Vegetable oil-based polymeric materials: synthesis, properties, and applications

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The use of vegetable oils as renewable raw materials for the synthesis of various monomers and polymeric materials is reviewed. Vegetable oils are generally considered to be the most important class of renewable resources, because of their ready availability and numerous applications. Recently, a variety of vegetable oil-based polymers have been prepared by free radical, cationic, olefin metathesis, and condensation polymerization. The polymers obtained display a wide range of thermophysical and mechanical properties from soft and flexible rubbers to hard and rigid plastics, which show promise as alternatives to petroleum-based plastics.

1. Introduction

The utilization of renewable resources in energy and material applications is receiving increasing attentions in both industrial and academic settings, due to concerns regarding environmental sustainability.[1,2] Nowadays, most commercially available polymers are derived from non-renewable resources and account worldwide for approximately 7% of all oil and gas used.[2] With the continuous depletion of fossil oils, dramatic fluctuations in the price of oil and environmental concerns, there is an urgent need to develop polymeric materials from renewable resources.[3]

The most widely used renewable raw materials include vegetable oils, polysaccharides (mainly cellulose and starch), wood and proteins.[4] A variety of chemicals have been prepared from these biomass-derived materials. For instance, bio-oils and syngas (mainly CO and H_2) are obtained by the pyrolysis of wood and agricultural wastes.[5] Bio-oil can be upgraded for applications as transportation fuels,[4] while syngas can be converted to methanol,[6] both of which can be used in chemical industry.

Vegetable oils represent another promising route to renewable chemicals and polymers due to their ready availability, inherent biodegradability and low toxicity. In fact, industrial uses consumed 15% of all soybean oil from 2001 to 2005.[7] Vegetable oils have been used in paints and coatings for centuries, because the unsaturated oils can oligomerize or polymerize when exposed to the oxygen in air.[8] In recent years, biorenewable fuels, mainly biodiesel, which can be used as an alternative engine fuel, have been prepared from vegetable oils by pyrolysis, catalytic cracking, and transesterification.[9]

During the last decade, a variety of vegetable oil-based polymeric systems have been developed.[10] Unmodified vegetable oils have been used to prepare biorenewable polymers by thermal[11] or cationic[12] polymerization methods, taking advantage of the carbon–carbon double bonds in the fatty acid chains. Modified

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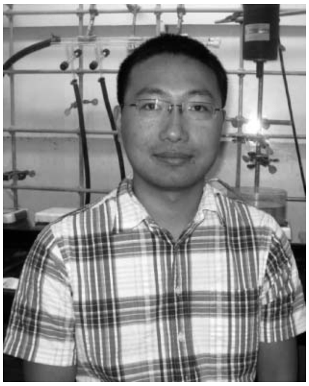

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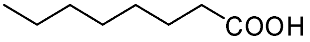
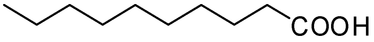
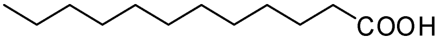
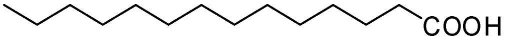
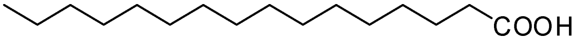
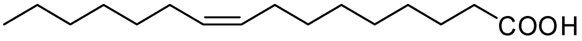
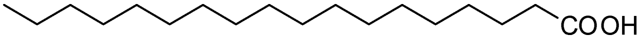
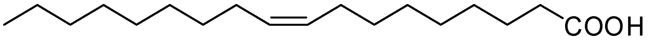
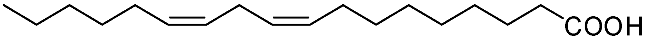
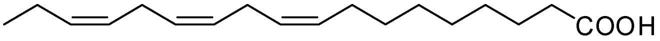
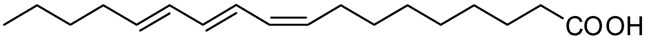
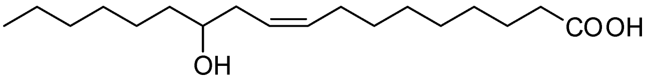
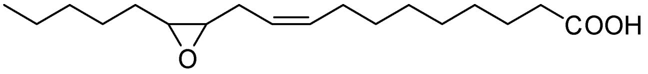
Table 1 Formulas and structures of the most important fatty acids[19]

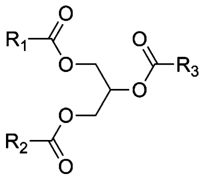
Fatty Acid	Formula	Structure
Caprylic	$C_8H_{16}O_2$	
Capric	$C_{10}H_{20}O_2$	
Lauric	$C_{12}H_{24}O_2$	
Myristic	$C_{14}H_{28}O_2$	
Palmitic	$C_{16}H_{32}O_2$	
Palmitoleic	$C_{16}H_{30}O_2$	
Stearic	$C_{18}H_{36}O_2$	
Oleic	$C_{18}H_{34}O_2$	
Linoleic	$C_{18}H_{32}O_2$	
Linolenic	$C_{18}H_{30}O_2$	
α-Eleostearic	$C_{18}H_{30}O_2$	
Ricinoleic	$C_{18}H_{34}O_3$	
Vernolic	$C_{18}H_{32}O_3$	

vegetable oils with acrylic double bonds exhibit higher reactivities and can undergo free radical polymerization to afford thermosets with good thermal and mechanical properties.[13] Recently, relatively new polymerization methods, acyclic metathesis polymerization (ADMET)[14] and ring-opening metathesis polymerization (ROMP),[15,16] have been employed to synthesize vegetable oil-based polymers as well. Vegetable oil-based polyols are another promising monomer, which can react with diisocyanates to afford polyurethane elastomers,[17] as well as water-borne polyurethane dispersions,[18] which have various applications in foams, coatings, and adhesives.

Herein, we review the most recent advances in polymeric materials prepared from vegetable oils by free radical, cationic, olefin metathesis, and condensation polymerization. The synthesis of these vegetable oil-based monomers and polymers, as well as their structural-property relationships and applications, are discussed in the following sections.

2. The structures of vegetable oils

Vegetable oils are vital biorenewable resources extracted from various plants and are normally named by their biological source, such as soybean oil and palm oil. Chemically, vegetable oils consist of mainly triglycerides formed between glycerol and various fatty acids (Scheme 1).[19] Table 1 summarizes the most common fatty acids present in vegetable oils. As can be seen from the table, most fatty acids are long straight-chain compounds with an even number of carbons and the double bonds in most of these unsaturated fatty acids possess a *cis* configuration. However, some fatty acid chains, like those in ricinoleic and vernolic acids, bear functional groups, hydroxyl and epoxy groups respectively.[7] The physical state of vegetable oils depends on both the nature and the distribution of the fatty acids. Most vegetable oils are liquid at room temperature. Generally, higher melting point vegetable oils are obtained with more carbons in the fatty acid chain, a lower number of carbon–carbon double bonds, and an *E* (*trans*) configuration and conjugation of the carbon–carbon double bonds.[19]



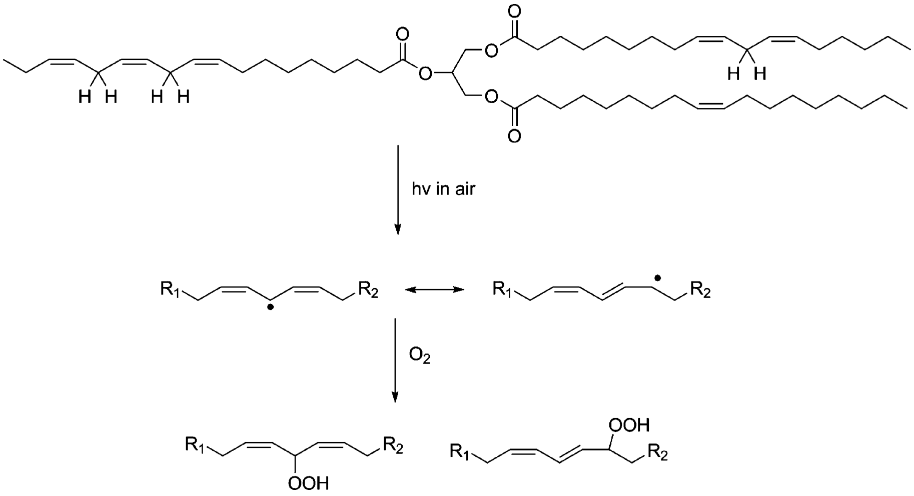
Scheme 1 Triglyceride structure of the vegetable oils (R^1, R^2, R^3 represent fatty acid chains).

Different vegetable oils contain differing composition of fatty acids depending on the plant and the growing conditions.[20] The fatty acid compositions of the most common vegetable oils are summarized in Table 2.[21,22] The chemical and physical

Table 2 Properties and fatty acid compositions of the most common vegetable oils[7]

			Fatty acids (%)				
Vegetable oil	Double bonds[a]	Iodine value[b]/mg per 100 g	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Palm	1.7	44–58	42.8	4.2	40.5	10.1	—
Olive	2.8	75–94	13.7	2.5	71.1	10.0	0.6
Groundnut	3.4	80–106	11.4	2.4	48.3	31.9	—
Rapeseed	3.8	94–120	4.0	2.0	56.0	26.0	10.0
Sesame	3.9	103–116	9.0	6.0	41.0	43.0	1.0
Cottonseed	3.9	90–119	21.6	2.6	18.6	54.4	0.7
Corn	4.5	102–130	10.9	2.0	25.4	59.6	1.2
Soybean	4.6	117–143	11.0	4.0	23.4	53.3	7.8
Sunflower	4.7	110–143	5.2	2.7	37.2	53.8	1.0
Linseed	6.6	168–204	5.5	3.5	19.1	15.3	56.6

[a] Average number of double bonds per triglyceride. [b] The amount of iodine (mg) that reacts with the double bonds in 100 g of vegetable oil.



