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Bio-Based Plant Oil Polymers and Composites

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BIO-BASED PLANT OIL POLYMERS AND COMPOSITES

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Preface

Most plastics are produced entirely from petroleum. However, the volatility of oil markets and diminishing petroleum reserves have motivated a desire to reduce dependence on petroleum products. Together with an increase in environmental awareness, this has promoted the development and use of alternative, biorenewable, environmentally-friendly plastics from biomass. The growing interest in replacing petroleum-based products by inexpensive, renewable, natural materials is important for sustainable development into the future and is already having a significant impact on the polymer industry and the environment. Plant oils represent one of the most promising renewable resources that can be used to create and develop a new class of bioplastics and composites with tailored multifunctional properties due to their unique chemical structure. Recently, polymers and composites derived from plant oil-based monomers have shown thermo-mechanical properties that rival those of their counterparts from petroleum because of the intrinsic structure and unique properties of plant oils. Additionally, new novel technology has improved the physical and thermo-mechanical properties of biobased polymers and enabled multifunctionality, such as antibacterial behavior, which further promotes their application in new areas, including sensors and medical devices.

In *Bio-Based Plant Oil Polymers and Composites*, we describe some of the latest technologies in the development of polymeric materials and composites from plant oils (thermoplastics, thermosets, nanocomposites, and fiber-reinforced composites) and summarize their applications. This book is likely to be of immediate practical interest to academic researchers, industrial scientists, engineers, and students in the fields of materials science and engineering and polymer science. The timeliness of the text owes to the increasing transformation from a fossil resource dependent society into a society dependent on renewable resources.

This book covers details of the preparation, characterization, and applications of vegetable oil-based polymers and composites. Chapter 1 describes sources, types, properties, structures, traditional usage, worldwide production (quantity/distribution), quality, and purity of plant oils. Chapter 2 describes important industry chemicals derived from plant oils, such as biofuels, lubricants, and adhesives, and examines their properties relative to their nonrenewable counterparts. Chapter 3 discusses the development of plant oil-based polyols for polyurethanes via different methods. This chapter also reports some critical applications of polyurethanes and waterborne polyurethane dispersions. Chapter 4 presents the development of plant oil-based polyhydroxyurethane and its advantages compared with traditional polyurethane products. Chapter 5 discusses the development of unsaturated polyester resins and its application as biomaterials and damping materials. Chapter 6 reports the fundamental aspects of plant oil-based polyether synthesis, processing, and characterization. Chapter 7 details the epoxidation method of plant oil, the ring-opening reaction of epoxidized vegetable oil by different initiators, and the polymerization of the epoxidized plant oils using different hardeners. Chapter 8 discusses polymer synthesis by various enzymes as well as modification of plant oil as monomers for polymeric materials by catalyzing oxidation, reduction, and transesterification reactions. Chapter 9 highlights substantial enhancement in mechanical, thermal, and dielectric properties of plant oil-based polyurethane by three different types of surface-modified and functionalized nanofillers including lignin, graphene, and carbon nanotubes. Chapter 10 presents plant oil-based composites reinforced with fibers, such as long glass fibers and banana fibers. The reinforcement mechanism and the treatment of fiber surfaces for improved interfacial strength are also discussed. Chapter 11 discusses the applications of plant oil-based products in structural health monitoring. Finally, Chapter 12 covers the current application of essential oils as pest control products and its prospection and future.

1 Introduction to Plant Oils

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1.1 Introduction

Plant oils is a class of lipids that have low melting points, are primarily long chain hydrocarbons, and have varying degree of unsaturation. Plant oils are a potentially renewable feedstock to a variety of industrial or consumer products that has not been fully exploited [1–3]. Plant oils can be classified into two main classes based on their biosynthetic origin namely, (i) fatty acids and their glycerol condensation products [4], and (ii) isoprenoid derived hydrocarbons and their condensation products. In most literature related to biorenewable feedstock, especially those focused on polymerization [5–22], fatty acid-derived oils bear the most significance since they can be extracted in significant quantities. Composition of fatty acids, and therefore their condensed triglycerides, show little variation within a species and has become a good target for chemotaxonomy [2]. Plant biosynthesis has evolved a mechanism to keep the melting points of fatty acids as low as possible, hence

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their oily nature. This evolutionary strategy has led to these fatty acids having, preferentially, functional groups that are associated with low melting points [2]. The isoprenoid-derived oils (commonly known as essential oils), though less explored, offer an opportunity to increase complexity of products derived from plant oils and as such are reviewed in this chapter alongside the triglyceride-based plant oils. Plant oils are chemically heterogeneous.

A majority of plant oils, however, has high quantities of triglycerides (>80%), with the rest of the oil being primarily di- and monoacylglycerols, phospholipids, terpenes, sterols, and fat-soluble vitamins. Plant oils are therefore named according to their biological origin – mostly based on the plant name; for example, soy oil and castor oil – even though every oil has unique physical (e.g., melting temperatures, density, and refractive index) and chemical properties. To assess the chemical quality of the oil, several metrics have been adopted. These metrics include (i) hydroxyl value (number of free –OH groups), (ii) acid value (free –CO_2H groups), (iii) olefin or iodine value (number of free C═C bonds), and (iv) peroxide value (measure of oxidative degradation) (Figure 1.1).

Plant oils have been used in many forms throughout the history of mankind. From lighting [4], lubricants [4], paints in ancient art [23], perfumes, fragrances, to polymer synthesis in recent years [14,24–27], humans have adopted plant-derived oils for a myriad of uses. More recently plant oils have come to prominence as an alternative source for products, like polymers, that have primarily been derived from petroleum. The challenge of sustainability in the petrochemical industry has pushed the need for other sources of industrial feedstock and/or more environmentally benign sources. Better agricultural practices have also helped promote biorenewables as a feasible source of industrial feedstock without jeopardizing global food security.

World production of oil producing crop has been on the rise since the 1980s with current production rising to billions of pounds per year (Table 1.1) [3,28]. Brazil, for example, is projected to produce 95.5 million tons of soybeans in 2015 (17% increase from 2014, and >500% increase since 1980) [28]. The ability

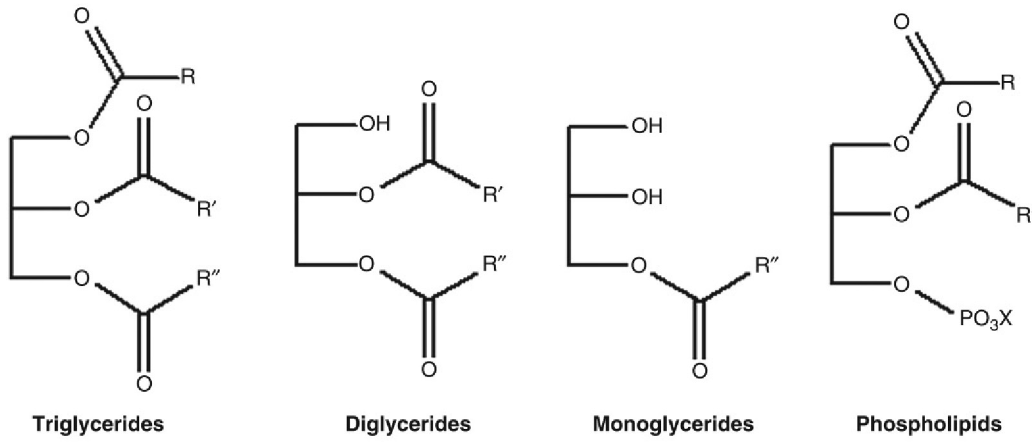

Figure 1.1 General chemical structure of triglycerides, the primary structure on which bulk plant oils are based. The structure is derived from condensation of a carbonyl moiety with a glyceride unit to give mono-, di-, or triglycerides. In some cases, the hydroxyl moiety of the parent glyceride unit contains a phosphate to give phospholipids.

Table 1.1 Production of Grains and Oil-Producing Crops Between 2001 and 2015 Shows Significant Increase in the Global Production (in Million Metric Tons) [28]

Year	Wheat	Coarse Grains	Total Grains	Oilseed	Cotton
2013	658	1136	2266	475	124
2014	715	1278	2471	504	120
2015	723	1272	2472	532	119

to optimize agricultural output, either through mechanization and better farming methods or science and technological advancements, has allowed previous low producing countries to emerge as leaders in cultivation of oil producing plants. For example, palm oil production in Malaysia has gained prominence due to the adaptation of the African palm tree in Southeast Asia while soybean farming in Brazil has benefited from mechanized farming [29,30]. It is projected that agricultural output for grains and oilseed will increase, especially with the developing and emerging economies adopting better farming practices.

