are being made by industrial and academic researchers to utilize renewable resources for the production of both chemicals and plastics [6].

A variety of renewable starting materials, like sugars and polysaccharides, vegetable oils, lignin, pine resin derivatives, and proteins, have been used to prepare polymeric materials [7,8]. Among these, vegetable oils, which are esters formed between glycerol and three fatty acids, are the most widely used renewable source in the chemical and polymer industries due to their inherent biodegradability, easy availability,

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low toxicity, and relatively low price [9]. It has been reported that 15% of vegetable oils have been used in the chemical industry from 2001 to 2005 [10]. Vegetable oils have been used as paints and coatings for thousands of years [11], because unsaturated oils oligomerize or polymerize to form crosslinked materials when exposed to the oxygen in air [12]. In recent years, vegetable oils have been used to produce biodiesel (fatty acid methyl esters), which can be used directly in conventional diesel engines [13]. Compared to diesel, biodiesel has advantages, including being degradable and non-toxic, releasing fewer emissions, and containing less sulfur [14].

Taking advantage of the functional groups in vegetable oils, namely the esters and carbon-carbon double bonds in the fatty acid chains, a variety of thermosets have been developed from vegetable oils [15]. The carbon-carbon double bonds can be polymerized by free-radical [16] or cationic [17] polymerizations to crosslink the triglycerides producing bio-based thermosets. The carbon-carbon double bonds in the fatty acid chains have also been conjugated to increase their reactivity and better thermosets can be obtained [18–20]. More reactive acrylate double bonds have also been grafted onto vegetable oil fatty acid chains; these acrylate groups can then be free radically polymerized to afford thermosets with good thermomechanical properties [21]. Carbon-carbon double bonds can also be easily converted to epoxy groups, which can be cured using a variety of chemicals to give bio-based thermosets [22]. Recently, the relatively new polymerization methods acyclic diene metathesis polymerization (ADMET) [23] and ring-opening metathesis polymerization (ROMP) [24] have been used to polymerize vegetable

oil-based monomers to produce thermosetting materials. Vegetable oil-based polyols have also been prepared to react with anhydrides [25], diacids [25] or diisocyanates [26] to give polyester or polyurethane thermosets.

Herein, we highlight the most recent advances in thermosets based on vegetable oils prepared by free radical, cationic, olefin metathesis, and step-growth polymerizations, epoxy curing reactions, and some other miscellaneous polymerization methods. Preparation of the monomers, crosslinking to form thermosets, and the structure-property relationships of the thermosets obtained are discussed in detail in the following sections. This review focuses primarily on work published in peer-reviewed journals, not the patent literature.

2 STRUCTURE AND PROPERTIES OF VEGETABLE OILS

In general, vegetable oils are triglycerides or triesters, consisting of three fatty acids condensed onto a glycerol unit. For any given vegetable oil, the triglycerides may contain a wide combination of fatty acid chains. The generic chemical representation of triglycerides is depicted in Scheme 1. The fatty acids differ from one another with respect to the length of the chains, the number and position of the carbon-carbon double bonds along those chains, and the presence and position of specific functional groups. The chemical structure of the most abundant fatty acids found in vegetable oils is shown in Scheme 2.
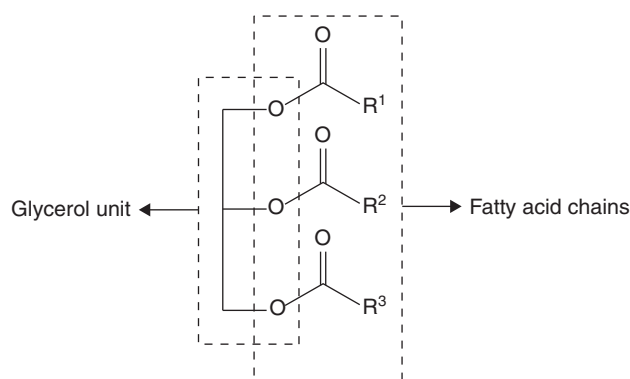
R^1, R^2, R^3 = distinct aliphatic hydrocarbon chains with varying length, number and position of carbon-carbon double bonds, and functional groups

Scheme 1 General chemical structure of vegetable oils.
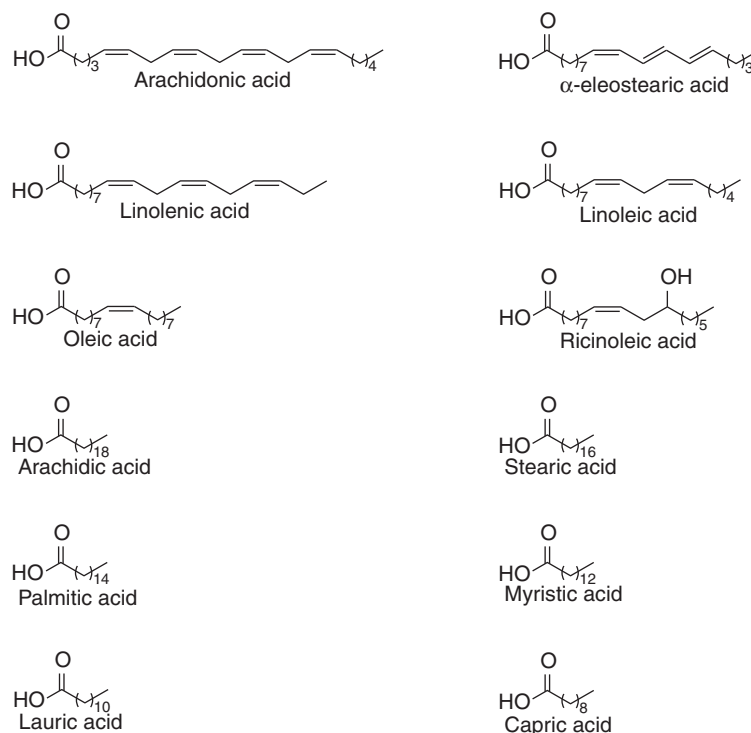
Scheme 2 Most common fatty acids present in vegetable oils and their chemical structure.

Because of the many possible combinations of fatty acids found naturally in the triglycerides of distinct vegetable oils, one needs to refer to the fatty acid composition of the various naturally-occurring oils. The fatty acid composition of any particular oil corresponds to the percentage of each fatty acid present in the collection of all of its triglycerides. Each distinct vegetable oil exhibits a distinct fatty acid composition, which is ultimately what defines the oil's physical and chemical properties. Intuitively, the fatty acid composition of distinct vegetable oils, and hence their properties, vary depending on the plants from which they are extracted, and their corresponding growing conditions [27]. Table 1 summarizes the fatty acid composition of the most widely used vegetable oils.

As can be seen from Scheme 2 and Table 1, naturally-occurring fatty acids contain an even number of carbon atoms, and most of the carbon-carbon double bonds present in the unsaturated fatty acids have a *cis* configuration and are non-conjugated. Overall, the reactivity of carbon-carbon double bonds in vegetable oils can be significantly increased upon conjugation [20]. For the remainder of this article, the term "conjugated oil" refers to oils in which all or the vast majority of the carbon-carbon double bonds are conjugated.

3 THERMOSETS FROM THE FREE RADICAL POLYMERIZATION OF VEGETABLE OILS

3.1 Non-modified Vegetable Oils

Very few reports of the preparation of bio-based resins using unmodified vegetable oils exist. This is possibly due to the low reactivity of regular vegetable oils. In the most popular application, highly unsaturated vegetable oils, also called drying oils, have been used in the paints and coatings industries for years. Such oils spontaneously auto-oxidize in the presence of the oxygen in air [28]. During auto-oxidation, the carbon-carbon double bonds in the oil self-polymerize to form a crosslinked network [16], following a free radical reaction pathway depicted in Scheme 3.

Without requiring any prior structural modification of the triglyceride structure, free-radical macro-initiators from linseed and soybean oils have been prepared and used to initiate the polymerization of methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA), resulting in grafted polyMMA and polyBMA copolymer thermosets [16,29]. Those materials are partially biodegradable and biocompatible due to the presence of vegetable oils, suggesting possible applications in tissue engineering [16,29].

Table 1 Fatty acid composition of most widely used vegetable oils.

Oil	Double bonds per triglyceride[a]	Linolenic acid ($C_{18:3}$) content (%)	Linoleic acid ($C_{18:2}$) content (%)	Oleic acid ($C_{18:1}$) content (%)	Stearic acid ($C_{18:0}$) content (%)	Palmitic acid ($C_{16:0}$) content (%)
Tung[b]	7.9	–	9	4	–	6
Linseed	6.6	57	15	19	4	6
Walnut	5.5	3	73	18	1	5
Low saturation soybean	5.0	9	57	31	1	3
Safflower	5.0	–	78	12	2	7
Sunflower	4.7	1	54	37	3	5
Soybean	4.6	8	53	23	4	11
Corn	4.5	1	60	25	2	11
Grapeseed	4.5	–	63	27	3	7
Canola	3.9	9	21	61	2	4
Sesame	3.9	1	43	41	6	9
Peanut	3.3	–	32	47	2	11
Olive	2.9	1	6	80	3	9
Castor[c]	2.7	1	4	5	1	2

[a]Average number of carbon-carbon double bonds per triglyceride.

[b]Approximately 84% of the fatty acid chains in tung oil are alpha-eleostearic acid, a naturally conjugated triene.

[c]Approximately 85% of the fatty acid chains in castor oil are ricinoleic acid.
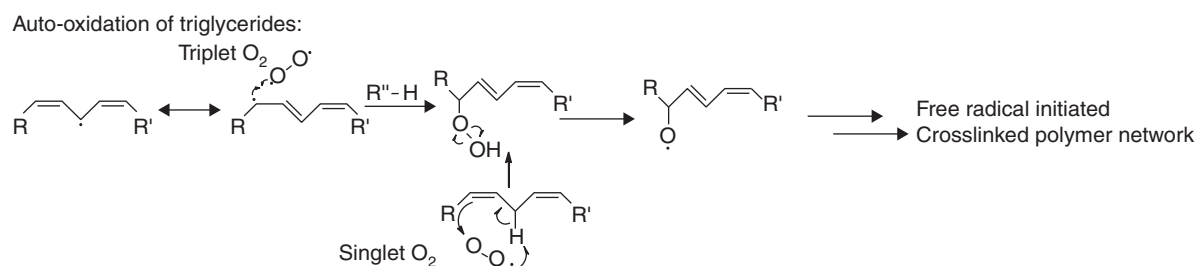
Scheme 3 Reaction mechanism for the auto-oxidation of vegetable oils in the presence of oxygen from air.

In an unrelated study, benzoyl peroxide was used as a free radical initiator for the preparation of rigid thermosets containing 30–65 wt.% of regular linseed oil, styrene (ST), and divinylbenzene (DVB). In these thermosets, an increase in the vegetable oil content typically causes an overall decrease in the mechanical properties [30].