Scheme 2 The auto-oxidation of drying oils in air.[23]

properties of the vegetable oils depend heavily on the degree of unsaturation, which can be determined by measuring the iodine value (IV). The IV value represents the amount of iodine (mg) that reacts with the carbon–carbon double bonds in 100 g of vegetable oil; the larger IV value indicates more carbon–carbon double bonds per vegetable oil triglyceride. Thus, vegetable oils can be classified as drying oils (IV > 130), semi-drying oils (100 < IV < 130), and non-drying oils (IV < 100). The IV values of common vegetable oils are summarized in Table 2 as well.

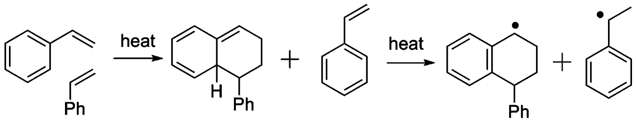
3. Vegetable oil-based polymers from free radical polymerization

3.1. Unmodified vegetable oils as monomers

The carbon–carbon double bonds in vegetable oils can be polymerized by free radical polymerization. Drying oils can undergo auto-oxidation with the help of an oxygen atmosphere to form peroxides (Scheme 2),[23] which undergo crosslinking through radical recombination to form highly branched or crosslinked polymeric materials.[24] Hazer *et al.* [24–28] have taken advantage of such peroxide processes of vegetable oils to form vegetable oil-based free-radical macroinitiators, which initiate the polymerization of methyl methacrylate (MMA) or n-butyl methacrylate (nBMA) to afford polymeric linseed oil (PLO)[28] and polymeric soybean oil (PSB)[24] grafted copolymers. It was found that the vegetable oil acts as a plasticizer and can make PMMA and PnBMA partially biodegradable and biocompatible. Moreover, fibroblast and macrophage cells adhere to these graft copolymers, suggesting possible uses in tissue engineering.[24,28]

Free radical polymerized soybean oil (polySOY) and isotactic poly(L-lactide) (PLLA) have been melt blended to increase the toughness of PLLA.[29] It was found that the gel fraction of the polySOY was a key variable in determining the blend morphology, while the tensile properties of the blends rely heavily on the morphology. The successfully prepared PLLA/polySOY blends have tensile toughnesses as high as 4 times greater than that of unmodified PLLA, with the corresponding strain at break values as high as 6 times greater than that of unmodified PLLA.[29]

Unlike other vegetable oils, tung oil consists of ~84% of α-eleostearic acid, which possesses a naturally occurring conjugated triene.[11] The high unsaturation and conjugation of the carbon–carbon double bonds makes this oil readily polymerizable. In 1940, Stoesser and Gabel[30] produced a tung oil-styrene copolymer by simply heating these materials at 125 °C for 3 d. However, tung oil constituted only 0.1–2.0% of the copolymer. Recently, Li and Larock[11] prepared a series of tung oil-styrene (ST)-divinylbenzene (DVB) copolymers containing 30–70 wt% of tung oil, which range from rubbery materials to tough and rigid plastics. These fully cured thermosets initiated by free radicals from simply heating ST (Scheme 3)[31,32] contained approximately 90–100% crosslinked materials, and possess glass transition temperatures of −2 °C to +116 °C, crosslink densities of 1.0×10^3 to 2.5×10^4 mol m^{-3}, coefficients of linear thermal expansion of 2.3×10^{-4} to 4.4×10^{-4} per °C, compressive strengths of 8 to 114 MPa, and compressive moduli of 0.02 to 1.12 GPa. The addition of metallic salts of Co, Ca, and Zr as catalysts accelerates the thermal copolymerization very effectively and thus increases the crosslink densities and properties of the resulting copolymers.[11]



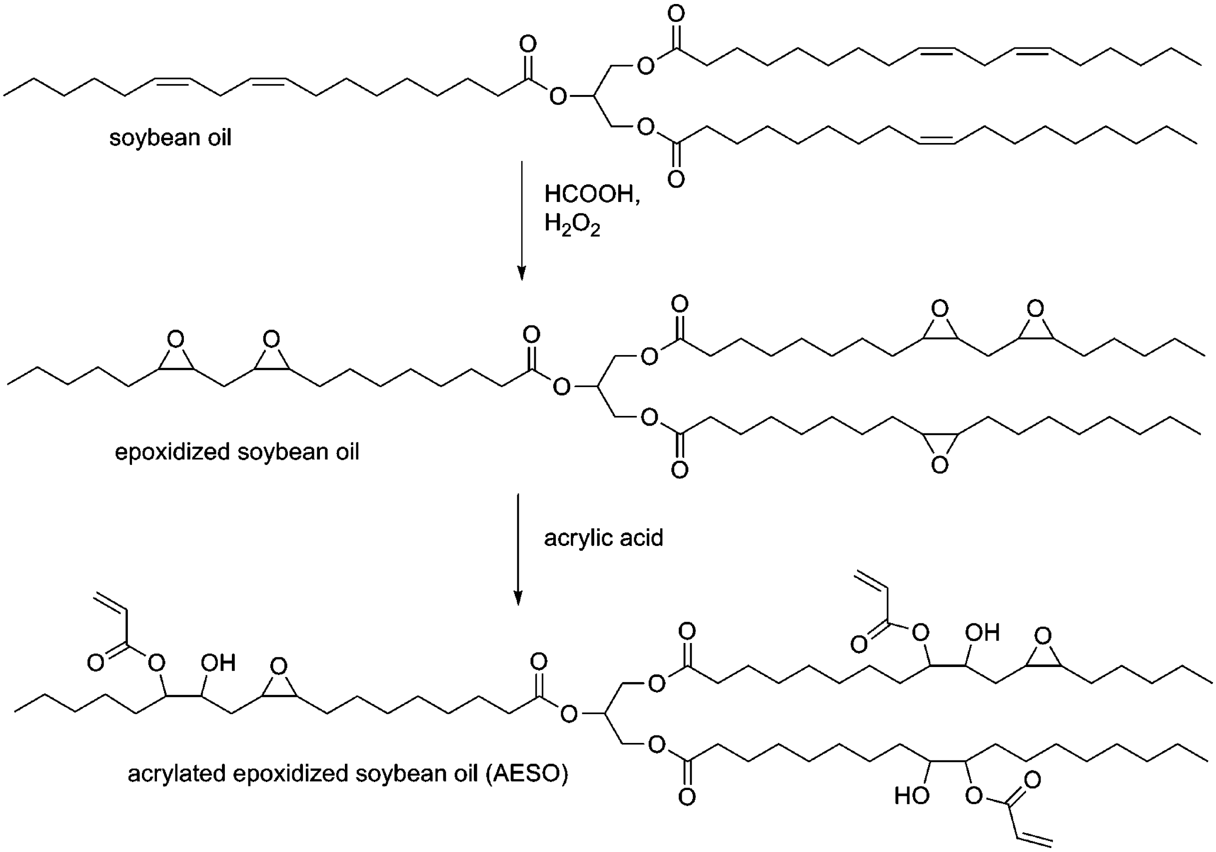
Scheme 3 Free radical formation by heating styrene.[31,32]

3.2. Monomers based on carbon–carbon double bond modifications in the vegetable oils

To make the nonconjugated vegetable oils undergo free radical polymerization more easily, conjugated linseed oil (CLIN) and conjugated low-saturation soybean oil (CLS) have been prepared using a rhodium-based catalysts developed by Larock *et al.*[33] These conjugated vegetable oils were subsequently copolymerized with styrene (ST), acrylonitrile (AN), dicyclopentadiene (DCPD) and DVB[34–36] initiated by thermally-produced free radicals[34] or azobisisobutyronitrile (AIBN).[35,36] The copolymers obtained incorporated up to 96 wt% of the conjugated oils, and a wide range of thermal and mechanical properties were obtained by simply changing the stoichiometry of the vegetable oils and the petroleum-based monomers.

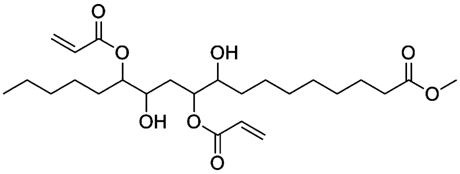
The carbon–carbon double bonds in the fatty acid chains of the vegetable oils can undergo various reactions to append different polymerizable functionalities, such as acrylates, to increase the reactivity of the vegetable oils. Acrylated epoxidized soybean oil (AESO), synthesized from the reaction of acrylic acid with epoxidized soybean oil (Scheme 4),[37] has been extensively studied in polymers and composites[13] and is commercially available under the brand name Ebecryl 860 from UCB Chemicals Company.[38] The acrylation reaction was found to have a first-order dependence on the epoxide concentration. However, the rate constant of acrylation increased as the number of epoxides per fatty acid decreased due to steric hindrance and the intermediate oxonium ion is apparently stabilized by local epoxide groups.[39]

AESO can be blended with reactive diluents, such as ST, to improve its processability and afford suitable AESO-ST thermosets and composites for structural applications.[13,40] The polymer properties can be controlled by changing the acrylate level of the triglyceride and by varying the amount of ST. Consequently, a range of properties and applications have been



Scheme 4 Synthesis of AESO.[37]