Plant oils are often obtained as a mixture of compounds making their use in polymer synthesis, in their crude form, a challenge. As a caution, however, the chemical composition of any plant oil can only be roughly defined since, like all natural product blends, it depends on (i) the plant cultivar, (ii) growing conditions, (iii) part of the plant from which the oil is extracted, and (iv) the health of the plant. Soy oil, for example, is rich in triglycerides (99%) but also contains about eight major fatty acids [31]. Besides variation in chemical identity, fatty acid chains in soy oil have different number of carbons and different degrees of saturation. Postextraction chemical modification, however, allows for the oils' complexity to be narrowed down for applications that require isotropic composition. In some cases, however, the diversity in chemical functionalities is desired. Paints and coating, for example, have been a historically unique application of plant oils since unsaturation in the oils leads to cross-linking and/or polymerization on exposure to ambient conditions.

This chapter reviews aspect of plant oils that are relevant to a multidisciplinary audience with a bias toward polymer synthesis and engineering application. Plant oils cover a breadth of compounds that would be difficult to review in a single chapter. The most pertinent information regarding biosynthesis, reactivity, sources, production, and processing is given.

1.2 Chemistry and Biochemistry of Plant Oils

With advances in genetic engineering, and a growing demand for plant-derived industrial feedstock, understanding the biosynthetic origin of a desired product can motivate genetic engineering of different organisms to maximize bioproduction. A brief overview of both the isoprenoid-derived oils (essential oils) and the fatty acid precursors to glycerides is given below. This is not an exhaustive review but rather points at the differences between the two mechanisms, with a special emphasis on key steps or unique intermediates.

1.2.1 Biosynthesis of Terpenoids

There are two major classes of plant oils, glycerides (major) and terpenoids (minor) [32,33]. Most low molecular weight plant oils belong to the terpene family, one of the most structurally diverse class of compounds [33]. Terpenoids are derived from an isoprene unit (Figure 1.2a). Terpenoids are structurally diverse and contain C═C, carboxyl and hydroxyl groups among others (Figure 1.2). The smaller terpenes (Figure 1.2b) can either be linear or cycloalkyls with various degrees of oxidation and stereochemical compositions. The ability of elongated isoprenes to cyclize can lead to aromatization to give elaborate structures that can be used in polymer synthesis (Figure 1.2c). Although less common, isoprenoids can condense with glycols through ether linkages (e.g., phytonyl glycerol, Figure 1.2b). These alkylated glycerols are structurally analogous to glycerides that are major components of commodity plant oils. There are also other terpenoid derivatives, like sterols, that are not of interest to the polymer community but have other uses as secondary metabolites (Figure 1.2d).

Polyisoprenoids, molecules derived from multiple IPP fragments, are biosynthesized through subsequent elongation of a dimethylallyl pyrophosphate (DMAPP) starting unit by IPP (Figure 1.2a). This elongation reaction is catalyzed by prenyltransferases like polyisoprenoid diphosphate synthases. The elongation reaction is a nucleophilic elimination of the allylic diphosphate on the growing chain with subsequent α-H elimination on the added IPP (Figure 1.2a). The subsequent α-H elimination on the IPP can lead to *cis*- or *trans*-olefins in the polyisoprenoid. The presence of electronic rich olefins on terpenoids opens the possibilities, at a first level, for cyclization, condensation, reduction, and/or oxidation (Figure 1.2b). Any other subsequent structural modification bestows this class of compound with complexity that would make them a rich entry point to biopolymer synthesis. Figure 1.2a and b shows some examples of structurally diverse molecules with potential for use as monomers. With increased structural diversity, however, the compounds are no longer oils but span a plethora of physical forms from waxy compounds to crystalline compounds like the steroids (Figure 1.2d).

Terpenes are, biosynthetically, derived from two isomeric compounds, isopentyl diphosphate (IPP) and DMAPP through successfully elongation [32,33], that is often accompanied by structural modifications through oxidation, reduction, or, cyclization (Figure 1.2c and d). There are two main biochemical pathways for the synthesis of the IPP precursor in plants, namely, the mavelonate (MVA) pathway and the methylerythritol (MEP) pathway – also referred as deoxyxylulose phosphate (DOX) pathway (Figure 1.3). The MVA pathway starts with Claisen condensation of acetyl coenzyme A (AcCoA) to an acetylacetyl CoA (AcAcCoA) (Figure 1.3a). This condensation reaction is then followed by an aldol condensation of the AcAcCoA with a third AcCoA to give 3-hydroxy-3-methylglutaryl-CoA (HMG-CoA), which is subsequently reduced to give mavelonic acid. Eventual reductive decarboxylation leads to the terpene-starting unit, IPP (Figure 1.3a). The MEP (DOX) pathway (Figure 1.3b) starts with condensation of pyruvic acid with glyceraldehyde-3-phosphate as catalyzed by 1-deoxy-D-xylulose-5-phosphate synthase (DXS) with a thiamin diphosphate cofactor (Figure 1.3b). Demethylation and reduction of the methylketone to an aldehyde followed by cytidinylation gives 4-diphosphocytidyl-2-C-methyl-D-erythritol. Subsequent C–2 phosphorylation followed by cyclization of the diphosphate leads to a rare cyclic diphosphate that is then dephosphorylated and reduced to give either IPP or DMAPP.