3.2 Modified Vegetable Oils

The free radical copolymerization of vegetable oils with petroleum-based comonomers requires that the carbon-carbon double bonds in the oil be sufficiently reactive in order to form a homogeneous material. It is known that conjugated double bonds form lower energy transition states than non-conjugated systems during free radical polymerization. This is due to stabilization of the transition state through better charge distribution in the intermediates, which results in an overall lower activation energy for the process when compared to the reaction of non-conjugated species. In short, conjugated vegetable oils are more reactive than their non-conjugated counter parts, and constitute better starting materials for the preparation of bio-based free radical thermosets. The conjugation of a variety of vegetable oils can be easily achieved in the presence of a rhodium catalyst in processes well described in the literature [18,20,31,32].

Translucent vegetable oil-based thermosets have been obtained by the free radical copolymerization of conjugated triglycerides and vinyl co-monomers [19,33]. The bulk free radical copolymerization of mixtures containing 30–75 wt.% of conjugated linseed oil with various amounts of acrylonitrile (AN) and DVB, initiated by 1 wt.% of azobisisobutyronitrile (AIBN) creates materials ranging from flexible to rigid thermosets [33]. Although the materials exhibit promising thermo-physical and -mechanical properties, it has been shown that these properties tend to decrease with increasing vegetable oil content. Soxhlet extraction experiments also revealed that the percentage of unreacted oil after the thermoset is cured to its maximum extent ranges from 4 wt.% to 39 wt.%, depending on the resin composition [33].

Soybean oil-based thermosets have been prepared by the copolymerization of mixtures containing 40–85 wt.% of conjugated low saturation soybean oil (CLS) with various amounts of AN, DVB, and/or dicyclopentadiene (DCPD) in the presence of AIBN [19]. The copolymers obtained exhibit 100% incorporation of the CLS when the amount of oil initially added ranges from 40 wt.% to 65 wt.% for DCPD-containing thermosets [19]. This higher oil incorporation, whenever DCPD is part of the resin, relates to the similar reactivity of both components. Similar to previous observations, when the oil content exceeds 70 wt.%, a large amount of unreacted oil is recovered from the final thermoset after 24 hours of Soxhlet extraction with methylene chloride [19]. A wide range of thermal and mechanical properties can be obtained by simply changing the stoichiometry of the resin components.

Alternatively, the carbon-carbon double bonds in the fatty acid chains of the vegetable oils can be allowed to react so as to incorporate polymerizable functionalities, such as acrylates, that increase the reactivity of the vegetable oils. For example, acrylated epoxidized soybean oil (AESO) has been synthesized by the reaction of acrylic acid with epoxidized soybean oil [ESO] [21]. The reaction scheme for the synthesis of AESO from ESO is presented in Scheme 4.

AESO can be copolymerized with ST to create thermosets with useful structural properties [34,35]. The polymer properties can be controlled by changing the acrylate level of the triglyceride and by varying the amount of ST. Recently, AESO was used to produce thermosetting foams with a high bio-based content. The cured foam's density was controlled by employing a partial vacuum before gelation and the resulting mechanical properties were comparable to those of semi-rigid industrial foams [36]. Besides soybean oil, acrylated epoxidized methyl oleate has been prepared in a similar manner and used in the preparation of a bio-based polymer by free radical emulsion polymerization [37]. The resulting polymer exhibits properties that may be of considerable interest for pressure-sensitive adhesive applications [37].

AESO contains both residual unreacted epoxy groups and newly formed hydroxyl groups, both of
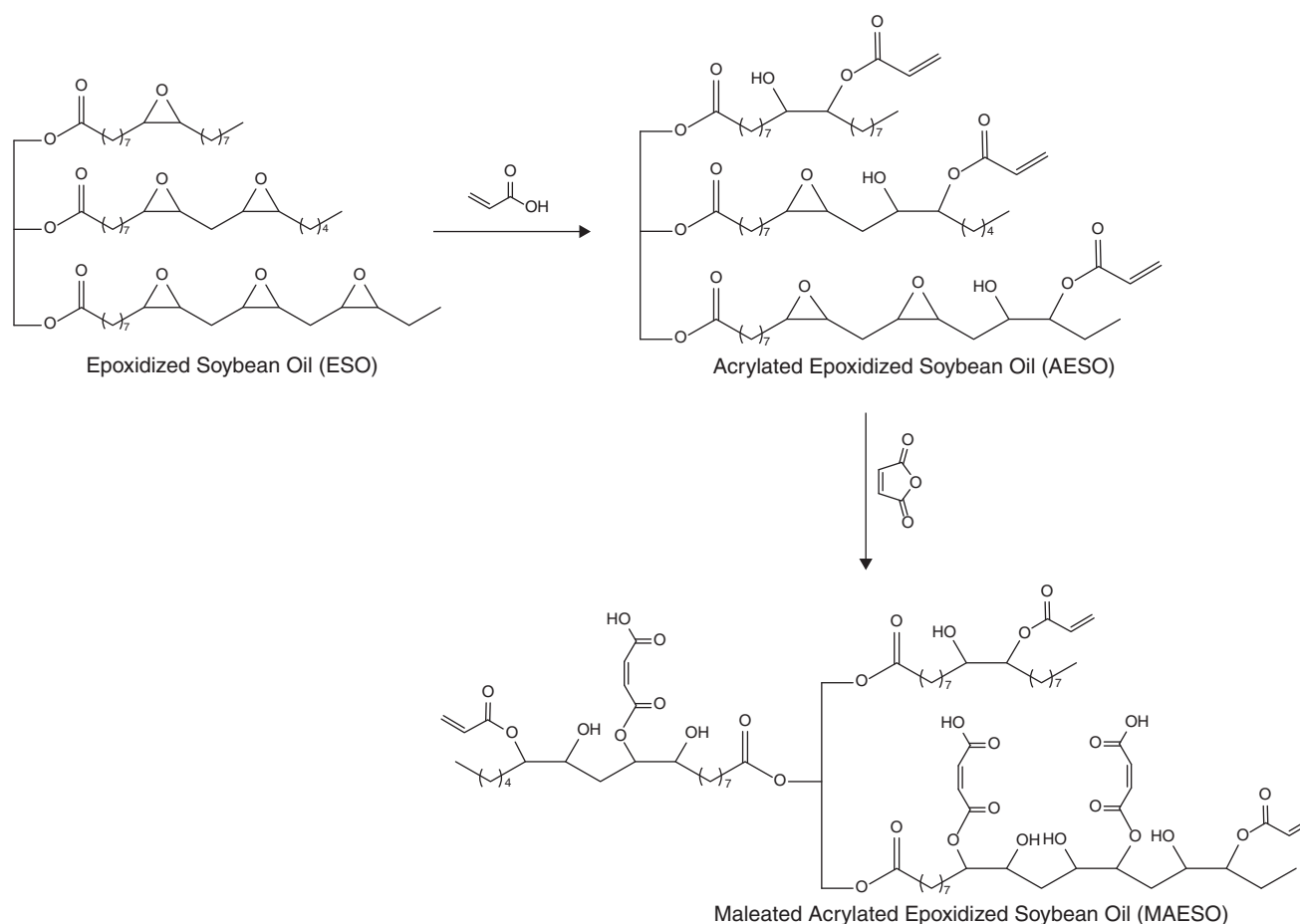
Scheme 4 Modifications of epoxidized soybean oil (ESO) to produce acrylated epoxidized soybean oil (AESO), and maleated acrylated epoxidized soybean oil (MAESO).

which can be used to further modify the triglyceride. Maleated epoxidized soybean oil (MAESO) is obtained by the reaction of AESO with maleic anhydride (MA), as depicted in Scheme 4. The copolymerization of MAESO and ST results in thermosets with higher crosslink densities, T_g's, and storage moduli than the corresponding AESO-based thermosets [21,37].

An alternate route for the preparation of acrylated triglycerides involves the oxidation of unsaturated vegetable oils with singlet oxygen to form hydroperoxides by a pathway similar to the one described for the auto-oxidation of vegetable oils. The hydroperoxides can be converted into secondary allylic alcohols, which can then be further reduced to saturated alcohols [38,39]. Both the saturated and the unsaturated alcohols are easily functionalized with acrylate groups. The acrylated triglycerides can be free radically polymerized in the presence of varying amounts of pentaerythritol tetraacrylate, providing a promising route to bio-based polymeric networks. These polymers show properties similar to those of other reported acrylated triglyceride-based materials [40].

Besides modification and functionalization of the carbon-carbon double bonds, structural changes involving the triglyceride ester groups is another promising approach for the preparation of reactive bio-based monomers. Along those lines, a series of rigid thermosets have been developed by the copolymerization of vegetable oil monoglyceride maleates with ST [41,42]. Scheme 5 shows the steps involved in preparation of the soybean oil monoglyceride (SOMG) maleate half esters. Bulk copolymerization of the SOMG maleates with 35 wt.% ST gives a rigid thermoset polymer with a T_g of approximately 135 °C and a storage modulus of 0.92 GPa at 35 °C [43]. In order to improve the properties of the SOMG maleate-ST polymers, neopentyl glycol (NPG) and bisphenol A (BPA) have been mixed with SOMG prior to being maleinized [43]. Similar materials have been prepared from linseed oil, leading to linseed oil monoglycerides (LOMGs), that have been copolymerized with 20–80 wt.% of ST [44].

When the same process was applied to castor oil, an overall increase in the modulus and the strength of the
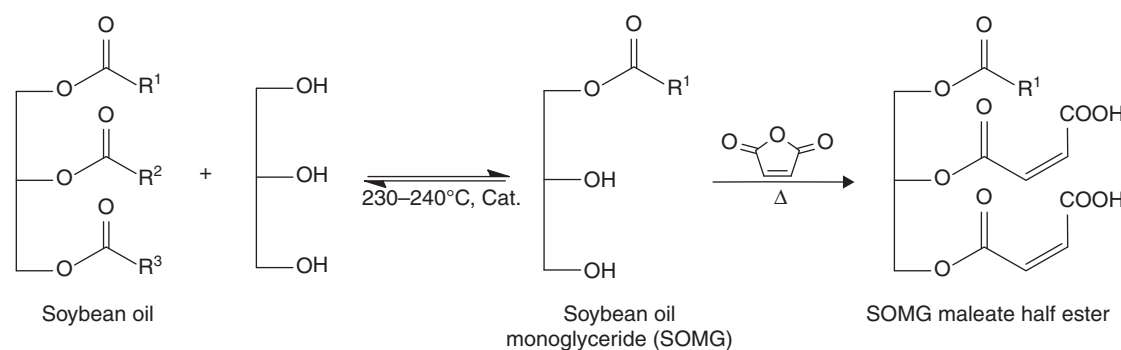
Scheme 5 Stepwise synthesis of vegetable oil monoglyceride (SOMG) maleate half esters from soybean oil.

resulting polymers was obtained. The fatty acid chains in this case also formed maleates and crosslinked, rather than just functioning as a plasticizer in the system [45,46]. The castor oil-based thermosets prepared in this fashion exhibit significantly improved properties compared to the soybean oil-based polymers [45].

