5 Producing Monomers and Polymers from Plant Oils*

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ABSTRACT

The integration of biobased industrial products into existing markets, where petrochemically derived materials currently dominate, is a worthy objective. This chapter reviews some technologies that have been developed including olefins of various chain lengths, photocurable polymers, vinyl monomers, and biobased oxygen-containing monomers. These products are needed in large markets, such as the lubricants market, where significant economic impact is anticipated. Also, potential uses are possible in products such as absorbent materials, adhesives, coatings, elastomers, latices, paints, plasticizers, plastics, printing inks, resins, surfactants, and textiles. This chapter is divided into several closely related sections on monomers and polymers. The first focuses on hydrocarbon-based monomers from fatty acids, followed by oxygen-containing monomers from lipids, then nonlipids. The final section reviews advanced polymerization of vegetable oils. Overall, the research in this area will eventually lead to the development of direct drop-in biobased replacements for nonrenewable commodity

* Mention of trade names or commercial products in this chapter is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture (USDA).
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chemicals. This will enhance the agricultural sector while simultaneously expanding our portfolio of renewable materials and reducing dependence on petroleum.

5.1 USE OF NATURAL FEEDSTOCKS TO PRODUCE INDUSTRIAL MATERIALS

The idea that natural materials can be used to replace petroleum products has been around as long as petroleum products themselves. There are several excellent reviews on several of these topics. Some recent examples include biomass processing [1], levulinic acid from carbohydrates [2], and polymer synthesis from caprolactone [3] and carbon dioxide [4,5]. Numerous comprehensive reviews relating to industrial applications of plant oils are also well represented, dating back more than 30 years [6]. Topics such as polymers [7–10] and lubricants [11] are particularly well covered. Other nonfood industrial uses of plant oils include detergents, paints, plasticizers, linoleum, textiles [12], adhesives, cosmetics, and many others [13]. Of course, no discussion of nonfood uses of plant oils would be complete without mentioning biodiesel. This fuel is now a worldwide industry and, along with other renewable fuels, has initiated an economic linkage between the energy and agricultural sectors [14,15]. The emergence of biodiesel has resulted in a dramatic increase in worldwide production of fats and oils, which has more than doubled since 1985 when annual production was only 68.2 million metric tons [16].

Despite these examples of commercial success, the industry has been hesitant to adopt naturally derived products in greater volumes. Much of this is owing to performance and cost differences, real or perceived, that accompany biobased materials. Natural oils and fats are rightly thought to have poor oxidation stability [17,18], a characteristic that carries through into many of the industrial products derived from them. In addition, the performance of many of these renewable materials is lower than those of the conventional petrochemical products they are intended to replace.

The cost competitiveness of natural products is also an issue. Many of these raw materials, although considered commodity products, are more costly than their petroleum counterparts. Additional issues such as the need for new processing technologies, feedstock variability and availability, and the food versus fuel debate leave only a limited pool of willing industrial adopters, even with favorable life cycle assessments [19] and biopreferred programs [20]. All of these potential pitfalls emphasize the importance of targeting specific market areas for incorporation of biobased products. Those are areas where cost competitiveness and performance equality are actually possible.

One approach around this problem is to provide industry with the building blocks that they already use, but made from natural sources as opposed to petroleum. This will overcome unwillingness by industry to use biobased products, because these materials will represent direct drop-in replacements for existing petrochemically derived products. Such an approach has already been applied to liquid transportation fuels [21], and some of the attempts to produce higher-value bio-based products, such as olefinic and oxygenated monomers, are detailed in this chapter.

5.2 RENEWABLE HYDROCARBON MONOMERS FROM FATTY ACIDS

The idea of producing hydrocarbons from natural fatty acids has been around for almost 100 years, where early work used alumina catalyst and heat to achieve deoxygenation [22]. Hydrocarbon monomers from renewable feedstocks are of particular interest now, considering the ubiquitous nature of industrial polymers encountered in every facet of modern life.