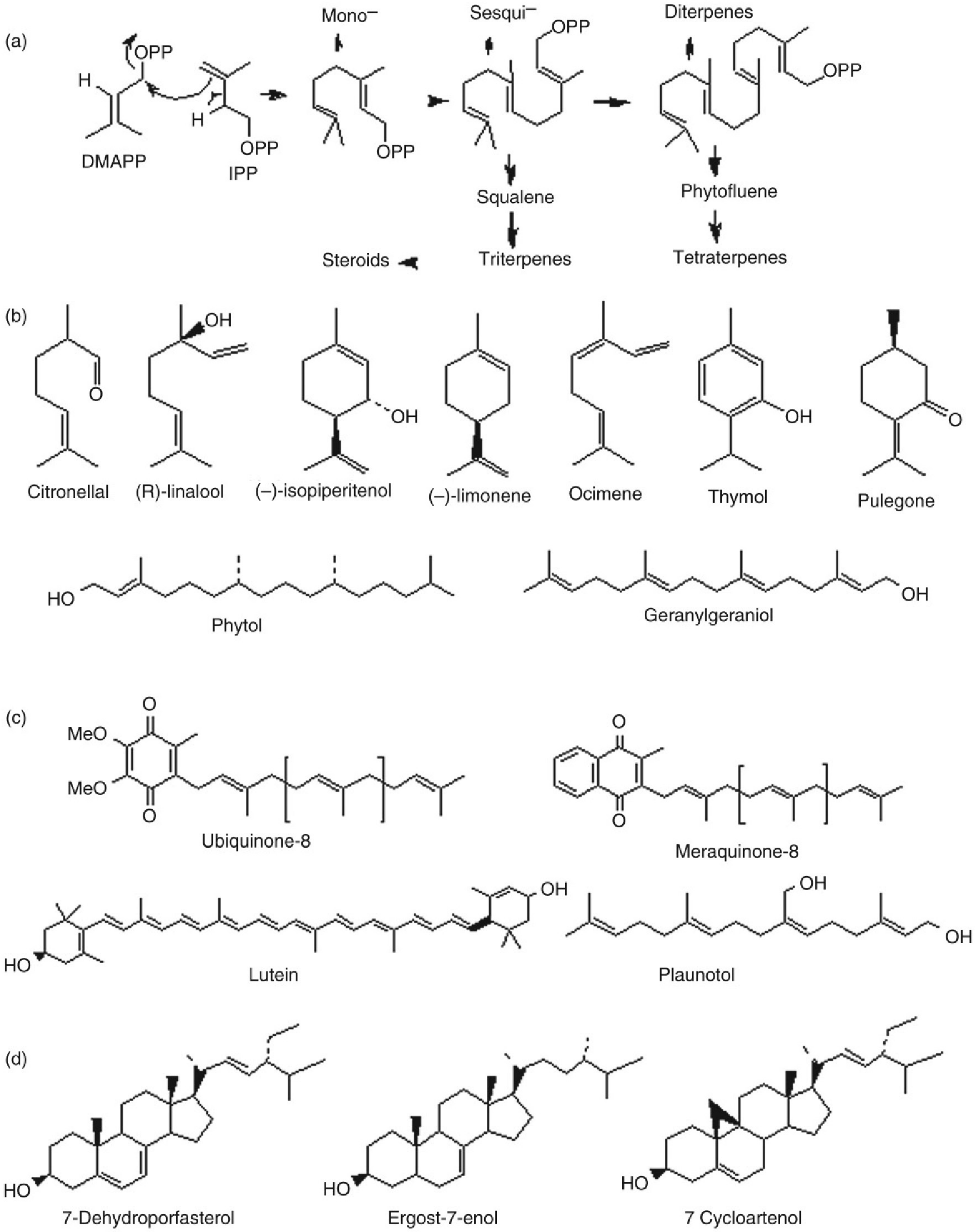

Figure 1.2 Overview of terpenes, a key class of molecules of essential oils. (a) Biosynthesis of terpenes from DMAPP and IPP to give monoterpenes or more elaborate structures. (b) Examples of chemical structures of commonly found terpenes, illustrating the structural diversity even in the low-molecular weight molecules. (c) Examples of polyolefin containing terpenes and/or other polymerizable groups. (d) Examples of structurally complex terpenes, a class dominated by steroids and related structures.

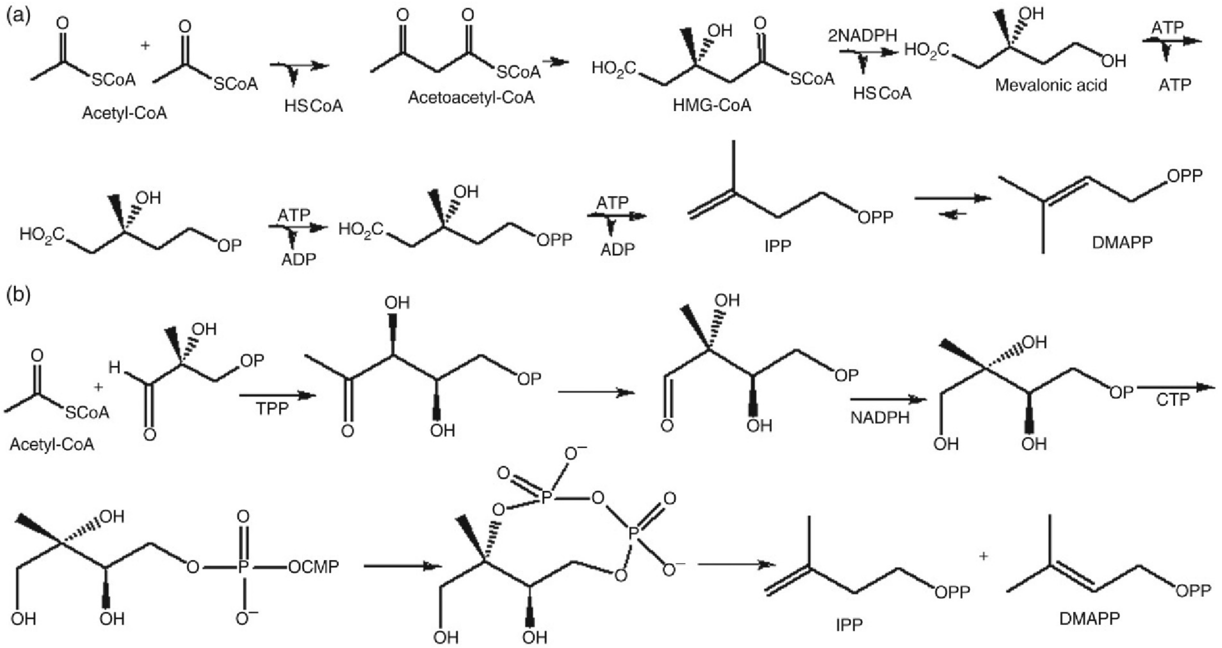

Figure 1.3 Biosynthesis of terpene precursors, dimethylallyl pyrophosphate (DMAPP) and IPP. (a) The MVA pathway, and (b) the DOX pathway also referred to as the MEP pathway.

1.2.2 Biosynthesis of Fatty Acids

Biosynthesis of fatty acid-derived oils is less elaborate compared to terpenoid-based oils. Glycerides (tri-, di-, and monoacylglycerides) are derived from condensation of fatty acids (see examples in Figure 1.4a) with a glycerol to give esters linkages. Since fatty acid are derived from acetyl CoA, they are limited in structural complexity – in comparison to terpenoids, but presence of olefins and hydrolyzable esters allows for simple transformations (Figure 1.4b). Fatty acids are derived from malonyl-Coenzyme A (malonyl CoA), which is synthesized by carboxylation of acetyl CoA by a biotinylated enzyme (Figure 1.4c). The malonyl CoA is sequentially elongated, 2 carbons at a time, by coupling with acetyl CoA. This elongation process (Figure 1.4c) is mediated by an acyl carrier protein (ACP) that is similar to a CoA with a difference that the phosphopantetheine group is attached to a serine rather than a nucleotide.

1.2.3 Chemical Reactivity of Plant Oils

Plant oils, fatty acids, or isoprenoid-derived, often contain C═C bonds, carboxylic acids, or hydrolyzable esters (Figure 1.4b). Presence of alkene moieties allows for, potentially, many reactions to be carried out on plant oils (Figure 1.5b). The greatest challenge is heterogeneity in composition of the oil, hence the need to assess functional group compatibility to allow for successful, or selective, transformation(s). Figure 1.5 gives a summary of potential reactions of alkenes (Figure 1.5b) and carboxylic acids/esters (Figure 1.5a). We only highlight key chemical transformation to illustrate the potential of these two functional groups, carboxylic acids and olefins, in increasing diversity