3.3 Thermal Polymerization of Vegetable Oils

With an average of 9.0 naturally conjugated carbon-carbon double bonds per triglyceride (84% of α-eleostearic acid), tung oil (TUN) is very reactive and can readily polymerize under mild reaction conditions. Copolymers containing 0.1–2.0% of tung oil and ST can be easily obtained by heating the materials to 125 °C for 3 days [47]. More recently, a series of copolymers of TUN, ST, and DVB, containing 30–70 wt.% of the oil, have been prepared by thermal polymerization at temperatures ranging from 85 °C to 160 °C [48]. The materials obtained range from elastomeric to tough and rigid thermosets, with glass transition temperatures in the range of −2 °C to +116 °C, and crosslink densities ranging from 1.0×10^3 to 2.5×10^4 mol/m^3 [48]. The addition of catalytic amounts of Co, Ca, and Zr salts accelerates the thermal copolymerization process and improves the properties of the resulting thermosets [48].

Similar materials have been prepared using 30–70 wt.% of conjugated linseed oil (CLO), in which 87% of the carbon-carbon double bonds were conjugated [49]. The material properties could be varied by simply adjusting the resin stoichiometry [49]. The use of a less reactive oil compared to TUN resulted in a microphase separation into an oil-rich and a DVB-rich phase [49]. Scanning electron microscopy (SEM) and proton nuclear magnetic resonance spectroscopic (1H NMR) results revealed the presence of soluble components in the final polymer matrix, consisting mainly of unreacted oil. These components were well distributed throughout the material, and left evenly spaced

nanopores after Soxhlet extraction with methylene chloride for 24 hours [49]. As observed for the TUN-based thermally produced thermosets, [48] the use of catalytic amounts of cobalt salts during the cure of the CLO-based resins resulted in an increase in the crosslink density [50].

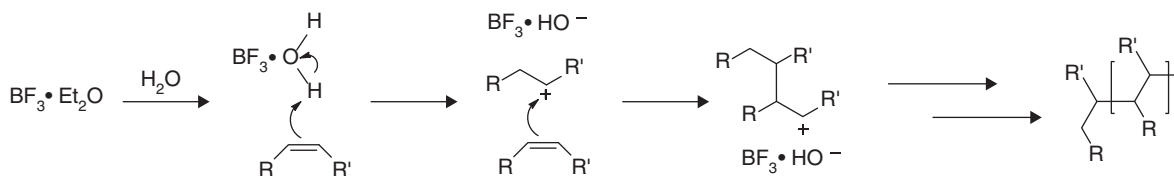## 4 THERMOSETS FROM THE CATIONIC POLYMERIZATION OF VEGETABLE OILS

4.1 Polymerization of the Carbon-Carbon Double Bonds

Besides the previously described free radical polymerization of the carbon-carbon double bonds present in vegetable oils, the cationic polymerization of triglycerides in the presence of petroleum-derived comonomers also yields thermosetting materials with a range of properties depending on the resin composition. The use of strong Lewis acids as initiators in the polymerization process avoids the entrapment of bubbles in the cured system, usually seen when free radical polymerization is employed, especially in the presence of AIBN. The cationic polymerization also limits crack formation related to shrinkage of the resin upon cure [6,17].

Scheme 6 illustrates the mechanism for the cationic polymerization of a simple olefin initiated by boron trifluoride dietherate (BFE). Because each unsaturated fatty acid chain in the triglyceride can participate in the cationic reaction, a three-dimensional crosslinked polymer network is formed.

As in the free radical polymerization process, very strong materials with room temperature storage moduli of approximately 2 GPa can be obtained by the cationic copolymerization of 50–55 wt.% of tung oil with DVB [51]. The gel time of these resins can be controlled by substituting up to 25 wt.% of TUN with oils having a lower degree of unsaturation, such as soybean oil

Cationic polymerization mechanism:

Scheme 6 Reaction mechanism for the cationic polymerization of simple olefins, initiated by boron trifluoride etherate.

(SOY), low saturation soybean oil (LSS), or CLS [51]. Similarly, mixtures containing 35–55 wt.% of regular corn oil (COR) or conjugated corn oil (CCO) with various amounts of DVB and ST afford polymeric materials with a range of mechanical properties [52]. An exponential increase in gel time is observed with increasing amounts of oil [52]. As expected, the gel times for resins containing conjugated oils are significantly shorter than for resins made from regular vegetable oils [52]. The cure temperatures also affect the gel time of the cationic resins. For example, when a resin containing 45 wt.% of COR, 32 wt.% of ST, 15 wt.% of DVB, and 8 wt.% of BFE initiator is cured at room temperature, the gel time observed is 116 minutes. At 15 °C, the same resin takes longer than 24 hours to completely gel [52]. Recently, the cationic polymerization of soybean oil, ST, and DVB with 4-vinylphenyl boronic acid [53] or 4-trimethylsilylstyrene [54] has afforded boron- and silicon-containing thermosets with flame retardant properties.

Extensive research has been conducted on the cationic copolymerization of SOY, LSS, and CLS with various petroleum-derived crosslinking agents. When 50–60 wt.% of SOY, LSS, or CLS are copolymerized with DVB, a densely crosslinked polymer network, interpenetrated by 12–31 wt.% of unreacted free oil or oligomers, is produced [55]. Poor miscibility between the oil and the BFE initiator results in micro-phase separation in the SOY- and LSS-based copolymers, with distinctly different crosslink densities in different parts of the bulk copolymer [55]. Modification of the BFE initiator with less reactive oils helps in the formation of more homogeneous materials, as well as in the conversion of vegetable oils into crosslinked thermosets [55]. The unreacted free oil or oligomers present in the final copolymers significantly affect the thermal stability of the thermosets. CLS polymers have the highest storage moduli and thermal stabilities, because they contain the least amount of unreacted free oil [55].

In order to increase the structural uniformity of crosslinked copolymers, ST has been added as a comonomer to the original composition of vegetable oil-based thermosetting resins [56]. With the substitution of 25–50 wt.% of DVB by ST, the overall properties of the resulting plastics are significantly improved [56]. When different crosslinking agents have been evaluated (norbornadiene, DCPD, and DVB), it was found that DVB exhibits the highest reactivity and thus gives the most promising crosslinked materials with good damping and shape memory properties. [57] An isothermal cure study of vegetable oil-based systems established that the ideal cure temperature is in the range of 12–66 °C, depending on the actual composition of the resin, while a DSC study revealed that the optimum concentration of the Lewis acid is 2 wt.% [48,58].

A study of the cationic copolymerization of regular and conjugated soybean oil (CSO) with DCPD in the presence of modified BFE indicated that the commonly used fish oil ethyl ester modifier is unnecessary when the polymerization involves the more reactive CSO [20]. A variety of other vegetable oils, including olive, peanut, sesame, canola, grapeseed, sunflower, safflower, walnut, and linseed oils have been cationically copolymerized with DVB and/or ST to form a range of thermosets with properties that can be tailored according to the desired applications [17]. Overall, the properties of the thermosets gradually increase with the number of carbon-carbon double bonds present in the oil [17]. However, it was found that the gel times of these copolymers are independent of the reactivity of the vegetable oil used [17]. A comparison of the tensile properties of bioplastics made by the cationic copolymerization of various vegetable oils in the presence of DVB is presented in Table 2.

More recently, Dilulin (the product of the Diels-Alder reaction of linseed oil with cyclopentadiene) and ML189 (the product of an "ene" reaction between linseed oil and cyclopentadiene) have been copolymerized with DCPD under cationic conditions [59]. The structures of Dilulin and ML189 are represented in Scheme 7. Owing to the similar reactivity of DCPD and the modified oils, uniform bio-based thermosets have been obtained from these cationic polymerizations [59]. As observed with SOY, LSS, and CLS [55,56], the Dilulin/DCPD and ML189/DCPD thermosets exhibit mechanical properties that increase with the amount of DCPD in the resin.

Table 2 Tensile properties of bioplastics made by the cationic polymerization of various vegetable oils.

Oil (wt%)	DVB (wt%)	Young's modulus (GPa)	Tensile strength (MPa)
Corn oil (45)[a]	15	0.05	4.6
Conjugated corn oil (45)[a]	15	0.07	7.0
Soybean oil (62)[b]	30	0.05	2.5
Olive oil (62)[c]	30	0.03	1.2
Peanut oil (62)[c]	30	0.04	1.7
Sesame oil (62)[c]	30	0.04	2.2
Canola oil (62)[c]	30	0.04	1.7
Linseed oil (62)[c]	30	0.10	5.6
Grapeseed oil (62)[c]	30	0.05	3.0
Sunflower oil (62)[c]	30	0.05	3.0
Safflower oil (62)[c]	30	0.06	3.1
Walnut oil (62)[c]	30	0.06	3.8

[a](Li and Hasjim, 2003)
[b](Li and Larock, 2001)
[c](Andjelkovic, 2005)
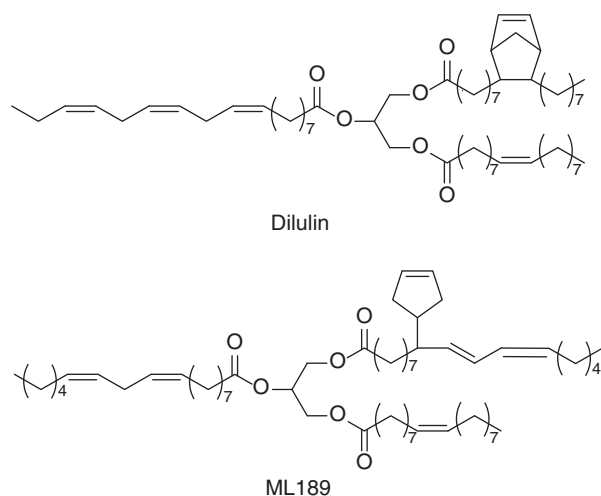
Dilulin

ML189

Scheme 7 Chemical structures of Dilulin and ML189.

## 4.2 Polymerization of Epoxidized Vegetable Oils

Latent initiators, such as benzylpyrazinium salts, enable controlled polymerizations. In fact, the activity of pyrazinium salts can be controlled by electronic modifications on the benzyl and pyrazine groups [60]. Latent cationic initiators are chemical compounds that are only activated under special conditions, such as heating or photoirradiation [60]. Epoxidized soybean and castor oils have been cationically polymerized in the presence of the latent initiator *N*-benzylpyrazinium hexafluoroantimonate [61]. Scheme 8 shows the general chemical scheme for such polymerizations using pyrazinium salts and their activation mechanism upon heating.

Cationic resins prepared from epoxidized castor oil (ECO) have been found to have higher T_g's and lower coefficients of thermal expansion than analogous resins prepared from epoxidized soybean oil (ESO). This is the result of increased intermolecular interactions in the ECO-based system when compared to the ESO-based polymer. [61] ESO and ECO have also been copolymerized with the diglycidyl ether of bisphenol A to give polymers with better mechanical properties [62,63]. For example, a copolymer containing 10 wt.% of ECO affords an epoxy resin with better interfacial mechanical properties. The addition of a large amount of soft segments to the ECO polymer results in a decrease in the crosslink density and an increase in the toughness of the final copolymer [61].