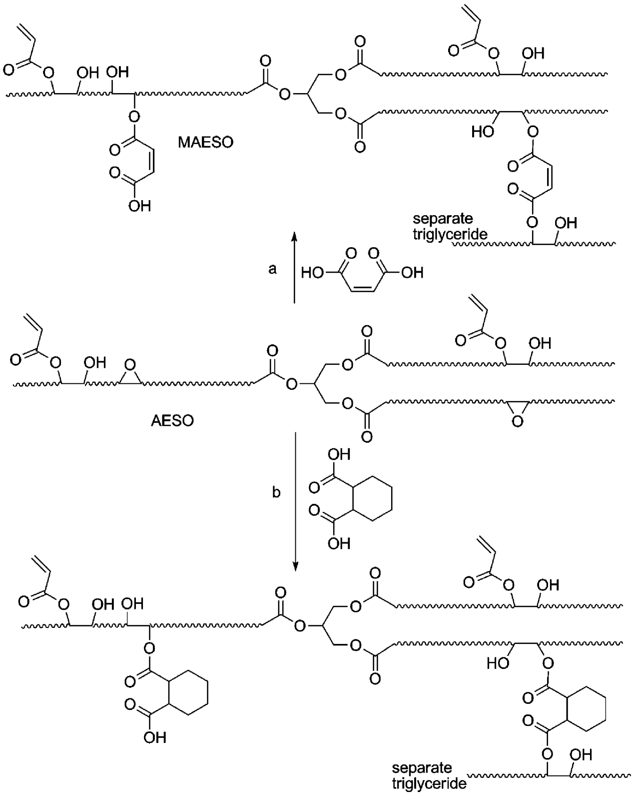
found for these biopolymers, making them suitable replacements for petroleum-based polymers. To make polymeric materials more biorenewable, a novel reactive diluent, acrylated epoxidized fatty methyl ester (AFAME) (Scheme 5), was used as a styrene replacement in polymerizations with AESO with the advantage of reducing hazardous air pollutant (HAP) emissions and health and environmental risks.[41] Recently, AESO/CO_2 was used to produce thermosetting foams with a high bio-based content. The cured foam's density was controlled by the application of a partial vacuum before gelation and its mechanical properties were comparable with those of semi-rigid industrial foams.[42] Besides soybean oil, acrylated epoxidized methyl oleate has been prepared in a similar manner and made to undergo free radical emulsion polymerization; the resulting polymer may be of considerable interest for pressure-sensitive adhesive applications.[43]



Scheme 5 Structure of an acrylated epoxidized fatty methyl ester (AFAME).[41]

AESO contains both residual unreacted epoxy groups and newly formed hydroxyl groups, both of which can be used to further modify AESO. As shown in Scheme 6a, MAESO obtained by reacting AESO with maleic acid introduces more carbon–carbon double bonds, as well as forming oligomers, which increase the entanglement density of the resulting biopolymers.[13,37] The MAESO-ST thermosets obtained exhibit higher crosslink densities than the corresponding AESO-ST thermosets, resulting in higher T_g values and improved room temperature storage moduli.[37] The reaction of AESO with cyclohexanedicarboxylic acid (Scheme 6b) also forms oligomers, as well as introducing stiff cyclic rings into the structure.[13]

Acrylate-containing triglycerides have recently been prepared by a new route, which involves an "ene" reaction with singlet oxygen.[44] As seen in Scheme 7a, a mixture of secondary allylic alcohols (HSO) can be obtained by singlet oxygen photooxygenation[45–47] and further reduction; these unsaturated alcohols can be further reduced to saturated alcohols (HSO[H]). These two novel hydroxyl-containing triglycerides are easily functionalized with acrylate groups (Scheme 7b) and free radically polymerized in the presence of differing amounts of pentaerythritol tetraacrylate, providing a promising route to polymeric networks. These polymers show properties similar to those of other reported acrylate triglyceride-based materials.[44] The allylic alcohols in HSO can react with chlorodiphenylphosphine to give allylic phosphinites capable of undergoing a [2,3]-sigmatropic rearrangement leading to tertiary phosphine oxides directly linked to the triglyceride (Scheme 8).[48] The phosphorus-containing triglycerides with different hydroxyl content that were obtained were further functionalized with acrylates and then were crosslinked in the presence of different amounts of pentaerythritol tetraacrylate. Interestingly, the phosphorus-containing polymers show flame-retardant abilities with increased limiting oxygen index (LOI) values.[48]

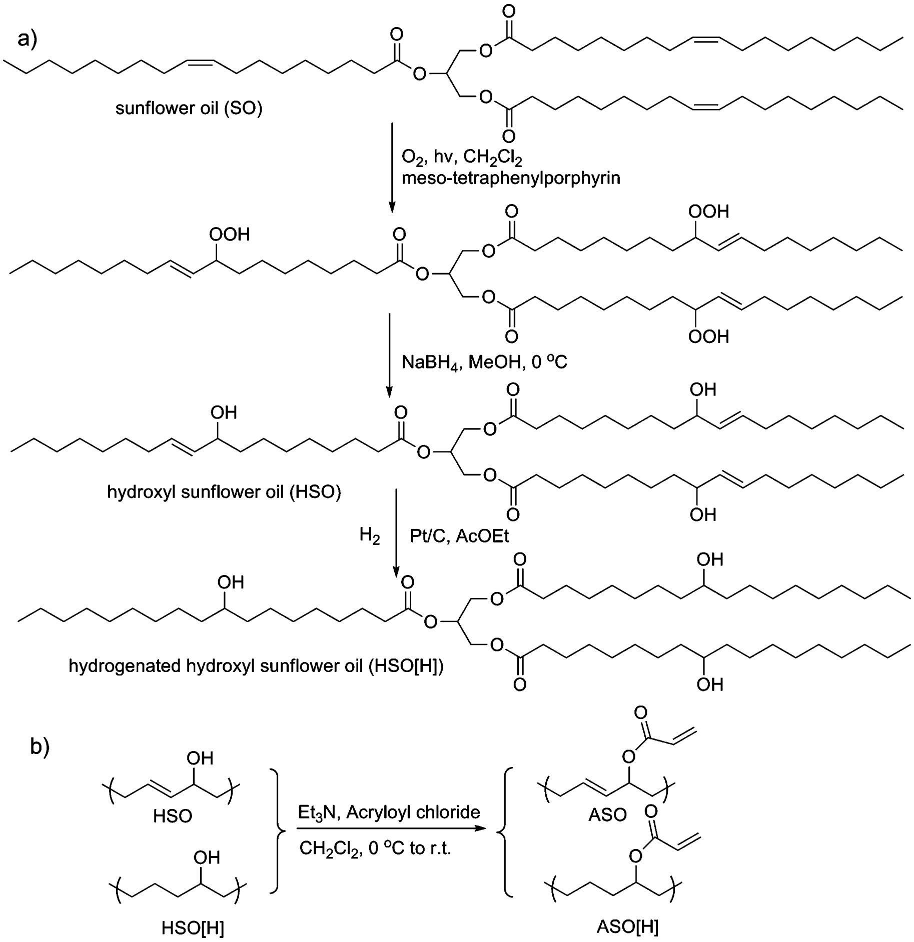


Scheme 6 Modification of AESO with (a) maleic acid and (b) cyclohexane dicarboxylic acid.[13]

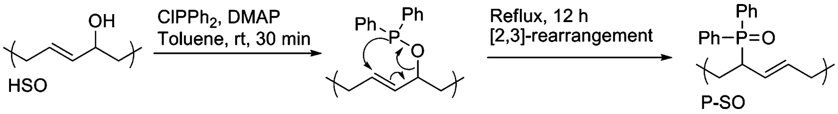
3.3. Monomers based on triglyceride ester modifications in the vegetable oils

Other than modifications of the fatty acid carbon–carbon double bonds, the incorporation of more reactive carbon–carbon double bonds through chemical modifications of the triglyceride ester groups is another promising approach to more reactive monomers. Wool and co-workers have developed a series of vegetable oil monoglyceride maleates copolymerized with ST to give rigid thermoset polymers.[49,50] Scheme 9 shows the preparation and polymerization of soybean oil monoglyceride SOMG) maleate half esters. The SOMG were obtained by transesterification of soybean oil and glycerol. The resulting material was then reacted with maleic anhydride (MA) to produce SOMG maleate half esters. Copolymerization of the SOMG maleates with 35 wt% ST gave a rigid, thermoset polymer with a T_g around 135 °C and storage modulus of 0.92 GPa at 35 °C. These materials show promising properties, making them suitable replacements for conventional petroleum-based plastics.[51] Besides bulk polymerization, emulsion copolymerization of the SOMG maleates with ST has also been carried out successfully without the addition of an emulsifier.[50]

To further increase the thermophysical and mechanical properties of the SOMG maleates-styrene polymers, neopentyl glycol (NPG) and bisphenol A (BPA) have been mixed with the SOMG. The mixtures were maleinized under the same reaction conditions used previously and the resulting maleates were then copolymerized with ST to give thermosets with better properties. For example, the polymer from SOMG/NPG/MA and ST displays a higher T_g value of 145 °C and an improved



Scheme 7 Synthesis of acrylate sunflower oil (ASO) and hydrogenated acrylate sunflower oil (ASO[H]) through singlet O_2.[44]



Scheme 8 Synthesis of phosphorous-containing triglycerides.[48]

storage modulus of 2.01 GPa at 35 °C. These improvements can be explained by the structural changes present in the polymer backbone.[51]

Linseed oil has been used to prepare linseed oil monoglyceride (LOMG) in a similar approach. The LOMG maleates obtained were copolymerized 20 to 80 wt% of ST to produce rigid, thermoset polymers. It was found that the copolymer with 40 wt% of ST gives a material with better mechanical and fracture behavior.[52]