There are three approaches to preparing hydrocarbons from fatty acids that have received significant attention: hydrogenation, decarboxylation, and decarbonylation (Figure 5.1). All are thermodynamically favored [23,24] to produce the desired hydrocarbon by elimination of carbon dioxide and/or carbon monoxide and/or water.
The hydrogenation of carboxylic acids and esters is the most straightforward and well studied [21,25]. A major drawback of this method is the requirement of hydrogen, which can be expensive, and its use increases the level of safety required. Additionally, it produces fully saturated hydrocarbons. These are not desirable for either fuel or lubricant applications owing to poor low-temperature properties such as pour point and cloud point.

Decarbonylation produces an unsaturated hydrocarbon as well as carbon monoxide through a mechanism that involves the coordination of a carboxylate moiety to the metal center of a catalyst in an oxidative addition. The first observation of this reaction, catalyzed by ruthenium and osmium, was made approximately 50 years ago [26]. Methodologies using palladium or rhodium catalysts to decarboxylate acids of 8 to 12 carbons were later developed [27,28] and, finally, extensions to biobased fatty acids were made [23,29–37]. Although catalytic, there are some drawbacks to this technology. First, for efficacy, the mechanism requires either the addition of or the in situ production of a hydrogen acceptor such as an anhydride. This disadvantage is best demonstrated by the example of the palladium-catalyzed decarbonylation of decanoic acid. Turnovers of up to 12,370 were observed when equimolar acetic anhydride was added, whereas less than 5 turnovers were noted without the anhydride [28].

Decarboxylation may produce either saturated or unsaturated hydrocarbons along with carbon dioxide as a by-product, which could be considered a drawback, since anthropogenic carbon dioxide emissions are implicated in global climate change. However, it is important to note that this carbon in the substrate that is converted to carbon dioxide is less than 6% of the carbon content of an 18-carbon fatty acid such as oleic acid. In other words, the amount of carbon dioxide produced is trivial compared to the carbon content of the biobased polymers possible using these monomers. Additionally, the carbon dioxide is essentially recycled back into the plant in the following growing season, thus leading to no net change in global atmospheric emissions. In contrast, carbon dioxide produced from petrochemically derived sources contributes to global anthropogenic greenhouse gas emissions because that carbon was sequestered from the atmosphere millions of years ago. Thus, a net increase in atmospheric carbon dioxide is caused by consumption of petroleum-derived products, whereas biobased materials that generate carbon dioxide are neutral or even potentially cable of causing a decrease with respect to carbon dioxide emissions. Also, hidden sources of carbon dioxide, such as those generated by the production of hydrogen, should be considered when comparing competing technologies from a carbon footprint perspective [38]. However, life cycle assessments [39] and the topic of green chemistry [40,41] as they relate to greenhouse gas emissions are beyond the scope of this introduction.

Thermal decarboxylation began with simple oxide materials [22] on various branched [42] and cyclic [43] compounds. A number of zeolites were also catalytically active [44–47] at temperatures
ranging from 370°C to 440°C. This technology is effective at producing fuels [14,48–50], but the reaction conditions are not amenable for the production of a narrow range of alkene monomers. More controllable chemistry is required to satisfy such industrial needs.

Addition of a metal catalyst that works in an oxidative mode is an approach that has gained attention. Silver in the +2 oxidation state initially coordinates to a fatty acid, which then undergoes an electron transfer that leads to a reduced silver species, a proton, and a carbonyl radical. Under most conditions, the carbonyl radical is unstable and will spontaneously decarboxylate to yield a hydrocarbon [51]. A copper cocatalyst is needed if an unsaturated hydrocarbon product is desired [52]. Although this reaction works under mild conditions, it leaves the silver and/or copper in an inactive oxidative state. Regeneration of the catalysts, therefore, requires an oxidant such as sodium persulfate.

Another method to reduce the reaction barrier to decarboxylation, without the need for sodium persulfate, is by manipulation of the isomeric structure of the substrate. Specifically, unsaturated carboxylic acids in which the double bond is conjugated or nearly conjugated with the carboxylate moiety exhibit significant enhancement in the rate of decarboxylation compared to isomers where the double bond is not proximate to the carbonyl. This is probably because of the availability of a cyclic transition state for the beta-gamma isomer, which is not possible in other isomers [42]. Therefore, decarboxylation can be conducted at considerably lower temperatures when the carboxylic acid moiety is conjugated with a double bond (Figure 5.2).