5 VEGETABLE OIL-BASED THERMOSETS FROM OLEFIN METATHESIS POLYMERIZATION

Since the discovery of the olefin metathesis reaction in 1964 [64], it has become more and more important in both organic and polymer chemistry. It is believed that the reaction occurs through a metallacyclobutane intermediate formed between and olefin and a metal alkylidene [65] (Scheme 9). Heterogeneous catalysts using transition metal oxides, such as Re_2O_7/Al_2O_3, MoO_3/Al_2O_3, and WO_3/SiO_2, with the advantage of easy separation and regeneration, have been used to effect the metathesis reaction in the early years [66]. However, reactions using these catalysts were hard to initiate and control, because very little of the active species
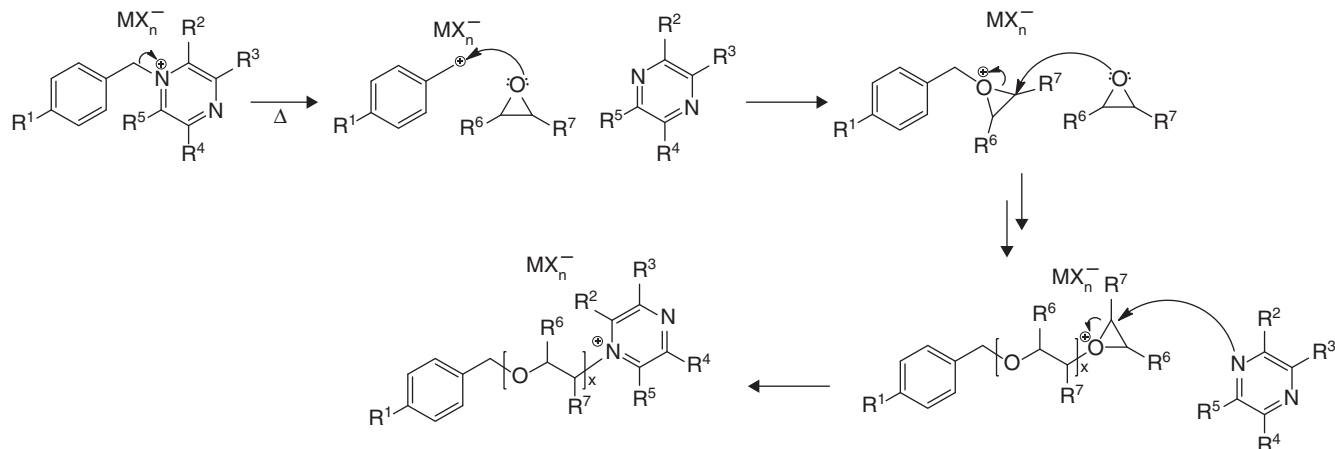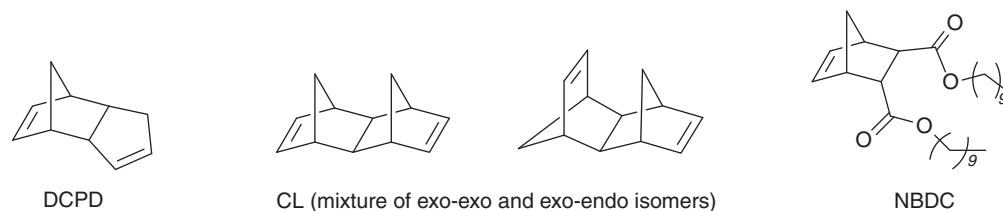
Where: $MX_n^- = SbF_6^-, PF_6^-, AsF_6^-, BF_4^-$

Scheme 8 Thermal activation, and cationic polymerization mechanism of pyrazinium salts.

Scheme 9 Mechanism of olefin metathesis.

DCPD

CL (mixture of exo-exo and exo-endo isomers)

NBDC

Scheme 10 Structures of DCPD and crosslinker (CL).

was formed in the catalyst mixture [67]. Furthermore, these early catalysts exhibited limited activity for the metathesis of certain functionalized olefins [66]. Later on, homogeneous catalysts, such as $WCl_6/(CH_3)_4Sn$ and $WOCl_4/(CH_3)_4Sn$, were developed and have been used to effect the metathesis of vegetable oil-based derivatives containing functional groups [68,69]. These homogeneous catalysts are cheap and can be prepared easily, but functional groups affect their efficiency significantly [66]. Recently, highly reactive metal alkylidene (carbene) complexes of a transition metal, including Ru, Mo, and W, have been developed [70–72]. Among these catalysts, well-defined ruthenium alkylidenes, such as $(Cy_3P)_2Cl_2Ru=CHPh$ [1st generation Grubbs catalyst (G1)], [70] can tolerate most important functional groups and are also stable to air and moisture. These catalysts dramatically facilitate olefin metathesis [67]. With the major advantages of these Grubbs catalysts, vegetable oil-based thermosets have been successfully prepared by ring-opening metathesis polymerization (ROMP) and acyclic diene

metathesis (ADMET) polymerization, which are discussed below.

5.1 Vegetable Oil-based Thermosets Prepared by ROMP

Monomers suitable for ROMP generally bear appended strained rings, such as norbornene groups. Dilulin, a commercially available norbornenyl-functionalized linseed oil (Scheme 7), has been copolymerized with dicyclopentadiene (DCPD) [73–75] and a bicyclic norbornene-based crosslinking agent (CL) (Scheme 10), [76,77] respectively. The thermosets obtained exhibit phase separations due to the large reactivity difference between Dilulin and the petroleum-based co-monomers. Increasing the amount of Dilulin results in lower glass transition temperatures, decreased thermal stabilities, and reduced mechanical properties. A cure experiment involving Dilulin and CL revealed that the rate of cure increases and the gel time decreases with an increasing CL loading, but the activation energy of the

cure does not vary systematically with the amount of CL [76]. A tandem cationic polymerization and ROMP between Dilulin and didecyl 5-norbornene-*endo*-2,3-dicarboxylate (NBDC) (Scheme 10) has resulted in rubbery thermosets with tensile test behavior ranging from relatively brittle (18% elongation) to moderately flexible (52% elongation) [78]. Increasing the loading of the NBDC decreases both the tensile stress and thermal stability of the thermosets.

Besides using Dilulin, a variety of chemical modifications have been used to introduce such strained rings into vegetable oils. Castor oil, where approximately 90% of the fatty acid chains bear hydroxyl groups, has been reacted with a commercially available bicyclic anhydride, bicycle [2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, to afford a norbornenyl-functionalized bicyclic castor oil derivative (BCO) (Scheme 11a) [79]. Thermosets have been prepared by copolymerizing BCO (55 to 85 wt%) with cyclooctene using 0.5 wt% of the 2nd generation Grubbs catalyst (G2). The glass transition temperature of these thermosets ranges from 1 to −14 °C, well below ambient temperature. It is observed that neat BCO does not undergo ROMP unless a certain amount of cyclooctene is present, because of the high viscosity of the BCO monomer, which results from the strong hydrogen bonding between the free carboxylic acids in the monomer [79]. Besides castor oil, fatty alcohols derived from soybean oil, Dilulin, ML189, and castor oil have also been reacted with the bicyclic anhydride to afford the corresponding norbornenyl-functionalized monomers, NMSA, NMDA, NMMA, and NMCA, respectively (Scheme 11b) [80].

Homogeneous thermosets have been obtained by polymerizing these monomers using 0.5 wt% of G2. The different groups appended to the fatty acid chains affect both the propagation process and the final thermosets properties. Compared to polyNMSA, polyNMDA and polyNMMA exhibit higher thermal stabilities and better mechanical properties due to the incorporation of side chains into the polymer matrix. The high viscosity of the monomers caused by the strong hydrogen bonding of the free carboxylic acids affects the properties of the thermosets as well [80].

Recently, novel castor oil-based ROMP monomers without free carboxylic acid groups, norbornenyl-functionalized castor oil (NCO) and norbornenyl-functionalized castor fatty alcohol (NCA), have been developed by reacting castor oil and the corresponding reduced fatty alcohol with norbornene carbonyl chloride (Scheme 12) [24]. The ROMP of different ratios of NCO/NCA using only 0.125 wt% of G2 results in rubbery to rigid biorenewable thermosets with crosslink densities ranging from 318 to 6028 mol/m^3. The increased crosslink densities enhance the thermomechanical properties and thermal stabilities of the thermosets obtained.

5.2 Vegetable Oil-based Thermosets Prepared by ADMET

ADMET polymerization has been applied to soybean oil using G1 as the catalyst to produce polymeric materials ranging from sticky oils to rubbers. [81,82] The polymerization proceeds in the absence of solvent
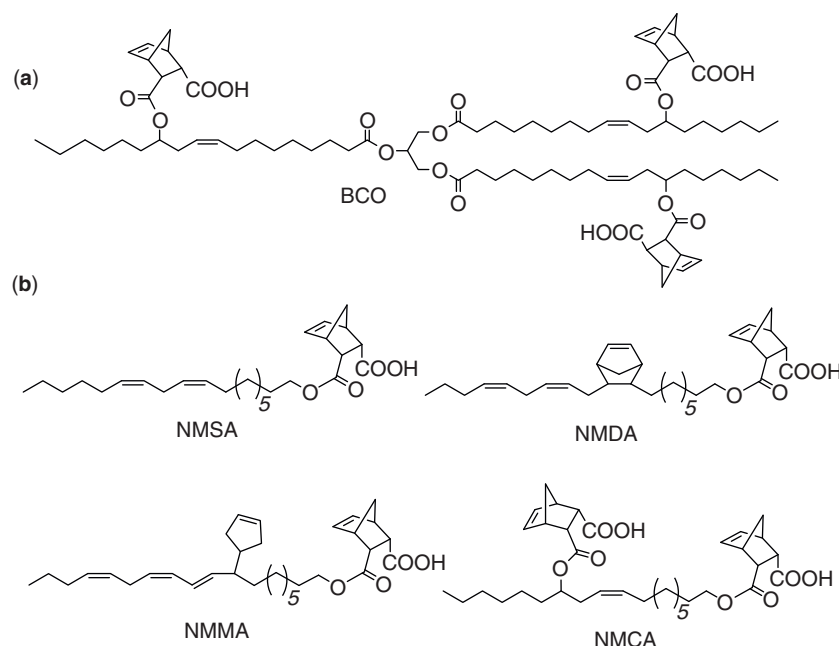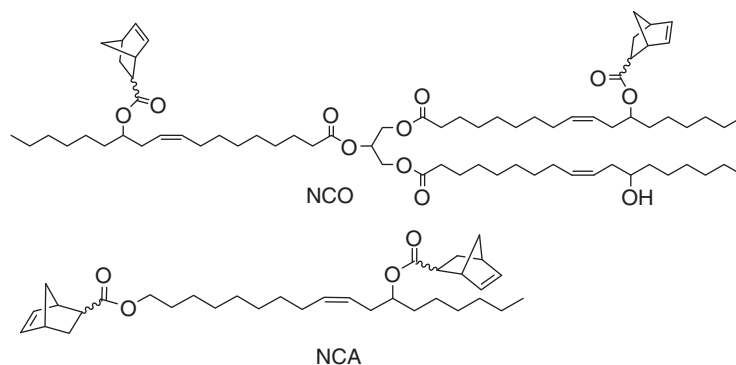

Scheme 11 Vegetable oil-based monomers for ROMP: (a) bicyclic castor oil derivative (BCO);[79] and (b) norbornene-functionalized fatty alcohols derived from soybean oil (NMSA), Dilulin (NMDA), ML189 (NMMA) and castor oil (NMCA) [80].

with a very low catalyst loading (0.1 mole%) under moderate temperatures and low pressures. Acyclic triene metathesis (ATMET) polymerization of a castor oil-based triene, glyceryl triundec-10-enoate, gives branched macromolecules by a simple one step, one pot procedure [83]. The molecular weight of the resulting polymer can be tuned by adjusting the ratio of the triene and a chain stopper, methyl acrylate (MA). High oleic sunflower oil with internal carbon-carbon double bonds has also been polymerized by ATMET polymerization using a 2nd generation Hoveyda-Grubbs catalyst to afford highly branched and functionalized polyesters [23]. The crosslinking was controlled by employing different loadings of MA. No crosslinking was observed for high oleic sunflower oil with the 1st generation Grubbs catalyst. A soybean oil-based monomer for ADMET polymerization (SESO) has been prepared by reacting epoxidized soybean oil (ESO) with 4-vinylbenzene sulfonic acid (4VBSA) (Scheme 13) [84]. ADMET polymerization of SESO with the 2nd generation Hoveyda-Grubbs catalyst with and without solvent gave approximately an 80% yield

of a thermosetting polymer. These new triglyceride-based benzene sulfonate polymers are rigid, non-hygroscopic polymers at room temperature. However, the hydrolytic stability of the polymer is low and fast hydrolysis occurs at 60 °C. Therefore, these new thermosets may find applications where heat and moisture triggered decomposition of a rigid plastic sample is needed [84].