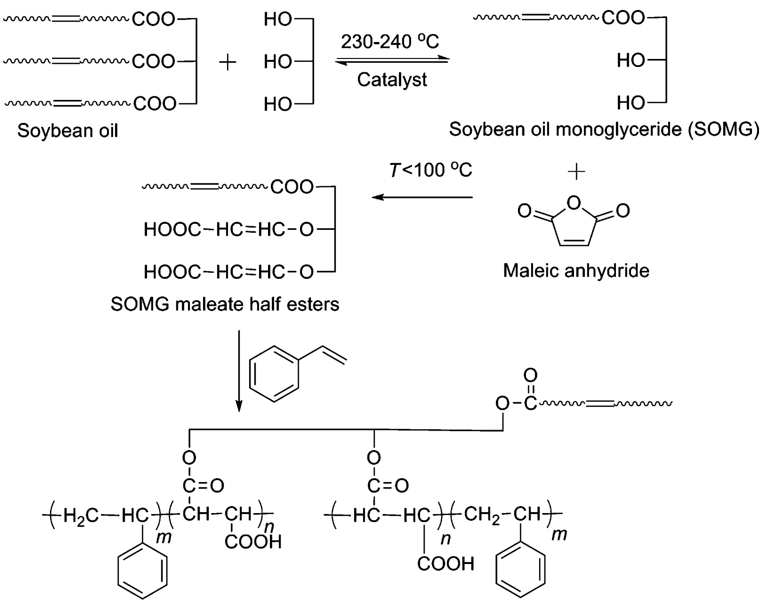
The fatty acid chains in SOMG or LOMG were not incorporated into the polymer backbone and acted as plasticizers reducing the overall modulus and strength of the resulting polymers. To overcome the plasticizing effect, castor oil, where approximately 90% of the fatty acid chains bear hydroxyl groups, has been used for alcoholysis with various polyols, such as pentaerythritol, glycerol and bisphenol A propoxylate, and then reacted with MA to give maleated alcoholyzed castor oils (MACOs).[53,54] The MACO-ST thermosets subsequently prepared exhibited significantly improved modulus, strength, and T_g values compared to soybean oil-based polymers. These novel castor oil-based polymers show properties comparable to those of high performance unsaturated polyester (UP) resins and show promise as a replacement for petroleum-based materials.[53]

A lipase catalyst has been used to prepare 2-(acryloyloxy) ethyl oleate (AEO) (Scheme 10).[55] AEO was polymerized by radical polymerization using benzoyl peroxide (BPO) to afford polymers with M_n in the range from 20 000 to 30 000 g mol^{-1}, while incorporating AEO into PMMA by the copolymerization of MMA with AEO resulted in a good coating material with a comparable surface hardness.

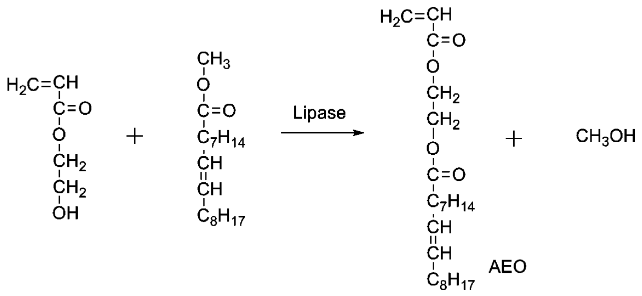
4. Vegetable oil-based polymers from cationic polymerization

4.1. Cationic polymerization of vegetable oil-based vinyl monomers

Lewis acids, such as $AlCl_3$, $TiCl_4$, $SnCl_4$, $ZnCl_2$ and $BF_3{\cdot}OEt_2$ (BFE) have been used to polymerize vinyl monomers cationically

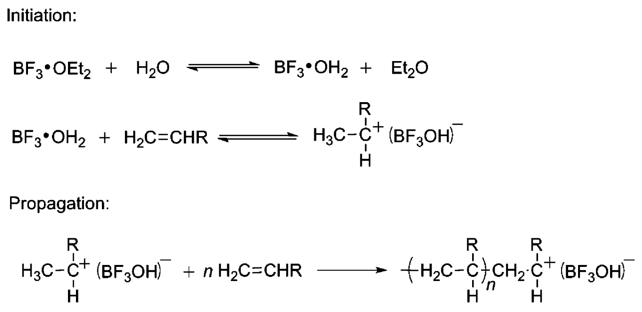


Scheme 9 Synthesis and polymerization of soybean oil monoglyceride maleates.[50]



Scheme 10 Preparation of AEO using a lipase catalyst.[55]

under relatively mild reaction conditions. Among these initiators, BFE has proven to be the most efficient and is commonly used in cationic polymerization of alkenes. Scheme 11 shows the generally accepted mechanism for such polymerizations.[56] The vinyl monomers must be nucleophilic enough to undergo protonation and subsequent polymerization.



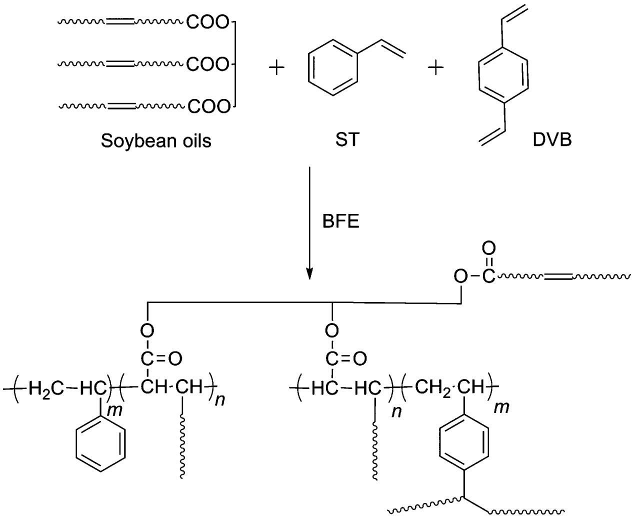
Scheme 11 Initiation and propagation of cationic polymerization with BFE.[56]

The carbon–carbon double bonds in ethylene and propylene can undergo cationic polymerization, but only give oligomers, because the relatively unstable carbocations formed favor secondary reactions, such as proton transfer, elimination, isomerization, and chain transfer, instead of chain propagation. Compared to ethylene and propylene, the carbon–carbon double bonds in vegetable oils are slightly more nucleophilic. Furthermore, the cationic intermediates produced from conjugated vegetable oils can be stabilized by the adjacent carbon–carbon double bonds. Thus, tung oil, containing a conjugated triene, is very reactive in cationic polymerization using the initiator BFE.[57] Vegetable oils in general are cationically polymerizable monomers, because their branched triglyceride structure leads to extensive crosslinking. Each unsaturated fatty acid chain in the triglyceride structure can participate in the cationic reaction. Thus, the secondary reactions which might normally occur during the polymerization process are not expected to inhibit the crosslinking process and a crosslinked three-dimensional polymer network can be formed.

The cationic polymerization of various soybean oils, such as regular soybean oil (SOY), low-saturation soybean oil (LoSatSoy oil or LSS) and conjugated LoSatSoy oil (CLS) have been extensively studied by Larock *et al.*[56,58–63] It was found that polymerization of the neat soybean oils affords low molecular weight viscous oils or soft rubbery materials, consisting of solid polymers and liquid oligomers, which are of limited utility.[56,62] Therefore, petroleum-based comonomers, such as ST and/or DVB, nobornadiene, and dicyclopentadiene (DCPD), have been used to copolymerize with vegetable oils to obtain better thermosets.[62] For example, the cationic copolymerization of SOY, LSS and CLS (50–60 wt%) with DVB initiated by BFE provides polymers ranging from soft rubbers to hard plastics depending on the comonomers and stoichiometry. Dynamic mechanical analysis (DMA) indicates that the resulting polymers are typical thermosets with moduli ranging from 4×10^8 to 1×10^9 Pa at room temperature, values which are comparable to those of conventional plastics.[59] The structure of the bulk polymer is a densely crosslinked polymer network mixed with a certain amount of unreacted free oil, which is found to largely affect the thermal stability of the thermosets obtained. The

CLS polymers have the highest moduli and thermal stabilities, because they contain the least unreacted free oil. Micro-phase separation occurs in the SOY and LSS/DVB copolymers mainly due to poor miscibility between the soybean oils and the initiator. Thus, a BFE initiator modified by the addition of Norway fish oil ethyl ester has been used to homogeneously copolymerize the various oils with DVB. The resulting bulk polymers exhibit higher conversion of the oils to crosslinked polymers than those utilizing BFE alone.[59]

To increase the uniformity of the crosslinked structure, the monofunctional monomer ST has been added to give soybean oil/ST/DVB copolymers and the mechanical properties of the resulting plastics are significantly improved.[58,61–63] Scheme 12 illustrates the cationic copolymerization of soybean oils with ST and DVB,[64] which provides a wide variety of viable polymeric materials with room temperature moduli ranging from 6×10^6 to 2×10^9 Pa and glass transition temperatures (T_g) ranging from 0 °C to 105 °C, which are thermally stable up to 200 °C in air. The thermophysical properties of the thermosets are considerably affected by the crosslink density of the bulk polymers and the yield of crosslinked polymers obtained after Soxhlet extraction largely depend on the concentration of the crosslinking agent, DVB. Furthermore, the reactivity of the soybean oils also affects the yield of the crosslinked polymers. Therefore, CLS affords thermosets with better properties compared to SOY and LSS.[58,62]



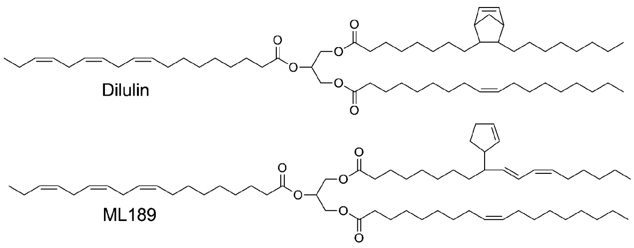
Scheme 12 Cationic copolymerization of soybean oils with ST and DVB.[64]