Heating plant oils results in indiscriminate isomerization [53], but controlled isomerization is needed to obtain well-defined industrial products. Iodine [13], enzymes [54], and organometallic complexes with complicated phosphine ligands [55–59] isomerize double bonds in plant oil-based materials. Transition metal carbonyls and related complexes are especially effective. In one route, iron carbonyl was used to isomerize fatty acids [60], but this catalyst is difficult to work with because of its volatility. In contrast, triruthenium dodecacarbonyl is easy to handle and will spontaneously form a catalyst precursor when reacted with a carboxylic acid [61]. This precursor facilitates isomerization of alkenes, with [62] or without [63,64] added phosphine ligands. Isomerization of the double bond of an unsaturated fatty acid into a position where subsequent decarboxylation occurs at a lower energy level is possible utilizing this precatalyst.

![Diagram](https://example.com/diagram.png)

5.3 RENEWABLE OXYGENATED MONOMERS FROM UNSATURATED LIPIDS

Renewable oxygenated monomers from plant oils have been known for decades. Classic examples include azelaic (nonanedioic), adipic (hexanedioic), and brassylic (tridecanedioic) acids, which are polymer building blocks made from ozonolysis of oleic, petroselinic, and erucic acids, respectively [65–67]. Furthermore, sebacic (decanedioic) acid is obtained via caustic oxidative cleavage of ricinoleic (12-hydroxyoctadec-9-Z-enoic) acid [68]. Linear renewable diacids are used in the manufacture of commercially important polymers as well as fragrances, lubricants, and adhesives [69]. Addition of carbon monoxide to double bonds of fatty acids also yields diacids. A branched 19-carbon diacid is produced from oleic acid. Such diacids have broad applications as monomers for lubricants, plasticizers, polyurethanes, epoxy resins, coatings, and transparent polyamide plastics [70].

5.3.1 MONOMERS BASED ON CARBON MONOXIDE ADDITION

Carbon monoxide reacts with unsaturated lipids in at least three ways: hydroformylation (oxo reaction), the Reppe reaction, and the Koch reaction (Figure 5.3). Hydroformylation yields an aldehyde intermediate that can be readily converted to an acid, alcohol, or amine to provide a 19-carbon diacid, hydroxy acid, or amino acid [70–73]. Hydroformylation of polyunsaturated fatty acids gives polyacids, polyols, or polyamines [73,74]. The Reppe reaction introduces carboxyl groups directly to unsaturated fatty acids, thereby bypassing the aldehyde intermediate [70]. Using ammonia instead of water during the reaction yields a fatty amido acid [75]. The Koch reaction is performed at lower temperature and pressure than those for the Reppe reaction but requires concentrated sulfuric acid as both a coreagent and a solvent [75]. Unlike ozonolysis, which yields linear diacids shorter in length than the starting acid, carbon monoxide addition results in branched diacids with one more carbon than the starting acid.

5.3.2 MONOMERS FROM DIMERIZATION OF FATTY ACIDS

Dimerization affords branched diacids (dimer acids) with twice the number of carbons as the starting acid. Dimer acids are prepared by heating unsaturated fatty acids under pressure in the presence of an acidic clay catalyst. Condensation of dimer acids with diamines yields polyamide resins useful as curing agents and coatings [75]. Additionally, ene reactions of unsaturated fatty acids with maleic

FIGURE 5.3 Reactions between carbon monoxide and lipids which produce lipids with increased functionality.
anhydride yield diacids. For instance, addition of maleic anhydride to oleic acid in the presence of a Lewis acid catalyst results in a 22-carbon branched diacid. Subsequent condensation with polyols affords copolymers useful as adhesives, film formers, and tackifiers [76].