The ADMET polymerization of a castor oil-based diene, 1,3-di-10-undecenoxy-2-propanol, with 10-undecenol as a renewable comonomer to end-cap the polymer chains (Scheme 14a) provides a polyol potentially useful for the preparation of polyurethane thermosets [85]. Furthermore, the ATMET polymerization of glyceryl triundec-10-enoate, using 10-undecenol to end-cap the polymer chains, affords castor oil-derived branched polyols (Scheme 14b) [86]. These polyols have also been reacted with 4,4'-methylenebis(phenyl isocyanate) (MDI) to prepare polyurethane thermosets. Interestingly, both the polyurethane thermosets prepared from the above two methods show good shape memory properties [85,86].
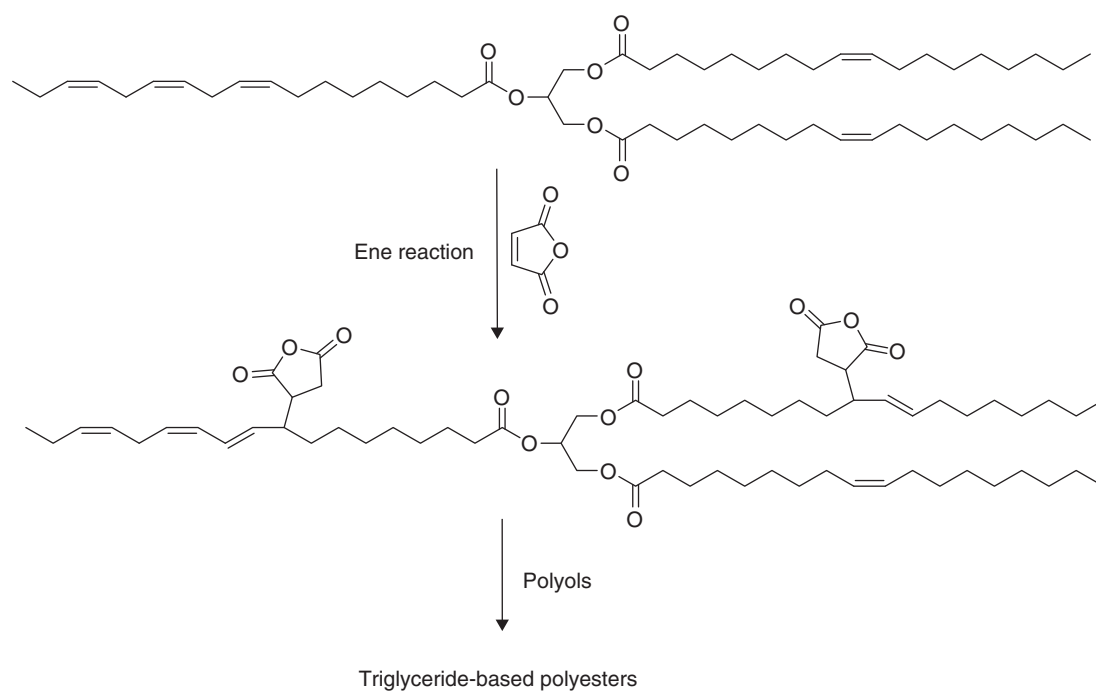

Scheme 12 Structures of NCO and NCA [24].
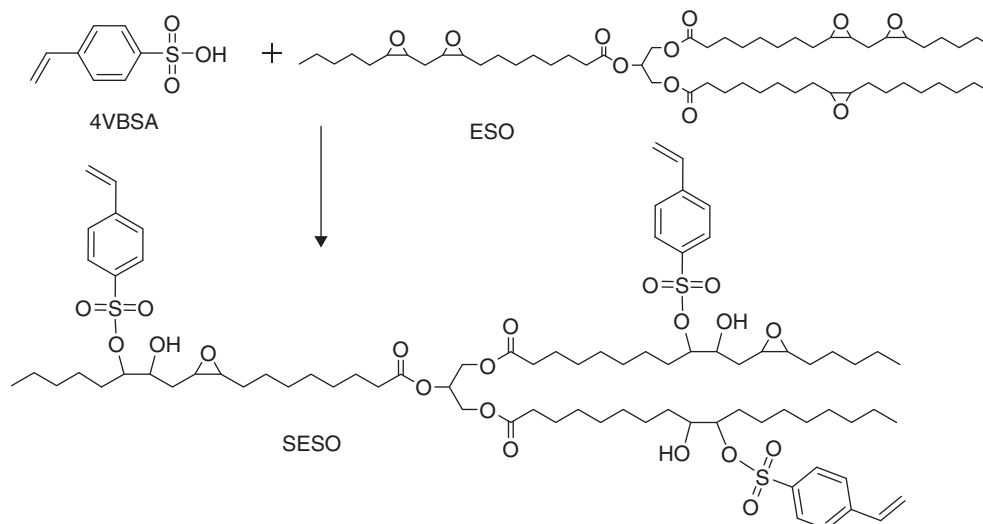
Scheme 13 Structure of soybean oil-based monomer (SESO) for ADMET [84].

Scheme 14 Vegetable oil-based polyols prepared from ADMET [85–87].

Vegetable oil-based phosphorus-containing polyols have also been prepared (Scheme 14c) [87]. Acrylate groups can be further connected to these polyols and thermosets containing phosphorus, which show good thermal stability and good flame retardancy, can be obtained after radical crosslinking [87].

6 VEGETABLE OIL-BASED THERMOSETS FROM STEP-GROWTH POLYMERIZATION

6.1 Vegetable Oil-based Polyesters/Polyamides

Vegetable oils with their internal carbon-carbon double bonds and inherent triglyceride ester groups can be easily functionalized and polymerized to provide polyester materials [88,89]. Oil collected from Nahar seeds has been reacted with glycerol to prepare polyols, which have been further reacted with acid anhydrides to afford polyesters [25]. These polyesters with interesting properties, like high resistance to dilute HCl acid, distilled water, and NaCl salt solution, may find applications in surface coatings and composite binders [25]. Soybean oil triglycerides have been reacted with maleic anhydride using an ene reaction to introduce maleate residues into the triglyceride structures (Scheme 15) [90]. The soybean oil-based anhydrides have been reacted with several different kinds of polyols to provide a variety of polyester thermosets. It has been observed that succinic anhydride groups on the triglyceride are less reactive than maleic anhydride toward polyols [90].

Vegetable oil-based polyesters with residual hydroxyl or carboxylic acid functional groups can be further reacted with other kinds of polymers. Polyester

Scheme 15 Polyester formed between a vegetable oil-based anhydride and polyols [90].

triols prepared by the transesterification of methyl esters of ricinoleic acid with trimethylol propane have been reacted with MDI to afford polyurethane thermosets [91]. These flexible thermosets display low glass transitions and have mechanical properties comparable to those of petrochemical polyurethanes, except for lower shore A hardness values [91]. Epoxy resins with residual epoxy groups have been reacted with vegetable oil-based hyperbranched polyesters in the presence of a poly(amido amine) [92,93]. Employing these highly branched polyesters, relatively hyperbranched epoxy thermosets have been modified to afford tough and flexible thermosets [92]. Due to the low viscosity of the vegetable oil-based polyesters, they can act as reactive diluents for epoxy resins, which results in paints with high solid content and low volatile organic compound (VOC) emissions. These paints may find applications in the automotive and wood industries [93].

Taking advantage of the carbon-carbon double bonds in oleic acid, vegetable oil-based polyesters have been prepared from oleic acid, glycerol and phthalic anhydride through free-radical copolymerization with methyl methacrylate (MMA) [94]. An increased MMA loading led to faster polymerization rates, higher molecular weights and higher glass transition temperatures. All of the coatings obtained exhibit excellent adhesion properties, while coatings with more MMA show better water and alkali resistance [94]. Incorporation of small amounts of an organo-nanoclay significantly improves the thermomechanical and biodegradation

properties of vegetable oil-based polyesters [95]. Silver nanoparticles have also been embedded in these materials to introduce antimicrobial properties into the vegetable oil-based polyesters [96].