Besides soybean oils, corn oil and conjugated corn oil have been copolymerized with ST and DVB cationically and the thermosets obtained exhibit commercially viable thermophysical and mechanical properties as well.[65] Recently, a range of thermosets have been prepared by the cationic copolymerization of olive, peanut, sesame, canola, corn, soybean, grapeseed, sunflower, low-saturation soy, safflower, walnut, and linseed oils with ST and DVB.[22] It was found that the gelation times of these copolymers were independent of the degree of unsaturation of the vegetable oil. The thermal transitions of the thermosets showed no observable dependence on the reactivity of the vegetable oil and the mechanical properties showed a gradual increase with increasing oil reactivity.[22]

Microwave irradiation has been observed to accelerate the cationic polymerization of soybean oil/ST/DVB noticeably over a conventional heating cure sequence, and the cure time was considerably shortened.[66] The copolymers obtained under conventional heating and under microwave irradiation show similar thermal and mechanical properties. Recently, the incorporation of Si and B compounds into cationically-polymerized soybean oil/ST/DVB systems resulted in fire retardation.[67] The boron-containing copolymers were found to be more efficient flame retardants. Moreover, reactive flame retardants show significant improvements compared to the corresponding additive flame retardants, because the reactive flame retardants have improved dispersion in the copolymer or their presence in the polymer chain promotes crosslinking and char formation.[67]

Dicyclopentadiene (DCPD) (~$0.29/lb), an inexpensive monomer, can be used to replace DVB (~$3.00/lb) in cationic copolymerizations with soybean oil (SOY) and 100% conjugated soybean oil (C_{100}SOY) catalyzed by Norway fish oil (NFO)-modified or SOY- and C_{100}SOY-diluted BFE.[68] The NFO-modified catalysts result in enhanced SOY-DCPD copolymer properties, while NFO can be completely omitted as a catalyst modifier during synthesis of the C_{100}SOY-DCPD copolymer, suggesting the monomer reactivity order C_{100}SOY > DCPD > SOY.[68]

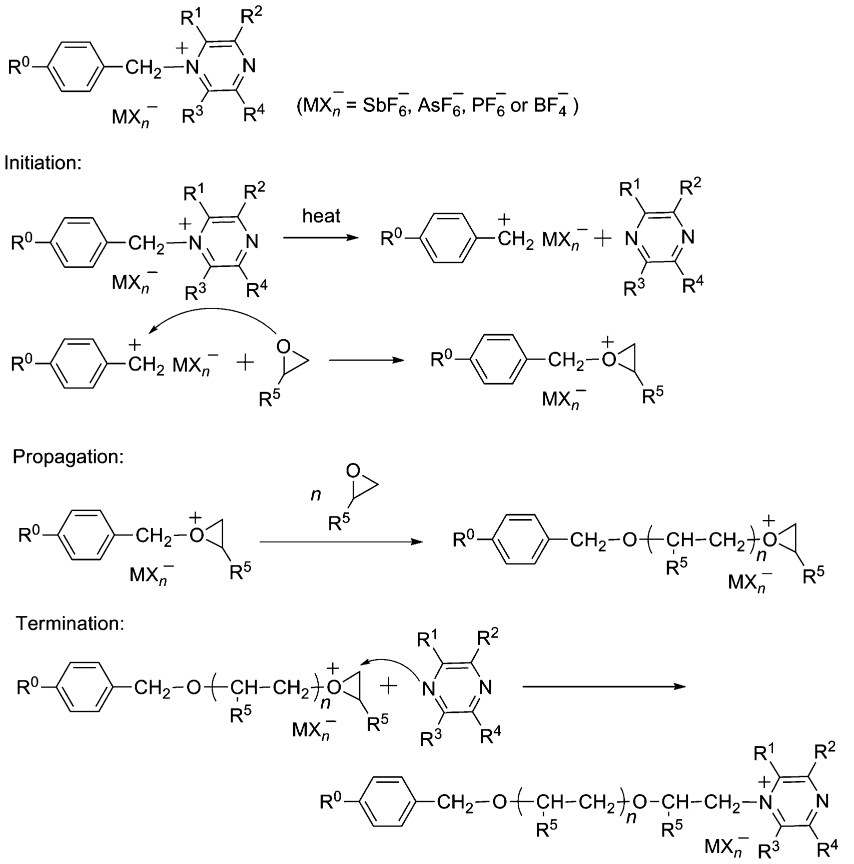
Recently, the modified linseed oils Dilulin and ML189, which have similar reactivity to DCPD, have been copolymerized with DCPD to give homogenous thermosets without using NFO-modified catalysts.[69] Dilulin and ML189 (Scheme 13) are commercially available oils. Dilulin is synthesized by a Diels–Alder reaction between linseed oil and cyclopentadiene,[70] while ML189 is obtained by an ene reaction between cyclopentadiene and the bis-allylic hydrogens in linseed oil.[71] The norbornene ring and the cyclopentene ring present in the linseed oil fatty acid chains of Dilulin and ML189 respectively increase the oils' reactivity and homogeneous polymers containing 57–97 wt% of Dilulin/ML189 are obtained without the use of fish oil-modified catalysts. The Dil/DCPD and ML189/DCPD copolymers obtained have T_gs ranging from 15 to 83 °C and 8 to 77 °C, respectively, and increase linearly with an increase in the amount of DCPD.[69]



Scheme 13 Representative structures of Dilulin and ML189.[69]

4.2. Cationic polymerization of vegetable oil epoxides

"Latent initiators" have been used to cationically polymerize epoxidized vegetable oils.[72–76] Latent initiators make possible controlled polymerizations where there is no activity under normal conditions, but active species are formed which will initiate polymerization only under certain situations, such as



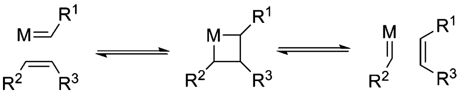
Scheme 14 Structure of benzylpyrazinium salts and their cationic polymerization.[77]

heating or photoirradiation.[77] Benzylpyrazinium salts have been used widely as thermally latent cationic polymerization initiators. Scheme 14 shows its structure and polymerization mechanism. The activity of pyrazinium salts can be controlled by electronic modification of the benzyl and pyrazine groups.[77]

Park *et al.*[76] polymerized epoxidized soybean oil (ESO) and epoxidized castor oil (ECO) cationically with a latent thermal catalyst, *N*-benzylpyrazinium hexafluoroantimonate (BPH). The cured ECO samples were found to have higher T_gs and lower coefficients of thermal expansion compared to those of ESO, resulting from an increased intermolecular interaction in the ECO/BPH system. ESO and ECO have also been copolymerized with the diglycidyl ether of bisphenol A (DGEBA) to give polymers with better mechanical properties.[72,73,75] For example, 10 wt% of ECO in DGEBA affords epoxy resins with better mechanical interfacial properties, because the addition of a large amount of soft segments in the ECO reduces the crosslinking density and results in an increased toughness in the blends.[75]

5. Vegetable oil-based polymers from olefin metathesis polymerization

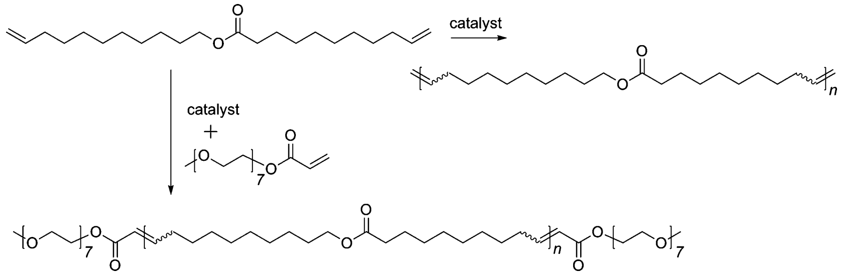
The olefin metathesis reaction was first discovered in 1964.[78] It is believed to occur through a metallacyclobutane intermediate formed between a metal alkylidene and an olefin[79] (Scheme 15). Transition metal salts combined with main group organometallic reagents or deposited on solid supports, such as WCl_6/Bu_4Sn, $WOCl_4/EtAlCl_2$, MoO_3/SiO_2, and Re_2O_7/Al_2O_3, were used to effect olefin metathesis in the early years.[80] However, these catalysts were difficult to produce and control due to the fact that very little of the active species was actually formed in the catalyst mixtures.[80] Later on, highly reactive molybdenum and tungsten alkylidenes developed by Schrock *et al.*[81] with the general formula $(ArN)(R'O)_2M{=}CHR$ were widely used, but these catalysts are extremely sensitive to moisture and air, which limited their applications.



Scheme 15 Mechanism of olefin metathesis.

In the mid-1990's, Grubbs *et al.* developed well-defined ruthenium alkylidenes, such as $(Cy_3P)_2Cl_2Ru{=}CHPh$ (G1).[82] This catalyst can tolerate most important functional groups and is also stable to air and moisture, dramatically facilitating olefin metathesis. The mono-substitution of PCy_3 with *N*-heterocyclic carbenes in G1 resulted in 2nd generation Grubbs catalysts (G2), which afford higher activity and better thermal stability and have further expanded ruthenium-alkylidene applications in olefin metathesis.[83]

The olefin metathesis of vegetable oil derivates, such as fatty acid esters, has been investigated since 1972.[84–88] This chemistry has converted biorenewable unsaturated fatty acid esters to useful chemicals and contributed to a sustainable chemical



Scheme 16 Vegetable oil-based polymers and block copolymers obtained from ADMET polymerization.[93]

industry. A number of catalyst systems have been examined for these procedures. For example, heterogeneous supported rhenium oxide catalysts show activity at room temperature and can be regenerated many times. Homogeneous well-defined ruthenium catalysts are very effective and show high turnover numbers.[89,90] Besides producing chemicals, olefin metathesis has been used to produce vegetable oil-based polymers primarily by acyclic diene metathesis polymerization (ADMET) and ring-opening metathesis polymerization (ROMP), which are discussed below.