5.3.3 CASTOR OIL-BASED MONOMERS

The principal fatty acid in castor oil is ricinoleic acid (Figure 5.4), which is both hydroxylated and unsaturated. As a consequence of its unique multifunctional composition, castor oil is used extensively as an industrial oil. In addition to sebacic acid mentioned previously, ricinoleic acid is used to produce a variety of products including estolides via polycondensation; polyols by transesterification with diols or other polyhydroxylated compounds; 10-hydroxydecanoic acid by low-temperature alkali cleavage; and 10-undecenoic (undecylenic) acid from pyrolysis [68, 77, 78]. Undecylenic acid is used as a platform chemical for the production of numerous monomers [79]. For example, polyamide 11 is obtained from 11-aminoundecanoic acid, which is prepared via an 11-bromo intermediate [68, 77, 78]. Dienoic monomers suitable for free radical or acyclic diene metathesis polymerization have also been prepared from undecylenic acid. These include allyl, vinyl, acrylic, and methacrylic ethers and esters, all of which have applications in the coatings industry [80]. Dienes suitable for acyclic diene metathesis polymerization include 10-undecenyl undecylenate and undecylenic acid moieties esterified to phosphorus-containing heteroaromatic cores as comonomers for flame-resistant polyesters [81, 82]. Finally, a variety of renewable monomers can be prepared via thiol-ene click chemistry in which thiolated compounds are added to undecylenic acid via a free radical mechanism to yield anti-Markovnikov products [83]. Such monomers are useful for production of ultraviolet (UV)–curable resins and coatings. Specific examples of monomers from undecylenic acid include those derived by addition of butanediol, thioacetic acid, thioglycerol, 4-hydroxybutanethiol, and methyl 2-mercaptoacetate, among others [83–85]. Methyl 9-decenoate (Figure 5.5 and next subsection), prepared by cross metathesis of methyl oleate with ethene (ethenolysis), represents the 10-carbon analogue of methyl 10-undecenoate [86].

5.3.4 MONOMERS SYNTHESIZED USING ALKENE METATHESIS

Olefin metathesis is a versatile method for building carbon–carbon bonds and has been exploited by the petrochemical industry for decades using molybdenum- and tungsten-based catalysts.

FIGURE 5.4 The structures of methyl oleate and the common fatty materials from castor and meadowfoam oils.
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The reaction proceeds by the cleavage and reformation of carbon–carbon double bonds and the simultaneous exchange of substituents. The fundamental metathesis transformations include self-metathesis, cross metathesis, ring-closing metathesis, ring-opening metathesis acyclic diene metathesis polymerization, and ring-opening metathesis polymerization. Application of metathesis chemistry to fats and oils was limited until the discovery of active ruthenium catalysts by Grubbs, which, in 2005, earned him the Nobel Prize in Chemistry [87]. Olefin metathesis is an appealing industrial reaction because it is cost effective and catalytic, generates almost no unusable by-products, and is easily scalable [88]. Major petrochemical applications of metathesis include conversion of relatively inexpensive propene into more valuable ethene and butene by the Shell Higher Olefins Process, to produce linear alpha olefins and their derivatives from oligomerized ethene [89].

Self-metathesis of fatty acids by using Grubbs catalysts is an efficient route to unsaturated diacids. For instance, self-metathesis of methyl oleate affords, as one of its products, an 18-carbon α,ω-diester which can be converted to an 18-carbon α,ω-dicarboxylic acid by hydrolysis of the ester groups [90]. Methyl 9-decenoate also yields an 18-carbon α,ω-dicarboxylic acid after self-metathesis and hydrolysis [91]. A mixture of diacids of differing chain lengths is obtained by isomerizing the double bonds in the fatty acids prior to self-metathesis or concurrently with the addition of isomerization catalysts compatible with ruthenium metathesis catalysts [92,93]. Metathesis itself may lead to isomerization, especially if older-generation molybdenum- and tungsten-based catalysts are used. Unwanted isomerization complicates the product mixture and reduces the yield of the intended product [94]. Fortunately, olefin isomerization during metathesis can be prevented with a radical quencher such as 1,4-benzoquinone [95]. Cross metathesis and hydrolysis of unsaturated fatty esters with short-chain unsaturated diesters yield diacids with chain lengths different from those of diacids obtained from self-metathesis. For example, methyl oleate cross metathesized with dimethyl 3-hexenedioate and diisopropyl 4-octenedioate generates 12- and 14-carbon unsaturated diesters, respectively [96].