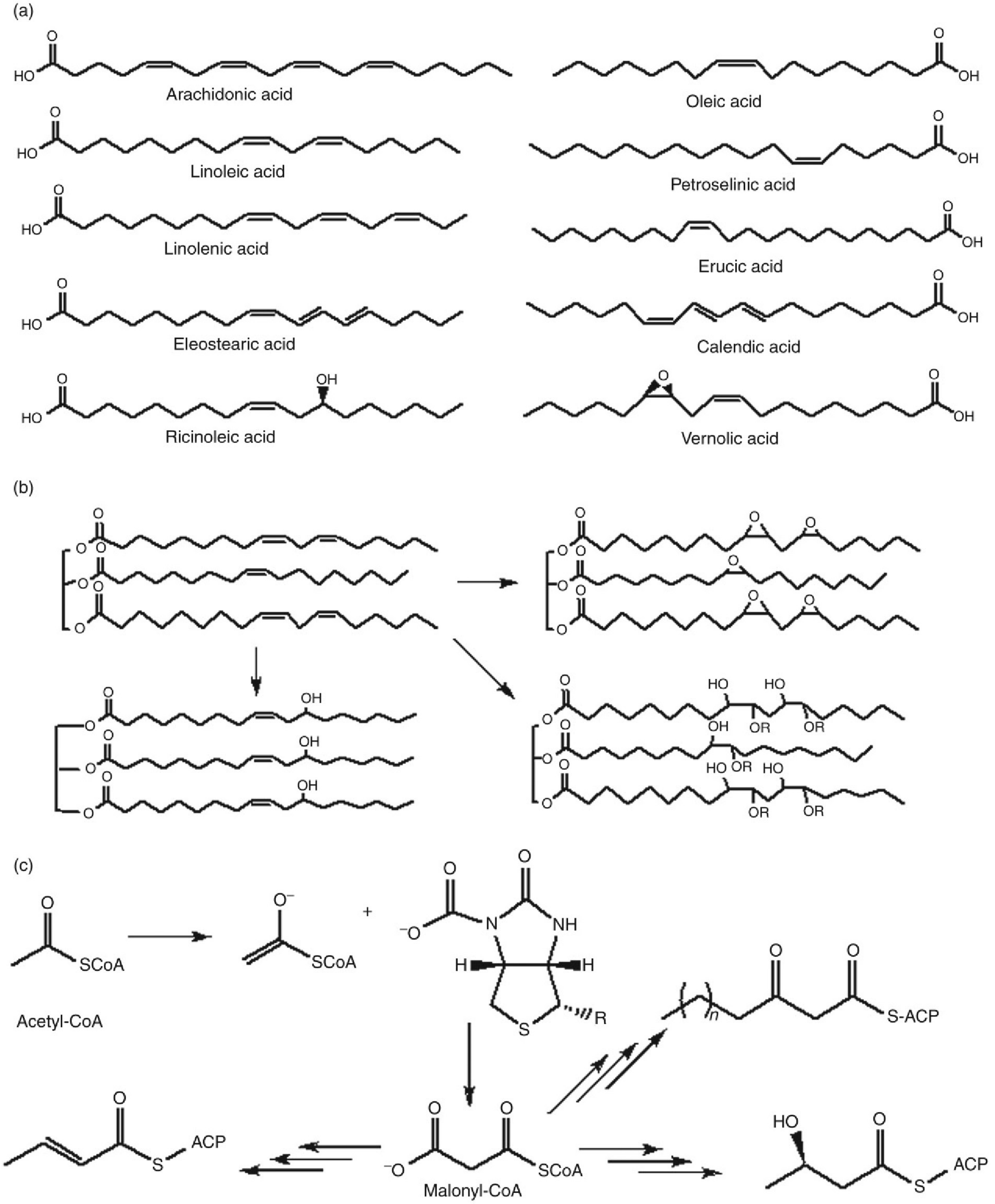

Figure 1.4 An overview of fatty acid derived oils. (a) Examples of common plant-derived fatty acids. (b) Triglycerides with examples of a variety of polymerizable or modifiable moieties to illustrate potential complexity and opportunities for further chemical elaboration or polymerization. (c) An abbreviated schematic of the biosynthesis of various fatty acids from malonyl-Coenzyme A (malonyl-CoA) that is derived from carboxylation of acetyl-CoA.

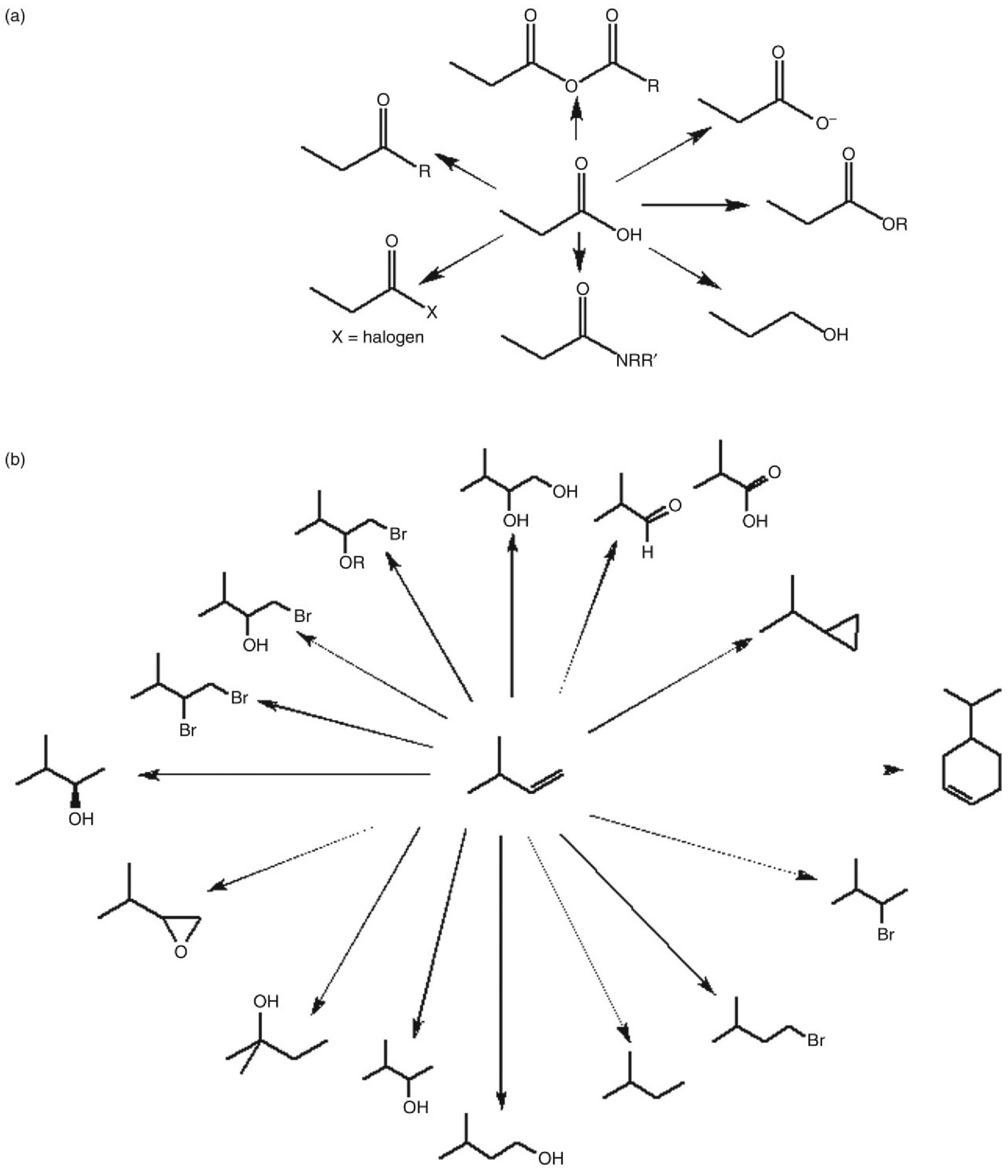

Figure 1.5 An overview of some reactions of carboxylic acids (a) and alkenes (b). The type of reactions range from simple carboxylate condensation to cycloadditions like Diels–Alder reaction and cyclopropyration in the alkenes.

of the reactive sites in plant oils. Detailed chemical transformations have been given in the literature [1,9,13,14,25–27,34–43]. For a discussion and practical guide on performing the chemical transformations listed below, the reader is referred to the Vogel's text on practical organic chemistry [44].

The chemistry of carboxylic acid and esters is dominated by the presence of an electrophilic carbon and the presence of a cleavable C—O single bond (for esters) or the acid proton (or analogous carboxylate anion) on the carboylic acid. From the carboxylic acid, direct or indirect condensation of the carboxylate with nucleophilic moieties can lead to amines, amides, esters, anhydrides, or acyl halides [45–49]. Reduction of the carboxylate leads to a terminal hydroxyl while activation of the –OH into good leaving groups, for example, a tosylate, allows for monoalkylation of the carboxylate using mild reagents to give ketones. These reactions can be used to create intermediate moieties that can be used to further increase structural diversity of the oils and/or alter the oils' properties and/or aid in processing.

Olefin chemistry is dictated by the presence of an electron-rich C═C bond. This allows electrophilic and/or nucleophilic addition across the π-bond. The addition can be symmetric or asymmetric depending on the functional groups adjacent to the olefin that may influence the sharing of the π-electron cloud. Common symmetric additions include bromination, hydrogentation, dihydroxylations, epoxidation, and cyclopropanation. Asymmetric additions are dominated by Markovnikov and anti-Markovnikov's additions, oxymercuration–demercurations, halohydrin formation, hydroboration–oxidations, and related reactions. Besides additions, olefins can undergo cycloadditions depending on other associated functional groups in the molecule. The most common cycloaddition reaction for olefins is the 4 + 2 Diels–Alder reaction in which an olefin reacts with a diene to give a cyclohexene [47] or the 2 + 2 reaction to give a cyclobutane [50]. Formation of three-membered rings [51] with either a carbon (cyclopropanation), oxygen (epoxidation), or sulfur (thiirane formation) can also be achieved either as a terminal product or as an intermediate structure to further chemical transformations.