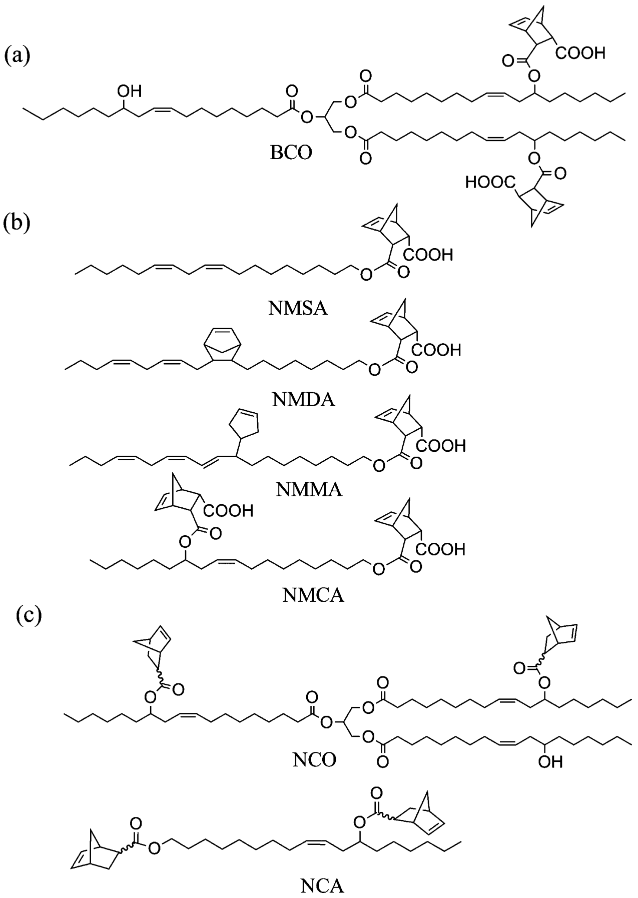
5.1. Vegetable oil-based polymers prepared by ADMET polymerization

The ADMET polymerization of soybean oil using the G1 catalyst has produced materials ranging from sticky oils to rubbers.[91,92] Recently, long-chain aliphatic α,ω-dienes from plant oil derivatives, such as undec-10-enyl undec-10-enoate, have been subjected to ADMET polymerization to give high molecular weight polymers and block copolymers (Scheme 16).[93,94] The molecular weight of the resulting polymers can be adjusted by varying the ratio of the monomer and the chain stopper. Telechelic polymers can be obtained using chain stoppers with different functional groups. Moreover, the ADMET polymerization of phosphorous-containing vegetable oil-based α,ω-dienes affords polymers with relatively good flame retardancy.[95] Acyclic triene metathesis (ATMET) bulk polymerization of glyceryl triundec-10-enoate has also been performed to give biorenewable branched polymers.[96] ATMET has also been used to polymerize high oleic sunflower oil to afford highly branched and functionalized polyesters.[97] The molecular weight of the polymers obtained could be tuned by varying the ratio of the triglyceride and methyl acrylate using an Hoveyda–Grubbs second generation catalyst. However, no cross-linking was observed when using the first generation Grubbs catalyst for the polymerization.

5.2. Vegetable oil-based polymers prepared from ROMP

ROMP polymerizes monomers containing strained rings, such as norbornene units. Vegetable oils need modification to bear such strained rings. The modified norbornene-containing linseed oil, Dilulin, has been copolymerized with dicyclopentadiene (DCPD)[98] or norbornene-containing crosslinkers[99] by ROMP to give a variety of thermosets. These thermosets exhibit phase separations due to the large difference in reactivity between Dilulin and the petroleum-based monomers.

Castor oil, where approximately 90% of the fatty acid chains bear hydroxyl groups, is a good candidate for chemical modification.[100,101] Castor oil has been reacted with a commercially available bicyclic anhydride bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride to give a norbornenyl-functionalized bicyclic castor oil derivative (BCO) (Scheme 17a).[15] BCO (55 to 85 wt%) has been copolymerized with cyclooctene catalyzed by 0.5 wt% of the G2 catalyst, affording transparent rubbery thermosets with T_g values ranging from −14 to 1 °C. Neat BCO does not undergo ROMP unless a certain concentration of cyclooctene is present, due to the high viscosity of the BCO



Scheme 17 Vegetable oil-based monomers for ROMP: (a) bicyclic castor oil derivative (BCO);[15] (b) norbornene-functionalized fatty alcohols derived from soybean oil (NMSA), Dilulin (NMDA), ML189 (NMMA) and castor oil (NMCA);[16] (c) norbornene-functionalized castor oil (NCO) and norbornene-functionalized castor oil alcohol (NCA).[102]

caused by strong hydrogen bonding between the free carboxylic acids in the monomer.[15]

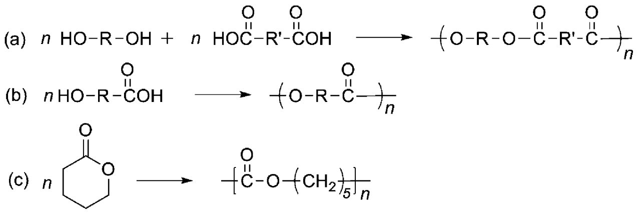
More recently, norbornenyl-functionalized fatty alcohols derived from soybean oil (NMSA), Dilulin (NMDA), ML189 (NMMA) and castor oil (NMCA) have been prepared (Scheme 17b) and polymerized with 0.5 wt% of the G2 catalyst.[16] The different groups appended to the fatty acid chains of these monomers affect both the propagation process and the final properties of the thermosets. PolyNMDA and polyNMMA exhibit Young's moduli and ultimate tensile strengths comparable to HDPE and poly(norbornene), and show promise as environmentally-friendly bioplastics with high performance.[16]

To eliminate the negative effect of the free carboxylic acid groups on ROMP, novel castor oil-based systems, norbornenyl-functionalized castor oil (NCO) and norbornenyl-functionalized castor fatty alcohol (NCA), have been developed by reacting castor oil and its fatty alcohol with norbornene carbonyl chloride (Scheme 17c).[102] The ROMP of NCO/NCA in different ratios with 0.125 wt% of the G2 catalyst resulted in rubbery to rigid transparent plastics with crosslink densities ranging from 318 to 6028 mol/m^3. The increased crosslink densities improved the thermophysical properties, mechanical properties, and thermal stabilities of the final thermosets.[102]

6. Vegetable oil-based polymers from condensation polymerization

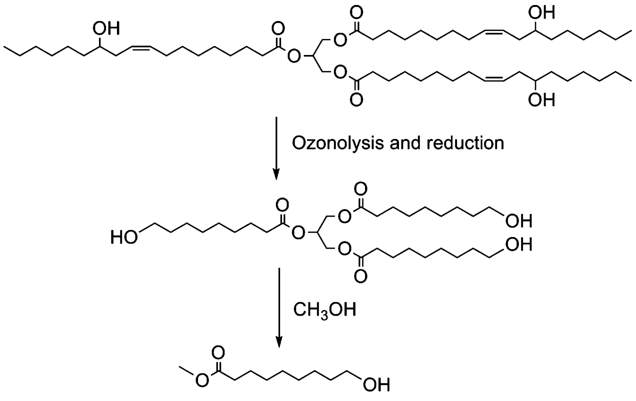
6.1. Vegetable oil-based polyesters

Polyesters can be obtained from vegetable oils by three main routes, polycondensation of a diacid and a diol or hydroxyl acids or by ring-opening polymerization of lactones (Scheme 18).[103] A vegetable oil monoglyceride, like SOMG (Scheme 9), can be reacted with an anhydride to give polyesters. Nahar seed oil monoglyceride has been reacted with phthalic and/or maleic anhydride to give polyesters, which have the potential to replace industrial polyester resins.[104]



Scheme 18 Polyester synthesis from (a) polycondensation of a diacid and a diol, (b) polycondensation of an hydroxyl acid, and (c) ring-opening polymerization of a lactone.

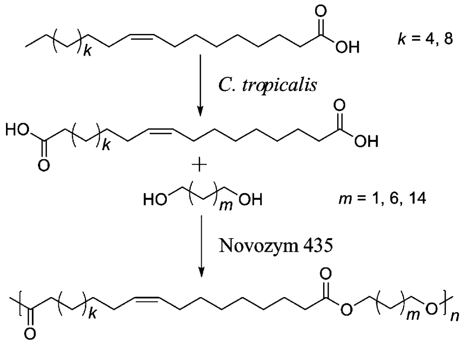
Vegetable oil-based thermoplastic polyesters have also been prepared.[105,106] Petrovic *et al.*[106] synthesized high molecular weight linear polyesters from the methyl ester of 9-hydroxynonanoic acid (HNME). High purity HNME was prepared by ozonolysis of castor oil and methanolysis of triglycerides (Scheme 19). Self-transesterification of HNME afforded a completely bio-based, high molecular weight polyester. The polyester is an analogue of polycaprolactone (PCL), but the longer hydrocarbon chain between ester groups results in a higher melting point (70 °C), a higher T_g (−31 °C), better thermal stability (~250 °C), and lower solubility in chlorinated solvents than PCL. These polyesters may have some interesting applications in industry and medicine as a replacement for PCL.