Cross metathesis of fatty acid alkyl esters with alkenes is a versatile route to fatty esters with double bonds located at specific positions. For instance, metathesis of ethene with methyl oleate yields methyl 9-decenoate and 1-decene (Figure 5.5), which can be used as the starting point for a variety of chemistries [86]. Metathetical cleavage of meadowfoam oil methyl esters (Figure 5.4) with ethene provides methyl 5-hexenoate along with 1-hexadecene. Subsequent self-metathesis of

methyl 5-hexenoate affords dimethyl 5-decenedioate as a diester suitable for polymerization [97]. Other alkenes such as 1- and 2-butenes, pentene, 1-hexene, 1-heptene, 2- and 4-octenes, 1-decene, and 1-octadecene have also been cross metathesized with plant oils and fatty esters [75,98,99]. Further transformation of these cross metathesized products at the double bond position yields various α,ω-bifunctional compounds suitable for polymerization, including diacids, amino acids, and cyano acids [100,101]. Additional functional groups can also be introduced by cross metathesizing fatty esters with functionalized alkenes such as methyl acrylate, allyl chloride, acrylonitrile, and fumaronitrile [102–107]. The nitrile group is then readily converted to an acid or amine, thus providing starting materials for the synthesis of polyesters and polyamides [100,101]. Similarly, α,ω-aminooesters are prepared from fatty esters via simultaneous cross metathesis with acrylonitrile and hydrogenation [108]. Lastly, cross metathesis of methyl oleate with 1-allyl-2,3-acetonide-glycerol followed by deprotection (to remove the acetonide-protecting group) and dihydroxylation of the double bond affords a fatty polyol [109].

In the industrial use of metathesis technology, the 18-carbon diacids from self-metathesis of oleic-rich oils serve as precursors to polyamides, polyurethanes, lubricants, and adhesives. Other products from the cross metathesis reaction with ethene of high-oleic plant oils to yield 1-decene and methyl 9-decenoate (Figure 5.5) are also industrially significant [88]. Decene is a valuable α-olefin used in the production of polyalphaolefins (PAOs) and other important chemicals [110]. However, markets for and applications of methyl 9-decenoate are still under development. In addition, practical and scalable methods for production of this emerging biobased chemical intermediate are needed. Existing literature on chemical modification of methyl 9-decenoate includes metathetical dimerization to yield an 18-carbon diacid, identical to that obtained from self-metathesis of methyl oleate [111]. Other chemical modifications include oxidative hydroformylation to yield an 11-carbon diacid for polyesters; derivatization to 10-aminodecanoic acid needed for nylon-10 production; and epoxidation to 9,10-epoxycyclo-

5.4 RENEWABLE OXYGENATED MONOMERS FROM NONLIPIDS

A number of nonlipid, biobased, polymerizable carboxylic acids can be obtained from fermentation of glucose and other simple sugars [25]. This also represents an important avenue in the synthesis of monomers from biobased materials.

5.4.1 ACRYLIC AND METHACRYLIC ACIDS FROM HYDROXYPROPYLIC AND ITAONIC ACIDS

The most commercially significant acids are succinic, lactic, itaconic, 3-hydroxypropionic and glutamic acids [117–121]. Subjection of these fermentative products to organic synthesis yields monomers such as maleic acid from 3-hydroxypropionic acid, acrylic acid from lactic and 3-hydroxypropionic acids (Figure 5.6), and methacrylic acid from itaconic acid (Figure 5.7) [122–126]. Noncarboxylic acid monomers obtained from simple sugars include 1,2-propanediol from lactic acid, 1,3-propanediol from 3-hydroxypropionic acid, 1,4-butanediol from succinic acid, and acrylonitrile from 3-hydroxypropionic acid [127–129]. Additionally, terephthalic acid can be obtained from simple sugars as well as from lignin [130].
5.4.2 Applications of Acrylic and Methacrylic Acids