Similar to vegetable oil-based polyesters, vegetable oil-based polyamides have been prepared as well. A linseed oil fatty amide diol has been reacted with ethylenediaminetetraacetic acid (EDTA) to form a polyesteramide, which was further cured with poly(styrene co-maleic anhydride) (SMA) to give an ambient cured polyesteramide [97]. The polyesteramide with 45 phr (parts per hundred parts of resin) of SMA showed the best corrosion resistance and the best physico-mechanical properties [97]. Copolyamides from soybean oil have been synthesized by the condensation polymerization of soybean oil-based dimer acids, diamines and amino acids [98]. The type and the content of the amino acids affected the chain structure and crystalline morphology of the final polyamides, but the incorporation of amino acids did not enhance their biodegradation [98].
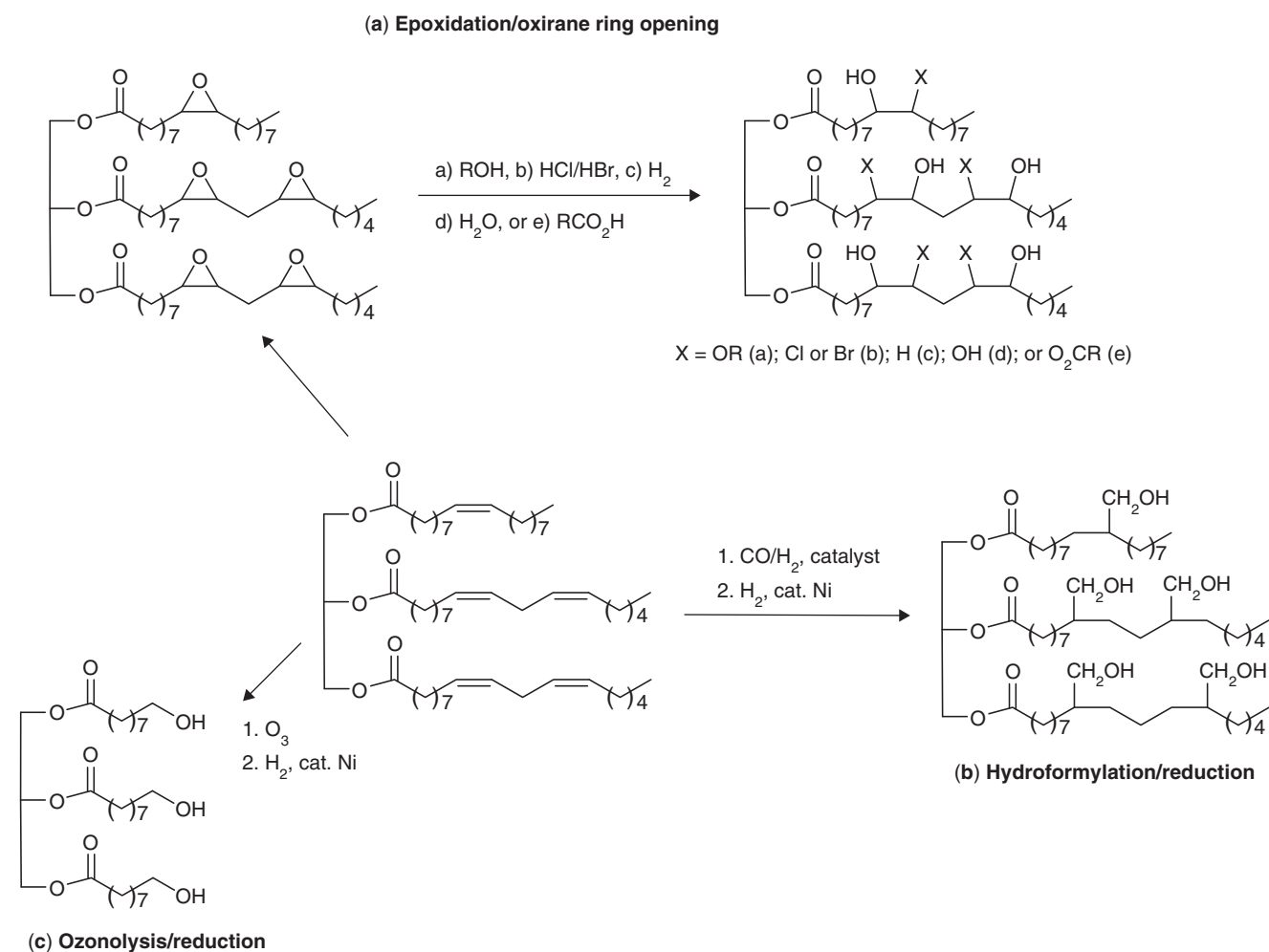
6.2 Vegetable Oil-based Polyurethanes

Castor oil, a naturally occurring plant oil with approximately 90% of the fatty acid chains bearing hydroxyl groups [99], has been used directly for polyurethane synthesis [100]. Polyurethane thermosets have been prepared by reacting castor oil with three different diisocyanates, toluene diisocyanate (TDI), isophorone

diisocyanate (IPDI) and hexamethylene diisocyanate (HDI), using dibutyltin dilaurate (DBTDL) as a catalyst [101]. All of the polyurethanes show good thermal stabilities, while the degree of swelling and thermomechanical properties are greatly affected by the nature of the diisocyanate [101]. Polyols from blending castor oil and poly(ethylene glycol) (PEG) have been used to synthesize biodegradable polyurethanes as potential candidates for biomedical implants and tissue engineering [102]. It has been observed that increasing the PEG-based polyurethane prepolymer content causes an increase in both the mechanical properties and the hydrolytic degradation. These materials also showed nontoxic behavior and good cytocompatibility when evaluated using L-929 fibroblast cells [102]. Castor oil has been transesterified with triethanolamine or glycerin to increase its hydroxyl functionality [103]. These polyols with high hydroxyl numbers have been used to prepare rigid vegetable oil foams with an apparent density of 50 ± 1 kg/m^3 and a compression strength around 200 kPa. Other than castor oil,

transesterification/transamidation reactions using other vegetable oils have also yielded a variety of polyols useful for polyurethane thermosets [103–105].

The carbon-carbon double bonds in vegetable oils can also be modified to append hydroxyl groups to the fatty acid chains. According to Scheme 16a, the ring-opening of epoxidized vegetable oils with a variety of chemicals gives different kinds of polyols for PU synthesis [100]. Polyols from mid-oleic sunflower, canola, soybean, sunflower, corn, and linseed oils have been prepared by the ring-opening of epoxidized vegetable oils with methanol [26]. Polyols from linseed oil give polyurethanes with the highest crosslink densities and best mechanical properties, while the polyol from mid-oleic sunflower oil gives a soft polyurethane with the lowest glass transition temperature and strength. The different polyurethane properties mainly result from different crosslink densities and less from the position of the reactive sites in the fatty acid chains [26]. The hydrogenation of epoxidized soybean oil using various times gave polyols with hydroxyl numbers

(a) **Epoxidation/oxirane ring opening**

X = OR (a); Cl or Br (b); H (c); OH (d); or O$_2$CR (e)

(b) **Hydroformylation/reduction**

(c) **Ozonolysis/reduction**

Scheme 16 Preparation of vegetable oil-based polyols through carbon-carbon double bond modifications.

ranging from 82 to 225 mg KOH/g. [106] Polyols with hydroxyl numbers above 200 mg KOH/g give glassy thermosets, while those below this value give rubbery thermosets. It has also been found that the heterogeneity of the polyols has a negative effect on the elastic properties only at low crosslinking densities. [106] Epoxidized soybean oil has also been ring-opened by different alcohols, such as methanol, glycerol, and 1,2-propanediol [107]. The polyols obtained also have a range of hydroxyl numbers and give both glassy and rubbery thermosets. Recently, epoxidized soybean oil has been ring-opened by a renewable chemical, lactic acid, to synthesize polyols [108]. These polyols bear two hydroxyl groups per epoxy group, leading to a unique crosslinking structure in the resulting polyurethanes, and the glass transition temperatures of the polyurethane thermosets obtained can be controlled over a broad temperature range. Dangling chains from fatty acid chains act as plasticizers and are generally considered to decrease the thermomechanical properties of the resulting polyurethanes. Polyols prepared from metathesized triolein without dangling chains increase the glass transition temperatures and also increase the solvent resistance of the resulting polyurethanes [109].

Polyurethane foams have been prepared from plant oil-based polyols. Two rapeseed oil-based polyols, with 2.5 and 5.2 hydroxyl groups per triglyceride, were prepared by partial epoxidation of the double bonds and overall oxirane ring-opening using diethylene glycol [110]. Foams prepared from the polyol with lower hydroxyl content had higher values of resilience and elongation at break, while foams prepared from the other polyol had higher tensile and compression strength and superior cell structure [110]. Polyols from ring-opening epoxidized palm oil using hexamethylene glycol have been used to partially substitute a petrochemical polyether-polyol in the preparation of flexible foams [111]. These palm oil-based polyols resulted in more uniform cell size, increased apparent density and considerably improved compressive stress [111].

Epoxidized soybean oil has been reacted with carbon dioxide to form carbonated soybean oil, and the ring-opening of the carbonated soybean oil with ethanolamine led to new polyols (Scheme 17) [112,113]. These polyols were allowed to react with blocked polyisocyanates to afford thermosetting polyurethanes with excellent thermal and electrical insulating properties. Blending these polyols with poly(propylene glycol) offered tunable physical and chemical properties in the final polyurethanes [113].

The carbon-carbon double bonds of soybean oil can be converted to aldehydes through hydroformylation using rhodium or cobalt catalysts, and the
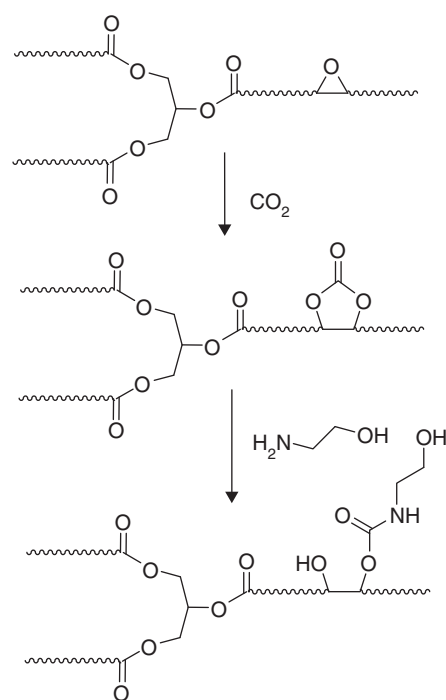

Scheme 17 Preparation of urethane-containing polyols through carbonated vegetable oil [112].

resulting aldehydes were reduced to primary alcohols (Scheme 16b) [114]. The rhodium-catalyzed reaction afforded a polyol in 95% conversion, which afforded rigid polyurethane thermosets. The cobalt-catalyzed reaction afforded a polyol in 67% conversion, leading to rubbery thermosets with lower mechanical strengths [114]. Polyols obtained from hydroformylation/reduction have been partially esterified with formic acid to prepare a variety of polyols with different hydroxyl numbers [115]. These polyols have been reacted with MDI to obtain polyurethane thermosets with different crosslink densities.

Polyols from canola oil with primary hydroxyl groups have been synthesized by ozonolysis and subsequent hydrogenation (Scheme 16c) [116,117]. These polyols when reacted with a fatty acid-derived diisocyanate, 1,7-heptamethylene diisocyanate, afforded thermosetting polyurethanes derived mostly from a lipid feedstock [116]. Compared to the commercially available diisocyanate, 1,6-hexamethylene diisocyanate, PUs from this fatty acid-derived diisocyanate have comparable thermomechanical properties within acceptable tolerances.

Recently, 2-mercaptoethanol was photochemically grafted onto vinyl groups of rapeseed oil through a thiol-ene addition to prepare bio-based polyols with an average functionality of 3.6 (Scheme 18) [118]. Thermosetting polyurethanes were obtained by reacting these polyols with MDI or HDI and their thermal
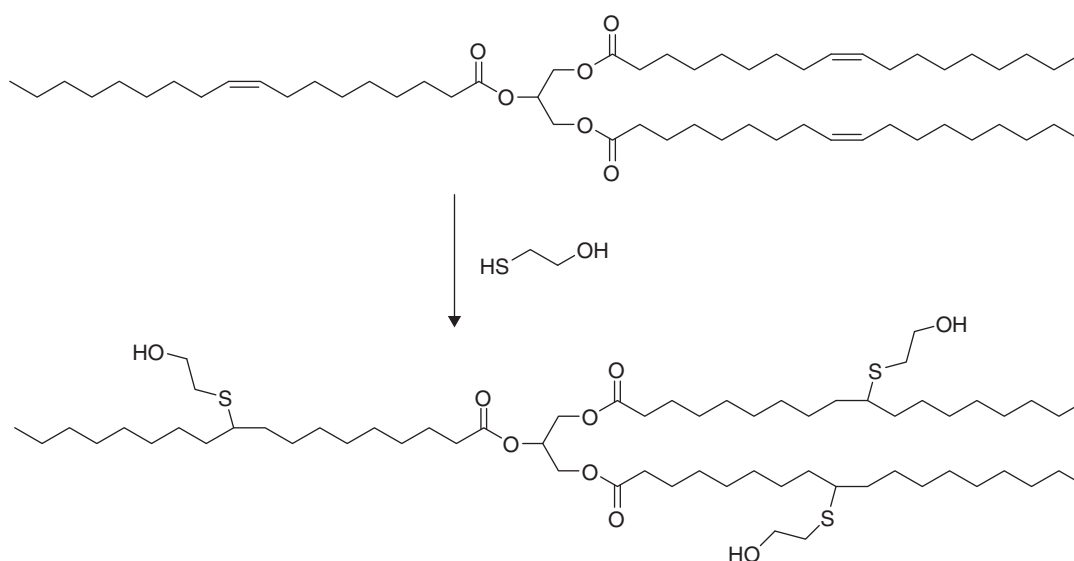
Scheme 18 Polyols from thiol-ene photoaddition of 2-mercaptoethanol onto vegetable oils [118].

properties were found to be similar to those from a commercial polyol (Desmophen 1150).