Scheme 19 Preparation of HNME from castor oil.[106]

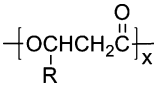
The castor oil-based hydroxyl acid, ricinoleic acid (RA), can be used to prepare polyesters as well. RA and lactic acid (LA) have been mixed in different ratios to prepare copolyesters by thermal polycondensation or by transesterification of high molecular weight PLA with RA and subsequent repolyesterification.[107–109] Interestingly, copolymers obtained by random condensation with more than 15% RA are liquid at room temperature, while copolymers made by transesterification with more than 50% RA are also liquid at room temperature. These polymers, especially the liquid polymers, might be used as sealants and injectable carriers of drugs.[107]

Biocatalytic provides another route to vegetable oil-based polyesters.[110–112] Recently, ω-carboxyl fatty acids, prepared by the whole-cell biotransformation of fatty acids, have been allowed to react with diols to prepare polyesters using immobilized *Candida antarctica* Lipase B (N435) as a catalyst (Scheme 20).[112] These polyesters containing carbon–carbon double bonds, which disrupt crystallization, have much lower melting points (23–40 °C) than analogous saturated polyesters (88 °C). Moreover, unlike polyesters from saturated diacids and diols, polyesters with unsaturation can be modified or crosslinked to develop curable coatings. Furthermore, functionalization of these polymers with bioactive moieties can be used for medical applications. These polyesters also exhibit high thermal stabilities.[112]



Scheme 20 Lipase-catalyzed polycondensation of unsaturated dicarboxylic acids with diols.[112]

Poly-3-hydroxy alkanoates (PHAs) (Scheme 21) are a class of polyesters produced by a large number of bacteria when subjected to metabolic stress.[113] The unsaturated carbon–carbon


$$\left[\mathrm{O\underset{R}{C}HCH_2\overset{O}{\overset{\|}{C}}}\right]_x$$

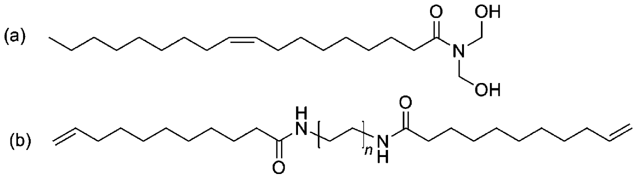
Scheme 21 Structure of a PHA.

double bonds in the alkyl side chain of PHAs can be further crosslinked to give elastomeric PHAs. It has been found that the double bond content greatly influences the autoxidation of medium chain length PHAs (mcl-PHAs).[114] A low amount of olefinic side chains (less than 10 mol%) resulted in chain scission, while samples with 50 and 75 mol % of an unsaturated moiety showed crosslinking after a few weeks. Hazer *et al.*[115,116] prepared bioelastomers by the autoxidation of mcl-PHAs consisting of a mixture of soybean oil fatty acids and octanoic acid in different weight ratios. These bioelastomers show improved mechanical strength after autoxidation. In addition, these elastomers contained no additional inorganic catalyst, which may be harmful to living systems in medical applications. In fact, *in vivo* experiments demonstrated that these PHA-copolyesters were biocompatible.[115] Other than fatty acids, linseed oil has been used as a carbon source for the production of PHAs.[117] UV-irradiation of these PHAs accelerated and enhanced the crosslinking reaction, resulting in an increase in the glass transition temperature of the polymers obtained from −51 °C to −32 °C.

6.2. Vegetable oil-based polyamides

Vegetable oil-based polyamides have been used in the ink and paint industries. Soy-based polyamides have been prepared and processed into dual-component toners, which exhibit printing performance comparable to that of a commercial toner.[118] Soy-based copolyamides have also been obtained by condensation polymerization of soy-based dimer acids, diamines and amino acids.[119] The chain structure and crystalline morphology, as well as the physical properties of the copolyamides, can be affected by the type and the content of the amino acids in the copolymers.

Another important polyamide, Nylon 11, has been developed from castor oil[120,121] using 11-amino-undecanoic acid as a monomer obtained from castor oil (10-undecenoic acid can be obtained from pyrolysis of castor oil). The product has excellent dimensional stability and electrical properties, a wide range of flexibility, a low cold brittleness temperature and good chemical resistance properties. Recently, vegetable oil-based fatty amide monomers, such as fatty amide diols (Scheme 22a) and castor oil amide-based α,ω-dienes (Scheme 22b), have been utilized to prepare polyamides by esterification[122] and ADMET polymerization,[123] respectively.

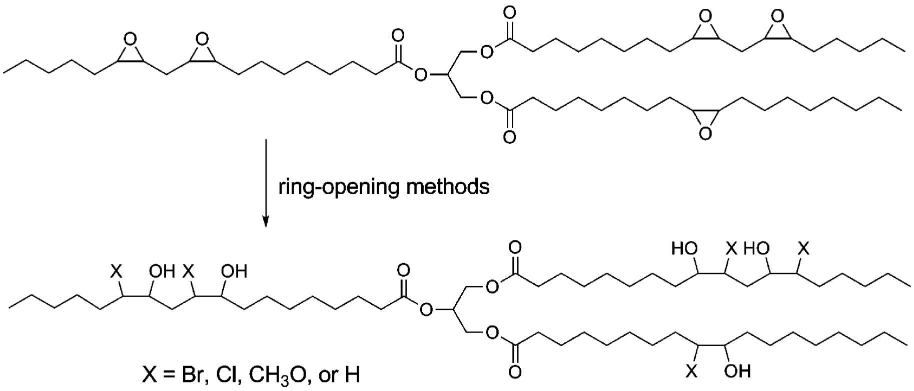


Scheme 22 Amide-based monomers from vegetable oils: (a) soybean oil-based fatty amide diols,[122] and (b) castor oil amide-based α,ω-dienes.[123]

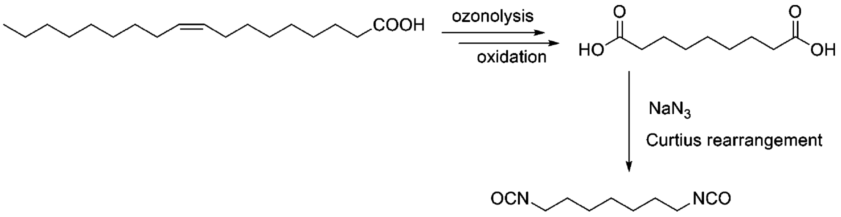
6.3. Vegetable oil-based polyurethanes

Vegetable oils can be converted into polyols, which can react with diisocyanates to give polyurethanes (PU).[17] Castor oil and its derivatives, such as ricinoleic acid, have been used to prepare PUs directly or after modifications.[124–126] These castor oil-based PUs display good mechanical properties, comparable to those of petrochemical PUs and may find applications as wood adhesives, flexible foams and hard elastomers. Polyricinoleate diols, obtained from the polycondensation (transesterification) of methyl ricinoleate with diethylene glycol as an initiator, have been copolymerized with diphenylmethane diisocyanate (MDI) and butanediol to prepare thermoplastic PUs.[127] Interestingly, "spherulitic-like" superstructures that are believed to arise from the nucleation and crystallization of the hard segments are observed in these polymers.

Vegetable oils other than castor oil can be used to prepare polyols by a variety of methods, such as ring opening of epoxidized plant oils (Scheme 23).[128] Polyols based on a variety of epoxidized oils (mid-oleic sunflower, canola, soybean, sunflower, corn and linseed oils) have been polymerized with MDI to give PUs.[129] It has been found that the differences in properties of these PU networks result primarily from different crosslink densities and less from the position of the reactive sites in the fatty acids. For example, linseed oil-based polyols, which have the highest functionality, afford PUs with higher crosslink densities and higher mechanical properties.[129]



Scheme 23 Vegetable oils prepared from epoxidized vegetable oils for polyurethane synthesis.[128]



Scheme 24 Synthesis of a diisocyanate from oleic acid.[132]

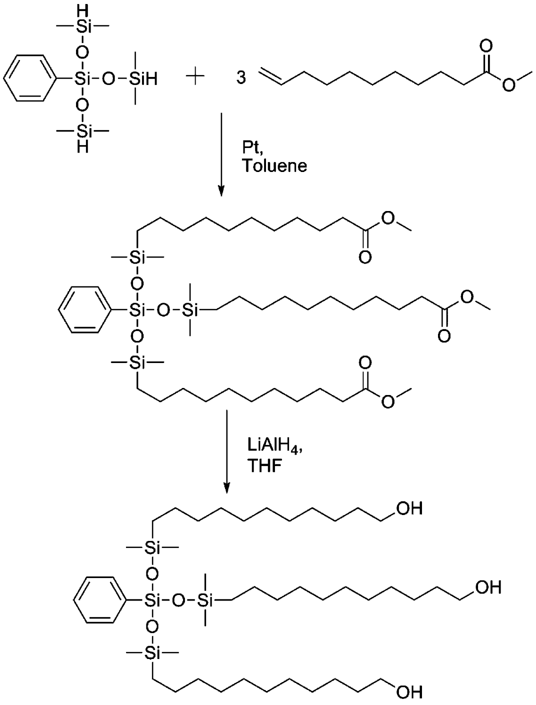
Vegetable oil-based polyols with a range of hydroxyl numbers have also been prepared by hydroformylation, reduction and partial esterification of the hydroxyl groups with formic acid. These polyols have been reacted with MDI to give PUs with different crosslink densities.[130] The heterogeneity of the polyols had a negative effect on the mechanical properties of the resulting rubbery PUs, while this effect was not obvious in glassy PUs. In addition, hydroformylation, followed by reduction, produces primary hydroxyl groups, which allow relatively better yields compared to hydroxyl fatty acids with secondary hydroxyl groups.[131]

Recently, diisocyanates derived from fatty acids have been synthesized. As shown in Scheme 24, ozonolysis and oxidation of oleic acid affords azelaic acid. This diacid has been converted to the corresponding 1,7-heptamethylene diisocyanate (HPMDI) *via* Curtius rearrangement.[132,133] Compared to the petroleum-based, commercially available 1,6-hexamethylene diisocyanate (HDI), PUs prepared from HPMDI have similar properties within acceptable limits.[132] HPMDI and HDI have also been used to prepare linear thermoplastic PUs.[133] The odd number of methylene groups in HPMDI affected the mechanical properties, because the crystal structure was less ordered and the strength of the hydrogen bonding was weaker.[133] Another biorenewable diisocyanate, L-lysine diisocyanate, has been reacted with a methyl oleate-based polyether polyol and 1,3-propanediol to give a series of PUs with different hard segment content.[134] The results revealed that the hard segment content is the main factor which affects the physical, mechanical, and degradation properties of these PUs.