Acrylic and methacrylic acids are of particular interest because their respective polymers have well-established industrial applications. For instance, methyl, ethyl, butyl, and 2-ethylhexyl acrylates are polymerized with several comonomers, including methyl methacrylate, vinyl acetate, styrene, acrylonitrile, and maleic anhydride, to yield commercially important coatings, plastics, adhesives, elastomers, fibers, absorbent materials, polishes, and paints [110,131]. The principal application of methyl methacrylate is homopolymerization to provide poly(methyl methacrylate) (Plexiglas®) as a lightweight and shatter-resistant transparent thermoplastic, which serves as a versatile alternative to glass. It is also an essential component in the polymer dispersion systems of coatings and paints [110,131,132]. Both acrylic and methacrylic acids and their corresponding esters are produced globally on a large scale, each exceeding 3 million metric tons of annual production. In addition, the market for each is projected to increase in coming years, especially in China and India. The rapidly growing construction industry in emerging economies, such as China and India, has propelled the growth of acrylic acid and its derivatives in the Asia-Pacific region. The current market prices for methyl methacrylate and acrylate esters are approximately $1.30/lb and $1.10/lb, respectively. These translate to total market values well in excess of $8 billion annually for each monomer [133,134].
5.4.3 Traditional Routes to Acrylic and Methacrylic Acids

The traditional petrochemical route to acrylic acid begins with catalytic oxidation of propene to yield acrolein followed by a second catalytic oxidation to provide acrylic acid (Figure 5.6) [110,131]. The classic route to methacrylic acid begins with condensation of acetone with hydrocyanic acid to give an acetone cyanohydrin intermediate (Figure 5.7). Dehydration and hydrolysis of the nitrile group with a stoichiometric excess of concentrated sulfuric acid at 140°C provide methacrylic acid along with ammonium bisulfate by-product that is produced in a ratio of 1.5:1 relative to methacrylic acid [110,132]. Both of these routes are environmentally unfriendly because they use nonrenewable starting materials, utilize stoichiometric amounts of harmful reagents, generate toxic intermediates, and, in the case of methacrylic acid, produce a large amount of low-value by-product. As a consequence, biobased routes to these industrial chemicals are of interest to overcome the deficiencies in the conventional petrochemical production methods.

Catalytic conversion of lactic acid to acrylic acid through dehydration has long been of interest. Unfortunately, side reactions leading to acetaldehyde, propionic acid, 2,3-pentanedione, and dilactide via decarbonylation/decarboxylation, reduction, condensation, and self-esterification, respectively, result in low yield and low selectivity [135,136]. Several methods of acrylic acid synthesis from lactic acid have been reviewed elsewhere [25,137]. Acrylic acid can also be obtained by catalytic thermal dehydration of 3-hydroxypropionic acid, at temperatures between 140°C and 160°C, in the presence of added copper powder to inhibit polymerization [137]. Methyl acrylate is obtained when methanol is present in this reaction [138]. Use of heterogeneous catalysts, such as NaH2PO4 and CuSO4, supported on silica gel and zeolite H-beta, has also been reported [139]. The key problems limiting commercial production of acrylic acid from lactic and 3-hydroxypropionic acids include low yield, high temperatures, high pressures, expensive catalysts, and difficulty in removing prevalent by-products due to poor selectivity [25,135]. Recently, a two-step catalytic process for production of acrylic acid at 300°C has been reported. In the procedure, glycerol was first dehydrated to acrolein using the catalyst Cs2.5H0.5PW12O40 supported on Nb2O5. This is followed by an oxidation step using vanadium–molybdenum mixed oxides supported on silicon carbide. Unfortunately, this method produces numerous by-products including propionic acid, acetone, allyl alcohol, acetol, acetaldehyde, acetic acid, carbon monoxide, and carbon dioxide [140].