Cleavage of the C═C bond can also be achieved through processes like ozonolysis to either give aldehydes or carboxylic acids. This cleavage has the advantage that, for plant oils, it can be used to reduce the size of the fatty acid chain while introducing reactive groups on the shortened oils or to alter their thermal properties (products of ozonolysis are more polar than the C═C bond). Olefin metathesis [45,46,51–55] can also be used to either cleave or couple olefins in plant oils. Through olefin cross-metathesis with a smaller olefin, the size of the fatty acid can be shortened; however, this is likely to occur alongside polymerization or cross-metathesis between the fatty acid chains. Olefin metathesis can also be used to alter the physical properties of an oil through controlled cross-linking to create large, oligomeric, macromonomers or to prepare polymers. A combination of the above reactions can be used to develop functional group selective chemistry based on the physical properties of the resultant compounds [52,54]. Where stereochemistry is desired, a plethora of chemical transformation exists to transform either one or both of the olefinic carbons into chiral centers [53]. Examples of chiral additions across olefins include asymmetric hydrogenation (Knowles or Noyori's catalysts), Sharpless bis-dihydroxylation using osmium catalysts, Jacobsen's epoxidation, asymmetric hydroboration–oxidation using chiral auxiliaries (e.g., isopinocamphenylboranes). Introduction of chiral centers requires the use of chiral auxiliaries and exploitation of sterics around the olefin.

1.2.4 Chemical Characterization

The development of plant oils as commercially viable chemicals, which was dominated for a long time by essential oils, has significantly evolved in line with development of analytical and separation techniques [56]. Due to their relatively low molecular weights and compositional diversity, gas chromatography (GC), mass spectrometry (MS), and liquid chromatography (LC) have been widely used to characterize their composition [56]. GC has a sufficiently high sensitivity that allows for even minor components of the oil to be analyzed. One disadvantage is the need for standards to ascertain the identity of the peak, although retention indices (RI) can be used to predict a possible structure assuming homology to known components. The use of RI is favorable to plant oils since structure similarities, due to a series of oils emanating from the same biosynthetic pathway, is very likely. A similar approach can also be used with LC for components that are not readily vaporized on a GC, for example, triglycerides and carboxylic acids. Since plant oils are isolated as mixtures, MS on its own cannot be used to characterize an oil blend without prior purification or isolation of individual components.

Supercritical fluids, with their high density, high diffusivity, and low viscosity, have been used as the mobile phase in chromatographic separation of plant oils. Capillary supercritical fluid chromatography (SFC) has shown reliable component quantifications of oxygenated compounds than GC [57,58]. Counter current chromatography (CCC), a form of liquid–liquid partition chromatography, has also been used to characterize plant oils.

Development in coupled (hyphenated) techniques, like GC–MS and LC–MS, has allowed for separation with concomitant identification of all components in an oil blend or other complex biological samples [56,59–61]. For low molecular weight compounds, GC–MS is used to generate a profile and identity for each of the components in the oil. For polar compounds, derivatization with nonpolar moieties is often used to allow for vaporization, promote uniform flow (sharp peaks), and prevent significant damage to the stationary phase of the GC column. Other coupled techniques that can be used to analyze plant oils are often technically involved, albeit with higher certainty in chemical structures in most cases. The recently reported LC–MS–NMR technique [59,60], for example, has great potential in plant oil analysis even though it is technically involving.

Chemical characterization of plant oils is often challenging and mischaracterization is possible due to structural homology and/or presence of difficult-to-resolve minor components. With techniques like GC and LC, there is potential for peaks to overlap leading to misidentification, although preparative techniques can be used to isolate pure components for full chemical characterization. Isolation of small pure quantities of plant oil components can be achieved through preparative thin-layer chromatography, preparative LC, distillation or chemical derivatization.

Other chemical characterizations that are used to identify chemical constituents of oils are ultraviolet (UV) spectroscopy, infrared (IR) spectroscopy, Raman spectroscopy and nuclear magnetic resonance (NMR).

1.3 Major Sources of Plant oils

The ISTA Mielke (Hamburg, Germany) recognizes 17 commodity oils and fats, 13 of which are vegetable oils. Vegetable oils can be sourced from (i) annual crops that need to be planted each year or season (e.g., canola, sunflower, soybeans, castor, and linseed), (ii) tree crops that take long time to mature but can be harvested for many years (e.g., coconut and palm tree), or (iii) as secondary products from plants grown for other purposes (e.g., cotton and soybeans). The focus of this section is not to review where the oils are derived from but to highlight the parts of the plants from which the oils can be derived. We highlight both glycerides- and isoprene-based oils.

Plant oils can be derived from many parts of the plant and a full review of the sources of plant oils is beyond the scope of this chapter. To give a few examples, leaves of Eucalyptus are used to produce significant amount of oils that are rich in citronellal. Southeast Asia and western Africa has also led the effort in production of palm oil, which is extracted from the fruit of the palm tree. Common plant oils, predominantly used in the fragrance and perfume industry, are derived from barks/wood (camphor, sandal wood), flowers (rose oil, chamomile, and jasmine), roots and rhizomes (valerian and ginger), fruits or fruit peels (palm or citrus oil), seeds and berries (almond oil, Juniper, anise oil, nutmeg oil), and resins (Myrrh, benzoin, and frankincense). Although there is a large diversity in the part of the plant from which the oil can be extracted, most oils have similar compounds, since they are derived from a limited number of biosynthetic pathways, albeit in varying concentrations. The part of the plant in which the oil accumulates depends on the evolutional role of these oils to the plants, with most of them having evolved as semiochemicals for *intra*- and *inter*-species chemical communication.

Understanding of the biosynthetic pathways and the role these oils play in the plant can potentially be used to develop genetic and/or external methods to increase yields. Several genetically engineered plants and/or enzymes have been developed to increase the production of the oils but the technology is not yet at an industrial scale.

1.4 Extraction and Processing of Plant Oils

1.4.1 Small-Scale Extraction and Processing

Extraction technique employed in obtaining plant oils depends on the required amount, desired purity, the part of the plant from which the oil is sourced and the use. For qualitative analysis, oils can be extracted directly from the oil glands or the stoma using glass capillaries, or headspace analysis for volatiles exudates. For semiquantitative amounts adsorbents can be used to obtain small quantities of the oil, especially exudates, sometimes without significantly affecting the plant. For laboratory scale oil extractions, soxhlet extraction or a Dean-and-Stark apparatus can be used to obtain gram quantities of oil. The soxhlet extraction is desired where the oil has a higher boiling point than the solvent, the source has high fiber/particulate content, or plant contains thermally degradable compounds that can contaminate the oil. The Dean-and-Stark apparatus is used to coevaporate the oil with a solvent in which the oil is immiscible, often hydrodistillation, with the oil accumulating in Dean-and-Stark apparatus. Immiscibility of oil and the solvent leads to a two-phase distillate that is readily separated.

More recently, the use of polymeric membranes to separate organic compounds either for the sake of purification [62–65] or during a chemical transformation [45,46,51–54,66–71] has been reported. The Bowden's approach to purification of fatty acids [62,63,65] relies on the selective transport across a thin polymeric membrane that can be tuned, through degree of cross-linking and/or swelling, to allow for efficient purification of plant oils.

1.4.2 Large-Scale Extraction and Processing

For large quantities, or processes where the oil is a starting material in a production process, distillation or cold press techniques are widely used [4]. Due to the wide variation in techniques that can be employed, detailed analysis of the processing of palm is used to illustrate the process.

1.4.2.1 Palm Oil

Palm oil producing trees are natives of West Africa but they were imported to Southeast Asia where, in some places, have become a major revenue stream. Extraction of the palm oil from the fruits involves cleaning and mechanical (screw) pressing of the palm fruits. The oil is then filtered, clarified, and purified to give the crude palm oil (Figure 1.6a). To obtain the major components, however, further chemical or physical refining is required (Figure 1.6b). The chemical process involves alkali neutralization followed by earth bleaching and deodorizing to give the refined neutral bleached palm oil (NBD PO). The physical refining process is analogous to chemical refining with the exception that the neutralization step is replaced with degumming. The degumming process is used to remove