A silicon-containing vegetable oil-based polyol has been prepared by the hydrosilylation of methyl 10-undecenoate with phenyl tris(dimethylsiloxy)silane, followed by reduction of the carboxylate group (Scheme 25).[135] The incorporation of silicon into the PUs does not change the thermal stability, but improves the thermal stability of the char under an air atmosphere. PUs with higher silicon content show interesting fire resistance properties due to the production of continuous layers of silica, which retard the oxidation of the char.[135]

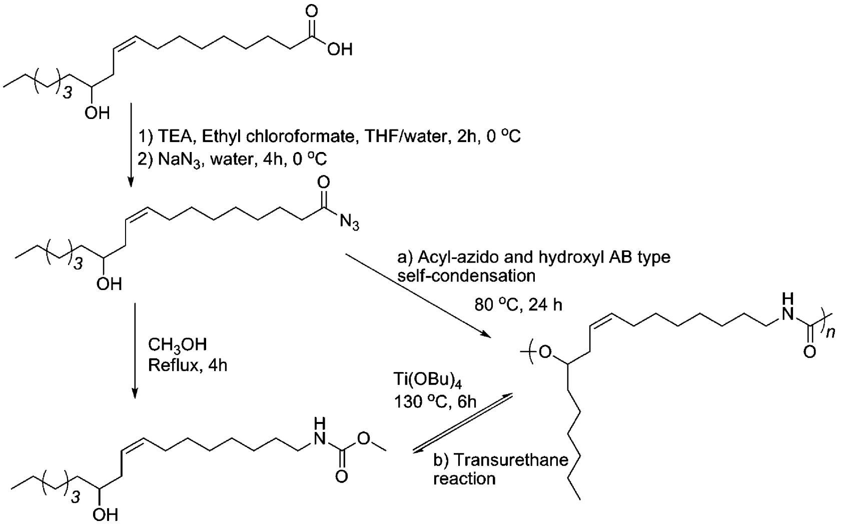
Self-polycondensation and transurethane approaches have been used to prepare PUs using methyl oleate or ricinoleic acid-based AB-type monomers (Scheme 26).[136] Two different glass transition temperatures for soft segments and hard segments were observed in these PUs, which indicates a phase-separated morphology. Both PUs obtained from ricinoleic acid by different methods had nearly the same T_g. Comparatively low molecular weights were observed for all PUs formed by both processes due to the formation of macrocycles.[136]

Environmentally-friendly, water-borne polyurethane dispersions (PUDs) with no volatile organic compounds (VOCs) have found wide applications as coatings, adhesives, and related end uses.[137–140] Previously, PUDs from castor oil[141] and rapeseed oil polyols[142] have been used to modify starch for the preparation of biodegradable plastics. The acrylic monomers, butyl acrylate and methyl methacrylate, have undergone emulsion polymerization in soybean oil-based anionic PUDs to give urethane–acrylic hybrid latexes.[143] The results suggest that the acrylates have been grafted onto the soybean oil-based urethane network by free radicals formed from reaction of the carbon–carbon double bonds in the fatty acid chains, leading to a significant increase in the thermal and mechanical properties of the resulting PUs when compared to the neat PUs.[143]

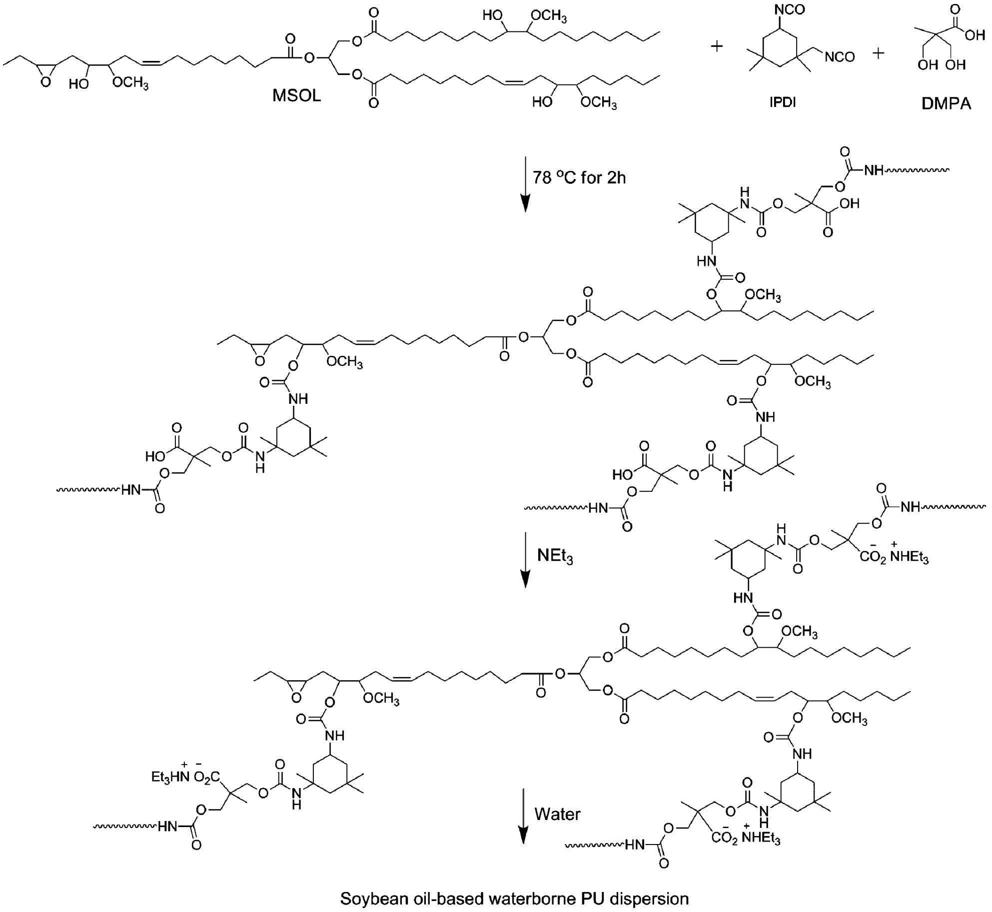


Scheme 25 Synthesis of a silicon-containing vegetable oil-based polyol.[135]

Methoxylated soybean oil polyols (MSOLs) with different hydroxyl numbers ranging from 2.4 to 4.0 have been used to prepare anionic PUDs (Scheme 27).[18] Polyurethanes obtained by reacting the MSOLs with isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA) have been neutralized by triethylamine and then dispersed in water to give soybean oil-based water-borne PUDs.[18] Increased OH numbers in the MSOLs significantly increase the crosslink density of the PUs, while increased hard segment content improves the interchain interactions caused by hydrogen bonding, resulting in biorenewable PUs ranging from elastomeric polymers to ductile plastics



Scheme 26 Synthesis of a PU from ricinoleic acid through self-condensation and transurethane approaches.[136]



Scheme 27 Preparation of soybean oil-based water-borne polyurethane dispersions.[18]

and rigid plastics.[18] These PUDs has been successfully used to prepare surfactant-free core-shell dispersions with 10–60 wt% of vinyl monomers.[144] The core–shell hybrid latex films obtained show a significant increase in thermal stability and mechanical properties compared to the neat PU films, due to grafting and crosslinking in the hybrid latexes.

Recently, vegetable oil-based cationic PUDs was firstly reported in the open literature.[145] *N*-Methyl diethanol amine (MDEA) has been used to replace DMPA in the anionic PUDs and the polyurethanes obtained have been neutralized by acetic acid and then dispersed in water to give cationic PUDs. Compared to anionic PUDs, cationic PUDs exhibit very high adhesion to a variety of ionic substrates, especially anionic substrates, like leather and glass, which suggest wide application as adhesives and coagulants.[146,147]

7. Summary and outlook

Vegetable oils and their derivatives have been employed as feedstocks for paints, lubricants, and coatings for a long time. Recently, polymeric systems based on vegetable oils have been developed using a variety of polymerization techniques, including free radical, cationic, olefin metathesis, and condensation polymerization. The polymers obtained range from linear thermoplastics to crosslinked thermosets, and soft and flexible rubbers to hard and ductile plastics. Some vegetable oil-based polymers show comparable or better properties compared to conventional petroleum-based polymers and may serve as replacements for them, providing solutions to increasing environmental and energy concerns.

Many challenging problems still exist and the development of better vegetable oil-based materials appears certain. For example, novel vegetable oil-based monomers can be prepared to replace petroleum-based portions of most of the current vegetable oil-based polymeric materials and thus increase the renewable resource content of the final resins. Moreover, controlled polymer architectures can be built based on vegetable oil-based monomers by employing living polymerization methods to expand the applications of these bio-based polymers. With the design and synthesis of new vegetable oil-based monomers and the incorporation of novel polymerization methods, a wider variety of renewable vegetable oil-based polymeric materials may be developed and used for various applications in the future.

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