5.4.4 Biobased Acrylic and Methacrylic Acids

Comparatively few biobased syntheses of methacrylic acid have been reported. One such approach is liquid-phase dehydration and decarboxylation of citramalic acid, at temperatures of 250–400°C and pressures of 3.1–27.6 MPa (450–4000 psi), in the presence of basic and/or acidic catalysts. Application of this methodology to maleic acid yields acrylic acid [141]. Another approach relies on biomass-derived ethene, carbon monoxide, and methanol in a two-step procedure referred to as the alpha process to yield methyl methacrylate [142]. The first step entails catalytic carbonylation of ethene in the presence of carbon monoxide to yield methyl propionate. In the second step, methyl propionate is converted to methyl methacrylate by using formaldehyde [143]. However, such a methodology requires considerable processing and purification of the biomass source to obtain the necessary chemical feedstocks, i.e., ethane, carbon monoxide, etc., and the processing steps themselves consume considerable quantities of fossil fuels. Another method involves conversion of citric acid to itaconic acid, followed by decarboxylation of itaconic acid in the presence of bases. Methacrylic acid could be formed under near-critical and supercritical water conditions [125]. However, appreciable accumulation of unwanted by-products such as 2-hydroxybutyric and crotonic acids was noted. In addition to low selectivity, high temperatures (>350°C) were required and yields are relatively low (70% or lower). In an optimized supercritical water procedure, selectivity was improved to over 90% and reaction temperatures were lowered slightly, to 245–270°C, and pressures were lowered to 3.1–20.7 MPa (450–3000 psi). However, stoichiometric amounts of base catalysts were...
used, and by-products such as crotonic and 2-hydroxybutyric acids were still produced along with propene.

5.5 RENEWABLE POLYMERS FROM PLANT OILS

Polymeric materials prepared from renewable natural resources are becoming increasingly important because of their low cost, ready availability, and possible biodegradability [144]. Plant oils are considered the most important class of agriculturally based raw materials for polymer synthesis.

5.5.1 WORLD PLANT OIL PRODUCTION

Worldwide plant oil production has increased continuously in the past decade, currently reaching more than 129 million metric tons annually [145]. The majority of growth has been in palm oil, representing more than 30% of plant oil production in 2007, with soybean (28%), rapeseed (15%), and sunflower (9%) accounting for most of the remaining production. Soybean oil is reasonably inexpensive and one of the most readily available renewable resource currently available in the United States. In addition to numerous applications in the food industry, soybean oil is utilized extensively to produce industrial products such as coatings, inks, plasticizers, lubricants, fuels, and agrochemicals [146–152]. Within the polymer field, plant oils have been utilized as toughening agents [153,154], polyol components in polyurethanes [155–157], polymeric surfactants [158,159], plastics [160–162], composites [163–165], and pressure-sensitive adhesives [166].

5.5.2 EPOXIDATION OF PLANT OILS

Plant oils can be chemically modified for use in most of these applications. The most common chemical modification is epoxidation, where plant oils are subjected to the Prilezhaev reaction. A percarboxylic acid, such as peracetic or performic acid, is generated in situ by the acid-catalyzed reaction of formic or glacial acetic acid with hydrogen peroxide. The peracid then reacts with olefinic moieties to yield epoxidized plant oils containing three-membered ring epoxy structures, also called oxiranes [75]. Epoxidized triacylglycerols have shown promise for use in industrial applications such as in coatings, inks, and adhesives [167]. Epoxidized plant oils can also be polymerized in the presence of curing agents, such as diamines [168], or by ring-opening catalysts such as Lewis acids [169]. This curing process transforms the relatively low-molecular weight oil into a highly cross-linked network with properties ranging from a high-viscosity liquid to a solid composite panel [170]. Generally, the curing agent attaches to one of the carbons of the epoxide group to yield an ester, ether, or amine linkage. This results in the formation of a hydroxyl group on the other carbon of the epoxide moiety. The most successful use of an epoxidized triacylglycerol is epoxidized soybean oil (ESO), which is commercially available under the brand name Vikoflex 7170 (Arkema). ESO is widely used as a nontoxic stabilizer and plasticizer and potentially can replace phthalates in plastic plasticizers, where it imparts desired properties such as increased flexibility, stability, and improved processing conditions [171].