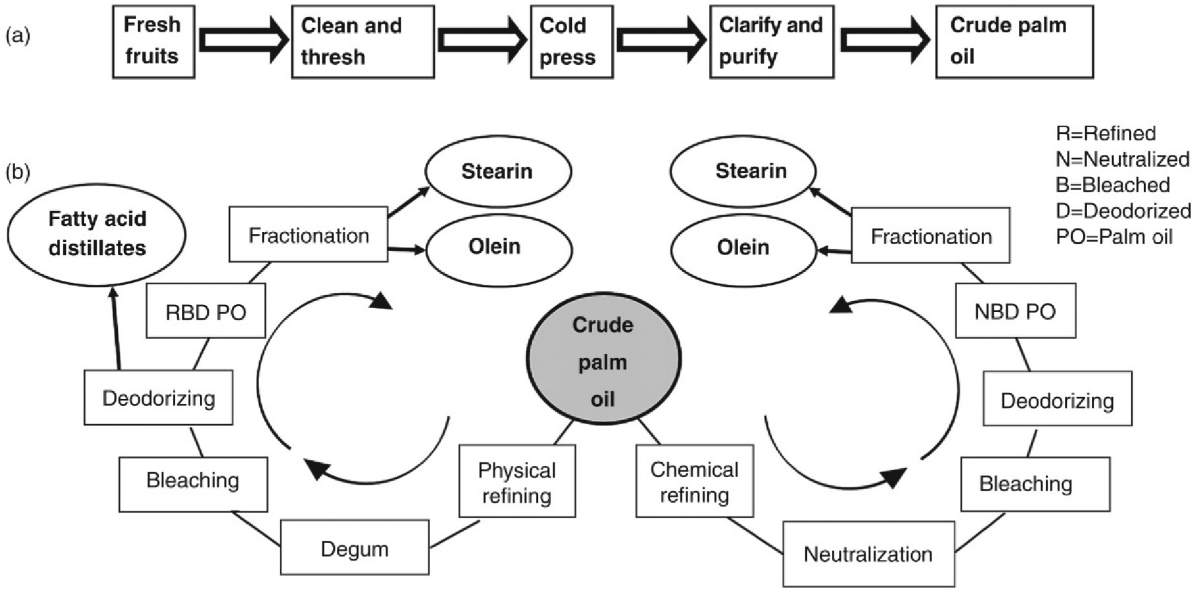

Figure 1.6 Processing of plant oils, palm oil as an example. (a) A general schematic of how palm fruits are processed after harvesting. The oil is extracted by cold pressing then purified to give industrial grade product. (b) The oil can then be refined through chemical or physical processes to give stearin and olein after fractionation.

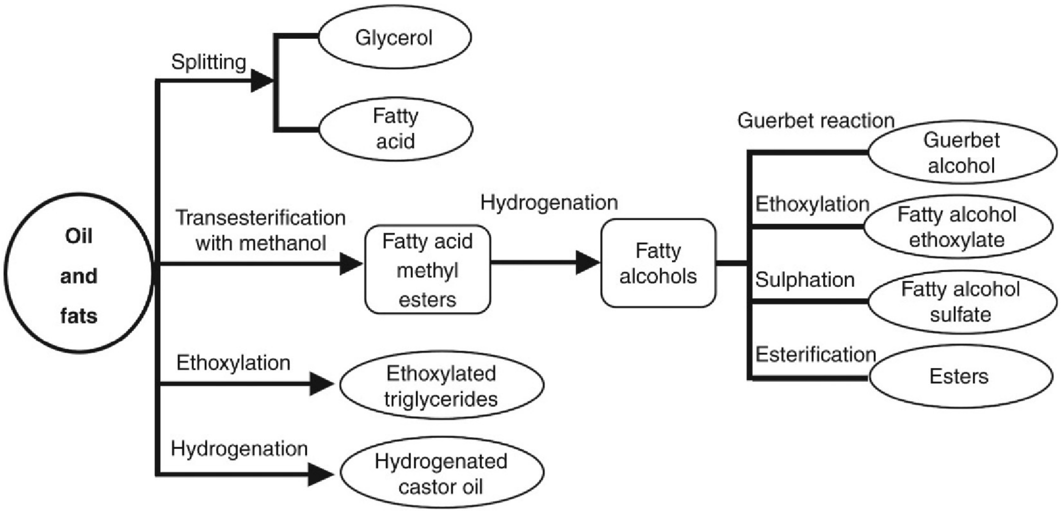

Figure 1.7 A general schema showing the processing of oils and fats into various chemical or reactive moieties using simple chemical reactions like esterifications of hydrogenation. The diversity of reactive moieties indicates the potential of oils and fats.

phospholipids analogous to the alkali neutralization (hydrolysis). Upon fractionation of the refined palm oil, stearin, and olein are obtained as the major products (Figure 1.6).

1.4.3 Postextraction Processing of Fatty Acids

Based on functional group diversity in the purified plant oil, several chemical processes can be used to improve the quality of the oil. Postextraction modifications can be used to introduce polymerizable chemical moieties in the plant oils. For polymer synthesis, although most oils contain polymerizable groups like epoxide, olefins, and hydroxyls, it is often desired to introduce moieties like norbornenes that can be polymerized using organometallic catalysts. Larock and coworkers, for example, have shown that by introducing norbornenes in castor oil and soybean oil, they can use the introduced norbornene to synthesize thermosets through ring-opening metathesis polymerization (ROMP) [13,14,25–27,43].

At an industrial scale, oils and fats can be saponified into the glycerol and fatty acids, hydrogenated to give saturated oil, or chemically modified to give derivatives of the triglycerides (Figure 1.7) [72]. Further processing can lead to alcohols, esters, ethers or other desired compounds. The postextraction modification depends on the use and possible chemical transformations based on available chemical moieties (Figure 1.7).

1.5 Outlook

The use of plant-derived oils is on the rise. With an increase in the need for biorenewable and sustainable engineering, plant-derived polymers are more desired. A challenge to the scientists and engineer in this field is to find means to use plant-derived materials without compromising food security. Genetic engineering has the potential to maximize plant oil production. This book addresses future prospects of plant oils in detail in later chapters.

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2 Plant Oil-Based Derivatives

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2.1 Introduction

The depleting of fossil resources, the ever-increasing emission of greenhouse gases and toxic waste, and stringent environmental regulation have triggered an increasing interest in developing industrially compounds and polymers from natural resources as an alternative of petroleum-based counterparts [1,2]. Various renewable resources are available, including cellulose, starch, natural oils, and sugars. Among them, plant oils are among the most promising options; they offer excellent properties, including world-wide availability, inherent sustainability nature, and relatively low price [3,4]. A large number of plant oils, such as soybean oil, rapseed oil, and palm oil, are considered to be the most important renewable feedstock processed in the chemical industry to decrease the dependence on depleting petroleum resources.

Vegetable oils are esters formed between glycerin and different fatty acids containing from 8 to 24 carbons and from 0 to 7 carbon–carbon double bonds (see Table 2.1), depending on the plant type and climatic conditions of harvest. Typical structure of vegetable oils is shown in Figure 2.1. Naturally existing carbon double bonds in most vegetable oils are located in the 9–16th carbon, which makes them less reactivity due to radical trapping by allyl hydrogens from methylene group between double bonds. However, in some oils, such as Tung oil, conjugated double bonds are available, which demonstrate high polymerization activity. Ester group is another

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Table 2.1 Degree of Unsaturation, Composition of Common Vegetable Oils

		Fatty Acid Composition (%)				
	Double Bonds	Palmitc	Stearic	Oleic	Linoleic	Linolenic
Castor	3.0	1.5	0.5	5.0	4.0	0.5
Corn	4.5	10.9	2.0	25.4	59.6	1.2
Linseed	6.6	5.5	3.5	19.1	15.3	56.6
Olive	2.8	13.7	2.5	71.1	10.0	0.6
Palm	1.7	42.8	4.2	40.5	10.1	-
Soybean	4.6	11.0	4.0	23.4	53.3	7.8
Canola	3.9	4.1	1.8	60.9	21.0	8.8

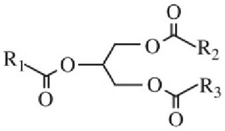
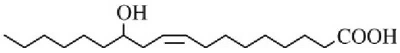
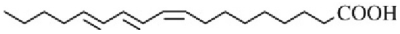
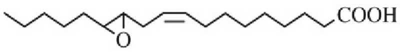


Figure 2.1 Typical structure of vegetable oils (R_1, R_2, R_3 represent fatty acid chains).

reactive site for most of vegetable oils, and some oils contain other reactive groups such as hydroxyl or epoxy as shown in Table 2.2. For example, castor oil contains 90% ricinoleic acid, which contains ne hydroxyl group on 12th carbon. Vernonia oil has a functionality of 2.8 epoxy rings per triglyceride. All these inherent functionalities offer the possibility of these renewable resources being transformed into industrially significant compounds (fatty acid, fatty amides/nitriles/amines, alcohols, ester derivatives, epoxy, conjugates) via several efficient chemical modifications. The basic oleochemicals are fatty acids (ca. 52%), the respective methyl esters (ca. 11%), amines (ca. 9%), and alcohols (ca. 25%) [1].