Vegetable oil-based polyurethanes with free carboxylic acid groups obtained by reacting methoxylated soybean oil polyols (MSOLs) with isophorone diisocyanate and dimethylolpropionic acid (DMPA) have been neutralized by triethylamine and dispersed in water to give waterborne anionic polyurethane dispersions (PUDs) [119]. These PUDs are environmentally friendly and contain no volatile organic compounds (VOCs). By using MSOLs with hydroxyl content ranging from 2.4 to 4.0 per triglyceride, rubbery and glassy thermosetting polyurethane coatings with Young's moduli from 8 to 720 MPa, ultimate tensile strengths from 4.2 to 21.5 MPa, and percent elongation at break values from 16 to 280% have been prepared [119]. By replacing DMPA with *N*-methyl diethanol amine (MDEA), polyurethanes containing amine groups can be obtained, which can be neutralized by acetic acid and dispersed in water to afford cationic PUDs [120,121]. Compared to anionic PUDs, cationic PUDs exhibit high adhesions to a variety of ionic substrates, especially anionic substrates, including leather and glass, leading to wide applications as coagulants and adhesives [122]. Furthermore, the cationic ammonium groups in the polyurethane backbones make these coatings antimicrobial to both gram positive and gram negative bacterials [123].

Free carboxylate groups in anionic PUDs can be further reacted with aziridine groups to prepare thermosetting coatings with higher crosslink densities [124]. When all of the carboxylate groups are reacted with the aziridine, the coating's Young's modulus and tensile strength increase from 14.5 to 125 MPa and 13.1 to 18.1 MPa, respectively. The thermal stability of the coatings was also increased after curing [124]. Polyurethane-silica nanocomposite dispersions with silica chemically connected to the polyurethane chains have been successfully prepared using a sol-gel process [125]. The incorporation of silica improved both the mechanical properties and thermal stabilities of the resulting coatings.

7 VEGETABLE OIL-BASED THERMOSETS FROM EPOXIDES

Epoxidized vegetable oils can react with a variety of cure reagents to give thermosets. Epoxidized linseed oil (ELO) has been reacted with three different amines, ethylenediamine, *p*-xylylenediamine, and triethylenetetramine, to afford crosslinked thermosets [126]. The thermoset from ELO and *p*-xylylenediamine is a very rigid material due to incorporation of the aromatic rings, which exhibits the highest decomposition temperature, but the preparation of this thermoset requires the highest curing temperature and longest reaction time [126]. Different amines and different ratios of the amine to the epoxy have been used to cure several epoxidized vegetable oils [127]. The diamine bis(*p*-aminocyclohexyl)methane afforded the highest performance and amine to epoxy ratios of 0.8 and 1.0 gave thermosets with superior performances [127]. Various amounts of epoxidized vegetable oils have been used as a reactive diluent for commercial BPA-based epoxy resins [128]. The epoxidized oil not only reduces the viscosity of the BPA-based epoxy resin, but it also enhances the thermomechanical properties of
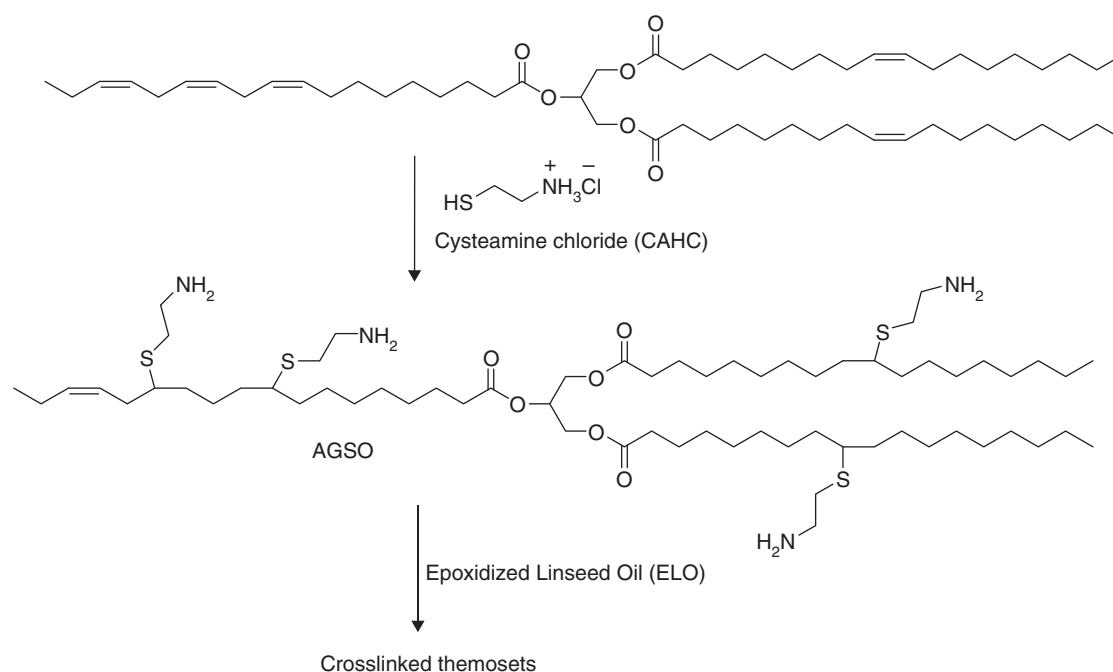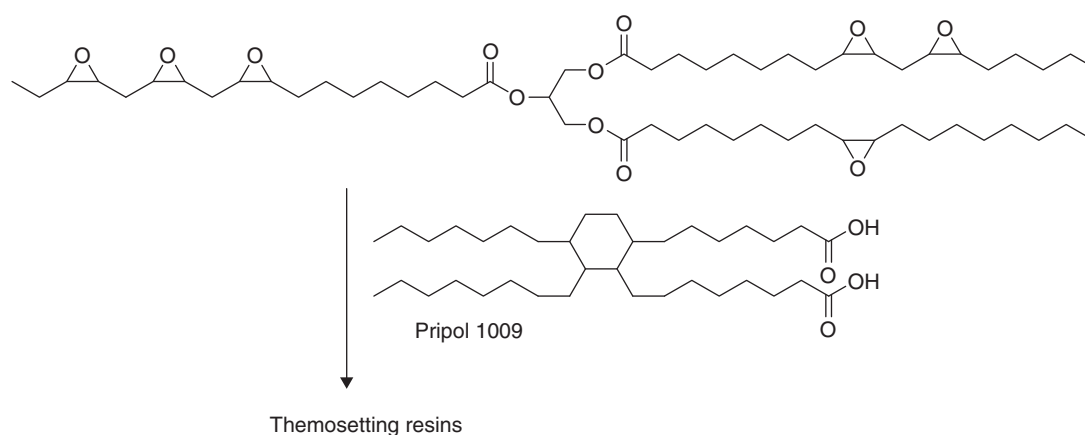
Scheme 19 Thermosets obtained by reacting vegetable oil-based polyamines with epoxidized linseed oil [130].

thermosets cured with a poly(amido amine) [128]. The kinetics of curing epoxidized soybean oil/diglycidyl ether of bisphenol A (DGEBA) with *p*-aminobenzoic acid have been investigated by differential scanning calorimetry (DSC). The activation energy of the curing reaction increase with increased ESO content, but the glass transition temperature decreases with more ESO [129]. The activation energy of the thermal degradation decreases with an increased loading of ESO [129]. A vegetable oil-based polyamine, prepared by a thiol-ene coupling of grapeseed oil (GSO) and cysteamine chloride (CAHC) (Scheme 19), has been used as a novel curing agent for ELO to prepare a fully bio-based epoxy resin [130]. The glass transition temperature of this thermoset was approximately –38 °C. Vegetable oils other than GSO can also be used to synthesize different vegetable oil-based polyamine curing reagents [130].
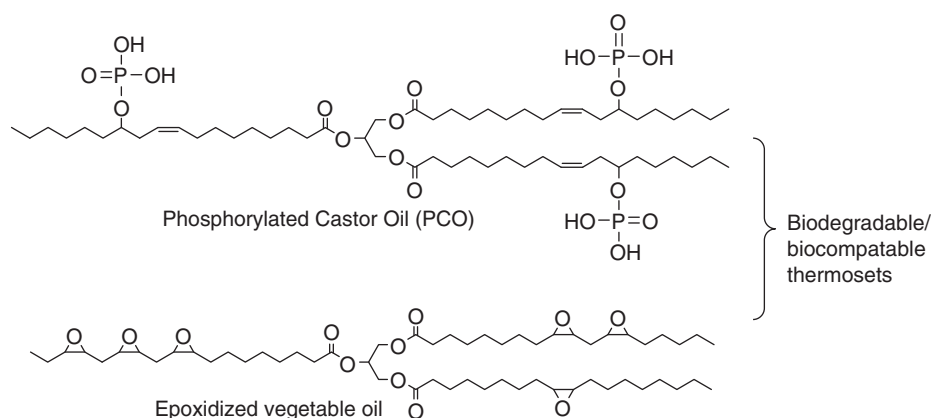
Vegetable oil-based polyols and epoxidized vegetable oils can be used to synthesize high molecular-weight epoxy resins by reaction with bisphenol A or low molecular weight bisphenol A-based resins [131,132]. The high molecular weight epoxy resins obtained were highly viscous liquids, which is very important from the point of view of processing and for applications as coating materials [131]. Recently, pressure-sensitive adhesives (PSAs) have been synthesized by polymerizing dihydroxyl-containing soybean oil with epoxidized soybean oil (ESO) and phosphoric acid in a one pot, single step, fast reaction at a moderate temperature (50 °C), and ESO PSA tapes were

produced at 110 °C within 30 seconds through a simple air drying process [133]. Due to their excellent thermal stability, transparency, chemical resistance, potential biodegradability from triglycerides, and comparable peel strength to commercially available PSAs, these PSAs may find broad applications, including uses in flexible electronics and medical devices [133].