5.5.3 ACRYLATED EPOXIDIZED SOYBEAN OIL (AESO)

AESO is synthesized by the reaction of acrylic acid with ESO (Figure 5.8) and is commercially available under the brand name Ebecryl 860 (UCB Chemical Company) [172]. AESO has numerous direct applications including surface coatings and films, inks, pressure-sensitive adhesives, and matrix material for fiber composites [173,174]. AESO is also a versatile chemical intermediate owing to the presence of residual reactive epoxy functionalities [172]. However, pure AESO polymers do not exhibit strong mechanical properties. They are amorphous cross-linked rubbers which cannot be processed into useful shapes. An approach to improve the mechanical properties of poly-AESO,
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or other polymeric material for that matter, is to use nanosized fibers and proteins as reinforcing fillers. O'Donnell et al. [175] prepared a composite of AESO resin and natural fiber mats made from flax, cellulose, pulp, and hemp. The composites are cured at room temperature, and a natural fiber reinforcement of 10–50 wt% increases the flexural modulus into a range between 1.5 and 6 GPa. Nanocomposites of AESO and organically modified montmorillonite have also been reported [176,177]. Shibata described the photocuring of AESO with a low-molecular weight organic substance, (R)-12-hydroxystearic acid (HSA), as a gelator [178]. Shibata found that the flexural strength and modulus decreased with increasing HSA concentration because the HSA crystalline phase was distributed heterogeneously in the cross-linked AESO resin matrix. The problem was that the cross-linked AESO has a lower affinity for HSA than that of a cross-linked ESO material. Habib and Bajpai [179] reported the preparation of coating films from AESO and trimethylolpropane trimethylacrylate with a benzophenone photoinitiator using a dimethylethanolamine activator. Polymeric films were formed under UV radiation and showed good thermal stability with a decomposition temperature of 200°C. However, no mechanical properties of the films were reported. López and Santiago [180] reported the reaction of AESO with butyl methyl acrylate and acrylamidomethyl cellulose acetate butyrate copolymers. They prepared composites based on these copolymers and carbon black conductive particles. They suggested the use of their composites for electrostatic protection and electromagnetic shields. They predicted that these conductive polymers would be useful for applications such as sensors for vapors, gases, and toxic or inert substances [181–183].

The previous studies indicate that smaller fillers and strong interactions between filler and the polymer matrix tend to improve the composite modulus. For example, soy-based protein is often used as renewable and reliable natural fiber filler. Its efficacy is enhanced by its structure where it forms fractal-like nanoparticle aggregates [184–186] that are rigid ~10 nm protein units with elastic moduli around 2 GPa [187]. It is an effective biomaterial for enhancing the mechanical properties of soft polymers. The conversion of wood and plant fibers into cellulose nanowhiskers/nanofibers has attracted much attention for the application of cellulose in polymer nanocomposites. Three-dimensional nanoporous cellulose gel has been readily prepared by an aqueous alkali hydroxide–urea solvent method developed by Cai et al. [188]. The resulting materials show high mechanical strength, high light transmittance, and high nanometer-scale porosity, owing to strong interchain hydrogen bonding and entanglement of cellulose chains [188–191]. They are useful in producing mechanically tough, foldable, and transparent cellulose bioplastics [192], and can be converted into hydrogels and organogels by solvent exchange processes [188–192].

5.6 CONCLUSION

Currently there is a need to increase the use of biobased materials in industry, especially in the lubricant industry. This review covers some developments relevant to the production of biobased drop-in replacements for petrochemicals. These include alkenes, which are important building blocks for PAOs and poly(internal olefin) lubricants. Also, acrylic acid and methacrylic acid are important in many commercial polymers. Development of biobased routes to existing industrial chemicals avoids the conundrum of new materials in search of a use or application. Also covered in
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this review is a process of using soybean oil directly through a method of epoxidation followed by reaction with acrylic acid. This process has potential for the manufacture of high-strength materials that can be easily cured into a variety of useful products.

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