The world production of major vegetable oils has risen from 95 million tons in 2002/2003 to 154 million tons in 2012/2013 at an average rate just over 5 million tons a year [1]. Soybean oil, palm oil, and rapeseed oil range highest world production of vegetable oils. Most of the global soybean oil production is located in North America and South America.

Table 2.2 Six Common Fatty Acids Composition in Vegetable Oils

Fatty Acids	Formula	Structure
Caprylic	$C_8H_{16}O_2$	
Palmitc	$C_{16}H_{32}O_2$	
Stearic	$C_{18}H_{36}O_2$	
Oleic	$C_{18}H_{34}O_2$	
Linoleic	$C_{18}H_{32}O_2$	
Linolenic	$C_{18}H_{30}O_2$	
Ricinoleic	$C_{18}H_{34}O_3$	
α-Eleostearic	$C_{18}H_{30}O_2$	
Vernolic	$C_{18}H_{32}O_2$	

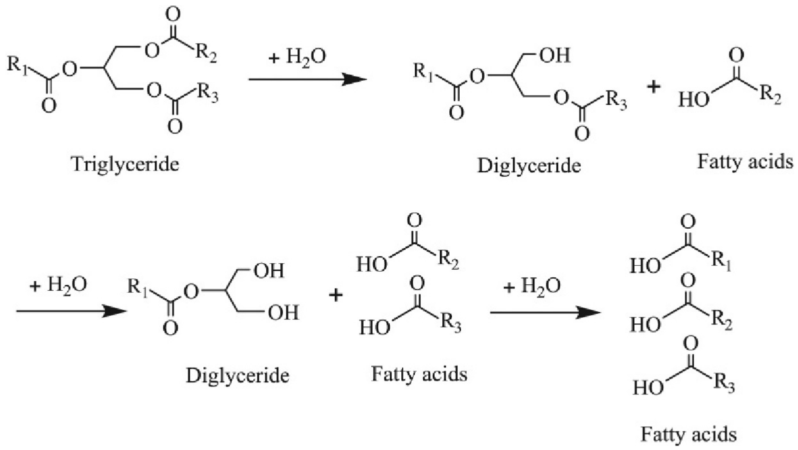


Figure 2.2 Hydrolysis of vegetable oils.

For example, in the United States, the three largest crops planted are corn, soybean, and wheat with planted acreage of 30%, 28%, and 23%, respectively. However, rapeseed production is the major crop in Europe, while palm oil dominates in Asia. These three oils are the most attractive for large-scale industrial products due to low price. From 2001 to 2005, 15% of soybean oil was used for industry application [5]. Although the majority of vegetable oils are primarily produced for food and feed purposes, minor vegetable oils such as castor and linseed oil are almost solely used for industrial applications.

Recently, there has been a steady growth in the use of plant oils in the painting and coating industries, such as shampoos lubricants, emulsifiers, cosmetics, plasticizers, biodiesels and pharmaceuticals, as well as various polymeric materials.

2.2 Plant Oil-Based Derivatives

2.2.1 Fatty Acids

The hydrolysis or saponification of different vegetable oils under the influence of water, temperature, pressure, and catalyst produces a mixture of C_6 up to C_{20} fatty acids. Partial hydrolysis of triglycerides yields mono- and di-glycerides and fatty acids, while complete hydrolysis generates glycerol and fatty acids as shown in Figure 2.2. Generally, the reaction between plant oils and water is pretty slow due to the hydrophobic nature of plant oils. Increased temperature or pressures improve the solubility of plant oils in water, leading to rapid hydrolysis rates [6]. Also, organic acid (such as HCl, H_2SO_4) and basic (NaOH) can be used to accelerate the reaction. When basic is used, the final product is fatty acid sodium salts, which are used to make soaps, skin products, candles, and perfumes.

Also, fatty acids provide useful chemicals for polymers development. For example, castor oil fatty acids were used as ring opener for preparation of polyols for polyurethane coating and foam [4].

2.2.2 Fatty Amides/Nitriles/Amines

Fatty amines can be obtained by hydrogenation of fatty nitriles, which are produced

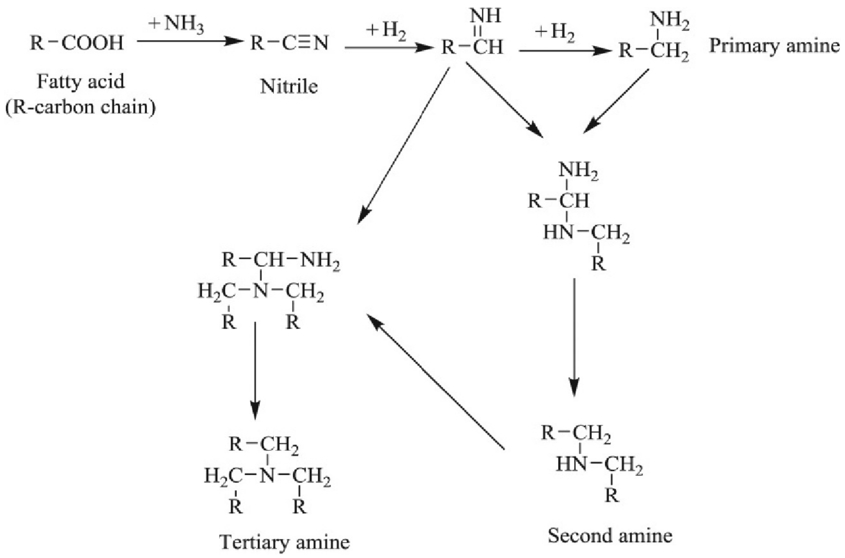


Figure 2.3 Preparation of fatty amides/nitriles/amines.

by the reaction between triglycerides, or fatty acids, or fatty esters and ammonia with elimination of two molecules of water at high temperature (423–723 K) in the presence of dehydrating catalyst (such as silica gel, alumina, or iron-based catalysts, and so on) [6,7]. Actually, the products from the hydrogenation of nitriles are mixtures of primary, secondary, and tertiary amines as shown in Figure 2.3. Excess of ammonia used in the process would prohibit the release of the ammonia, resulting in suppressing formation of secondary and tertiary amines. The choice of the hydrogenation catalyst also affects the selectivity of the process. For example, nickel or cobalt catalyst favored the formation of primary amines, while copper chromite catalysts promoted the formation of secondary amines. Primary amines and their salts find applications as flotation agents, anticaking and water-repellent agent, corrosion inhibitors, lubricating additives, bactericides, or additives for fuels and gasoline [8,9]. They are also intermediates for the production of quaternary ammonium salts. The secondary amines are used mainly as intermediates for the preparation of difatty dimethyl quaternary ammonium compounds.

2.2.3 Alcohols

Alcohols are obtained by conversation of plant oils directly, called polyols, or by catalytic hydrogenolysis of fatty acids or fatty esters derived from them, called fatty alcohols. The former are usually used to prepare polyurethane coating, foam, and dispersions. The hydroxyl groups in polyols are usually introduced in the react sites of double–double bonds located in the chain backbone of plant oils. The common alcoholysis methods that are used to prepare these polyols are as shown below.

1. Epoxidation/ring opening: Most vegetable oil-based polyols are produced by the epoxidation of vegetable oils, followed by oxirane ring opening with proton donors. Several proton donors can be used to ring open the epoxide, such as alcohol, acid.

2. Transesterification/amidation: Two common routes to synthesize vegetable oil-based polyols involve transesterification with various polyols, or amidation, typically with diethanolamine, of vegetable oils.
3. Hydroformylation/reduction: The hydroformylation/reduction of vegetable oils involves the addition of hydroxymethyl groups to the carbon–carbon double bonds in the fatty acid chains using a two-step procedure. In the first step, the vegetable oil is treated with syngas (a mixture of CO and H_2) in the presence of a Rh or Co catalyst to give aldehydes, which are then reduced with H_2 in the second step to yield hydroxyl groups.
4. Ozonolysis/reduction: This method involves the efficient cleavage of the carbon–carbon double bonds present in the fatty acid chains to give, under the right conditions, shorter chain alcohols. In the first step, an ozonide is formed by treating a vegetable oil with ozone, which is then reduced by zinc to give an aldehyde, and is further reduced with Raney nickel to the corresponding primary alcohol. The ozonide can also be treated with sodium borohydride to afford the primary alcohol directly.