Epoxidized vegetable oils can also be cured with carboxylic acids to produce thermosets. ELO has been allowed to react with a bio-derived diacid crosslinker (Pripol 1009) in the presence of several different amine catalysts to yield a 99.5% bio-derived, highly flexible transparent film with significant water resistance (Scheme 20) [134]. The carboxylate ions from Pripol 1099 act as nucleophiles to ring open the epoxide resulting in an alkoxide, which can be protonated to form an alcohol. The alcohol can continue to react with more epoxide to create a crosslinked network. The use of catalysts significantly enhanced the mechanical properties of the films. Compared to thermosets prepared without any catalyst, the tensile strength improved by up to 545% using 4-(dimethylamino)pyridine (DMAP) as a catalyst. The Young's modulus improved by up to 422% and elongation at break improved by 14–84% using 2-methylimidazole (2-MeIm) as a catalyst [134]. Biodegradable and biocompatible thermosets have been prepared by curing ESO and ELO with a phosphorylated castor oil (PCO) at 37 °C without any initiator or solvent (Scheme 21) [135]. These polymers can deform and return to their original dimensions even after 1000 repetitions of the cyclic compression

Scheme 20 Thermosets obtained by reacting an epoxidized vegetable oil with a bio-derived crosslinker [134].

Scheme 21 Biodegradable and biocompatible thermosets prepared from phosphorylated castor oil and epoxidized vegetable oils [135].

test. Cytotoxicity tests *in vitro* indicate that the polymers and their corresponding degradation products are compatible with the L929 cell line, and implantation of these polymers in animal skin shows that this kind of elastomer can be absorbed completely within 3 months [135].

Anhydrides have also been used to cure epoxidized vegetable oils [136]. BPA-based epoxies have been replaced by ESO or ELO and cured with anhydrides to give biobased epoxy thermosets [137,138]. Calorimetric studies exhibited a drop in reaction heat with ESO content, resulting from the lower reactivity of the oxirane rings in ESO due to steric constraints [138]. These bio-based epoxy thermosets incorporating ESO/ELO have higher elastic moduli and higher glass transition temperatures. Their Izod impact strengths and fracture toughness were significantly enhanced depending on the ESO/ELO content [137]. Epoxidized vegetable oils have been cured using a styrene maleic anhydride copolymer [139], maleic anhydride grafted polypropylene [140], and maleinized polybutadiene [141] to give a variety of thermosets. The molecular

weight and amount of these anhydride-containing polymers affect the thermomechanical properties of the final thermosets.

8 VEGETABLE OIL-BASED THERMOSETS FROM MISCELLANEOUS POLYMERIZATION METHODS

Click chemistry has been used to prepare vegetable oil-based thermosets [142,143]. Copper-catalyzed or thermal polyaddition between alkyne-containing vegetable oils and azide-containing vegetable oils has yielded a variety of thermosets (Scheme 22) [143]. The glass transition temperatures of the polymers obtained by the copper-catalyzed method (9 to 80 °C) were higher than those of the polymer obtained thermally (−13 to 45 °C), because the catalyst was trapped in the polymer network. However, the thermal approach requires less time and is higher yielding, indicating the suitability and ease of the click
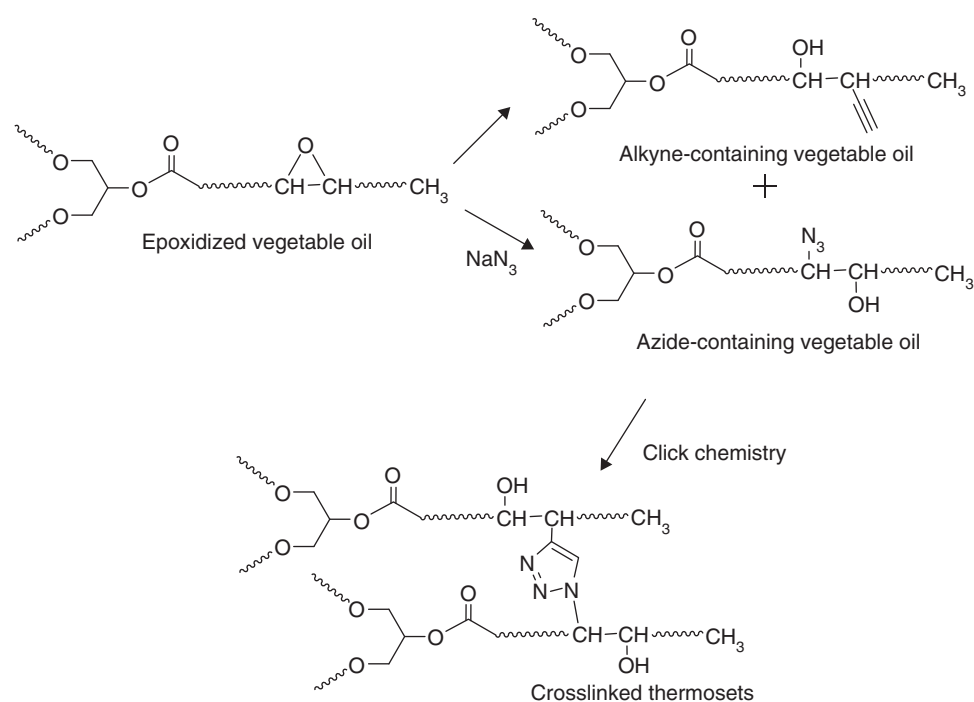
Scheme 22 Vegetable oil-based thermosets prepared from click chemistry [142].

polymerization for vegetable oil-derived alkynes and azides [143]. Recently, an alkyne-containing soybean oil has been reacted with several azide vegetable oils, including castor, canola, corn, soybean, and linseed oils, under thermal click chemistry conditions (without any solvent or catalyst) to afford fully crosslinked thermosets [142]. The tensile strength and glass transition temperature increased while the linear thermal expansion coefficient decreased in the series from the canola-derived polymer to the linseed-derived polymer. The castor oil-derived polymer behaved differently, because of the additional hydroxyl group per fatty acid [142].

A novel triglyceride containing an α, β-unsaturated ketone was prepared through photoperoxidation from high oleic sunflower oil using a one pot, environmentally friendly procedure [144]. The enone-containing triglyceride was crosslinked with diaminodiphenylmethane through an aza-Michael addition under mild conditions without the aid of a catalyst to give new thermosets (Scheme 23a) [144]. A phospha-Michael addition of diphenylphosphine oxide to the enone-containing triglyceride resulted in a novel phosphorus-containing vegetable oil (Scheme 23b), which was allowed to react with diaminodiphenylmethane by an aza-Michael addition to yield phosphorus-containing thermosets [145]. Limiting oxygen index (LOI) values from 26.4 to 35.0 for the final thermosets were obtained, indicating the flame retardant properties of the vegetable oil-based thermosets [145].

A thiol-ene reaction has also been used to prepare vegetable oil-based thermosets. Allyl acrylate and vinyl ether derivatives of castor oil were synthesized and cured with multifunctional thiols under UV light to prepare a variety of thermosets [146]. All of the materials show high solvent resistance and high hardness, and the final films contained approximately 40% vegetable oil [146]. Recently, acrylated castor oil has been cured with a thiol-containing polyhedral oligomeric silsesquioxane (POSS) using photo-crosslinking to obtain hybrid materials with no obvious phase separation, even if the content of the POSS is higher than 60% [147]. With the incorporation of POSS, the surface energy of the hybrid materials decreased, and the thermal stability increased, but the glass transition temperature decreased slightly. These vegetable oil-based hybrid materials show promise in coating applications [147].

9 CONCLUSION AND PERSPECTIVE

Vegetable oils have found applications in industry for many years. Recently, a variety of thermosets have been prepared from vegetable oils by a number of different polymerization methods. The thermosets exhibit a range of thermomechanical properties from soft and flexible rubbers to rigid and hard plastics. Some of the thermosets have properties comparable to their petroleum-based counterparts and show promise as replacements
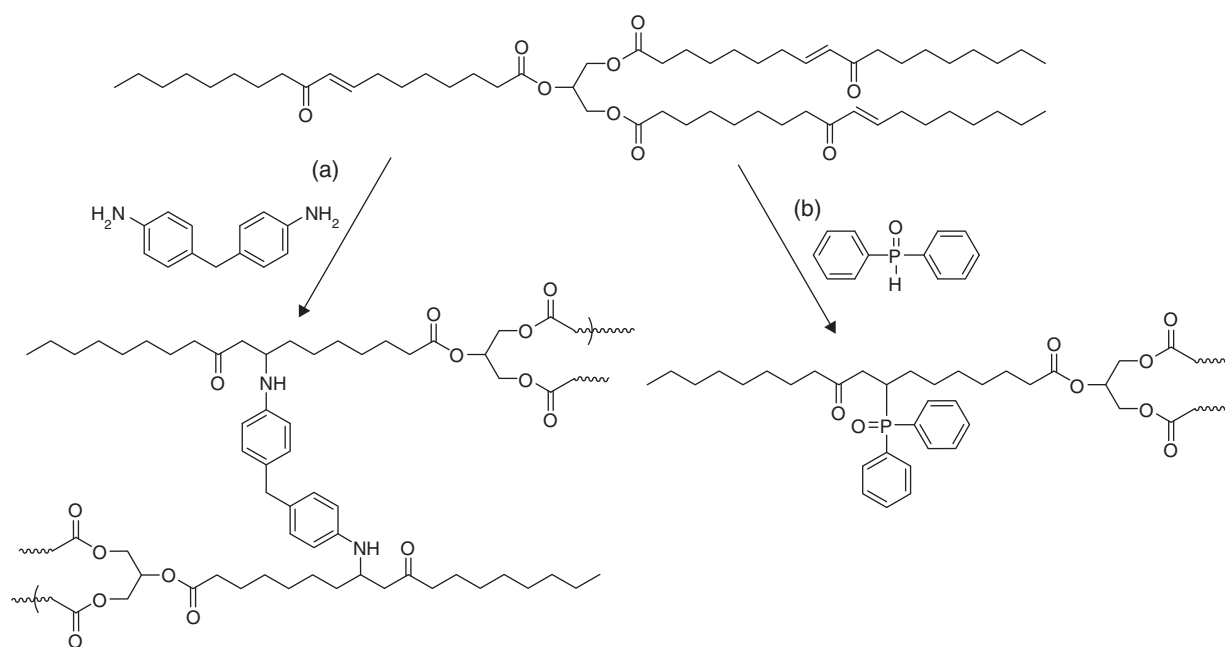
Scheme 23 (a) Thermosets from polymerization of an enone-containing triglyceride and an aromatic diamine, and (b) preparation of a phosphorous-containing triglyceride [144,145].

for commercially available polymeric materials, providing possible solutions to increasing environmental and energy concerns. Challenging problems still exist and the development of better vegetable oil-based thermosets appears certain. Petroleum-based comonomers can be replaced with renewable chemicals to prepare thermosets with a high loading of bio-based materials. The cure time for the thermosets needs to be reduced to ensure improved productivity and cost effectiveness. The cost of the vegetable oil-based thermosets should be reduced to compete with petroleum-based analogs. Genetic modifications of the plants may be used to give vegetable oils with desired fatty acid compositions for thermosets with specific properties. In general, interdisciplinary collaborations between scientists working in agriculture, biology, chemistry, and materials need to be established to make vegetable oils successful candidates for the thermoset industry, leading to a cleaner and greener future.

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