Based on these routes, several research groups are dedicated to combining the advantages offered by the modification of carbon–carbon double bonds and those offered by the modification of esters to develop high functionality polyols. For example, Kong used 1, 3-propanediol for ring-opening of epoxidized vegetable oils and transesterification with the triglycerides [10]. Lligadas developed oligomeric polyether polyols by ring-opening polymerization of epoxidized methyl oleate followed by reduction of the ester groups [11]. Epoxidation of vegetable oils, followed by reduction of epoxy groups and esters, is one method developed by Zhang to prepare high functional polyols from castor oil, soybean oil, and linseed oil for polyurethane coating [3].

Fatty alcohols are produced from hydrogenolysis of fatty acids or fatty esters catalyzed by copper chromite, palladium–rhenium, or rhodium–tin systems with large excess of hydrogen due to its low solubility in the reaction mixture, which introduces mass transport resistance and limits the concentration of hydrogen at the surface of the catalyst [12]. However, these catalysts are not selective toward carboxyl group and carbon–carbon double bonds. It is reported that zinc chromite catalyst, Zn–Cr catalyst, zinc–aluminum, iron–zinc, and zinc chromite show chemoselective reduction toward carboxylic group, preserving the double bonds [6,13,14]. One example of chemoselective reduction of fatty esters is production of oleyl alcohols, which is classified by refined, technical, and industrial according to their purity as shown in the figure. The refined oleyl alcohols are used primarily in cosmetic and pharmaceutical preparations. The technical grade of oleyl alcohol is used as a chemical intermediate for the preparation of surface-active agents such as ethoxylates, sulphates, and esters. The industrial grades of oleyl alcohol and their derivatives are widely used in lubricants and as petroleum additives [15]. Fatty alcohols by hydrogenation of fatty acids and their methyl esters are also used for the production of surfactants [1]. With their hydrophilic head and hydrophobic tail, fatty alcohols interpose themselves between water and water-insoluble substances. Properties of surfactants are additionally governed by the alkyl chain length of their hydrophobic

Table 2.3 Commercial Class of Oleyl Alcohol [15]

Class	Hydroxyl Value	Iodine Value	Cloud Point
Refinded	205–215	85–95	<10
Technical	205–220	80–90	<15
Industrial	205–225	65–75	<28

part: wetting agents (C8–C10), detergents (C12–C16), emulsifiers, and softeners (C18–C22) [16] (see Table 2.3).

The rapid emergence of biodiesel industry causes mass production of glycerol as an organic byproduct (a 10% byproduct of biodiesel production via the transesterification of vegetable oils), which attracts attention from both academia and industry to find application for this cheap renewable alcohol. With its three OH groups, several chemical pathways, such as oxidation, reduction, dehydration, esterification, etherification, were developed to transform it into a large number of chemicals as shown in Figure 2.4. For example, oxidation toward primary and secondary OH in glycerin using stoichiometric mineral acid or fermentation routes produce glyceric acid, dihydroxyacetone, and hydroxypyruvic acid, which find application in medicine, cosmetics [6]. The

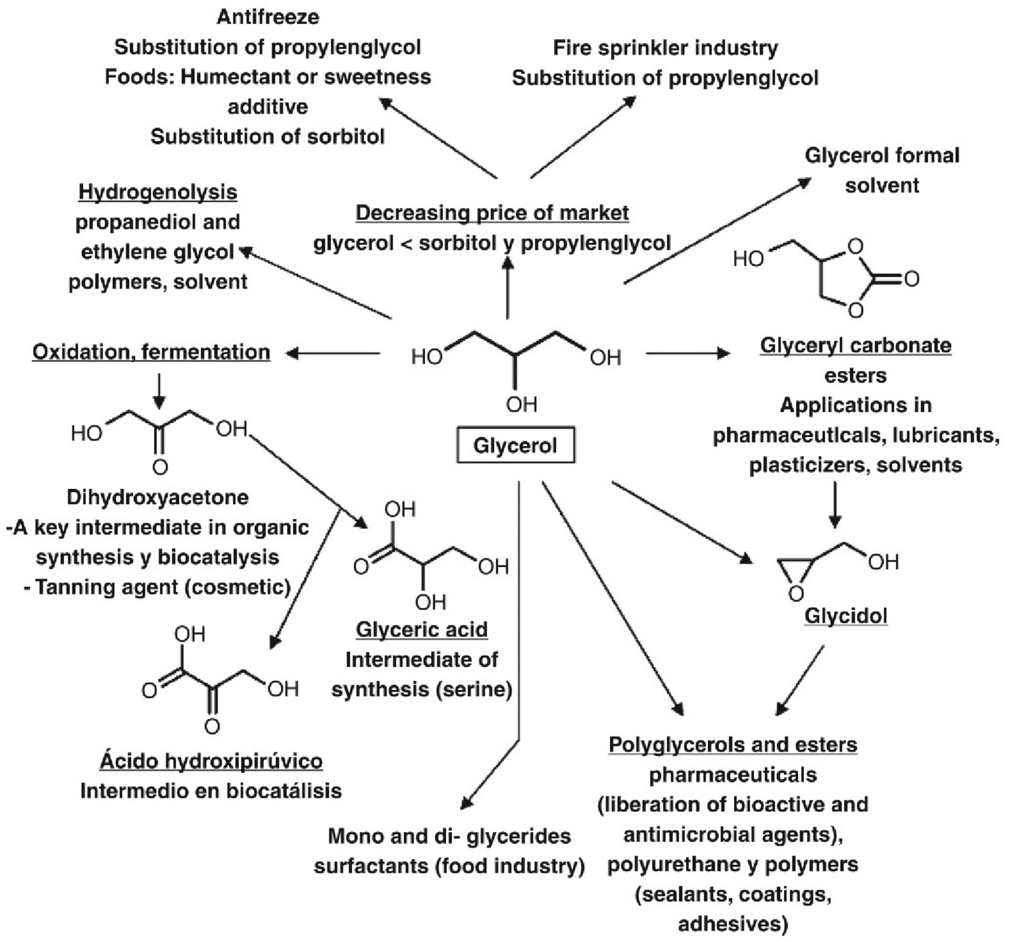
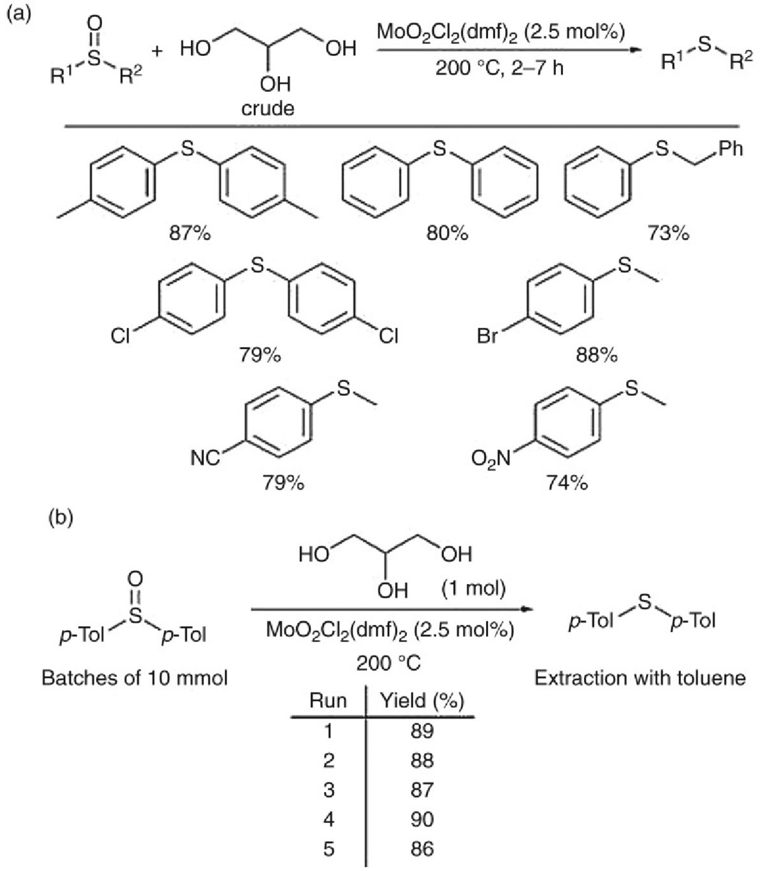


Figure 2.4 Possible application and transformation of glycerol [6].



Run	Yield (%)
1	89
2	88
3	87
4	90
5	86

Figure 2.5 (a) Mo-catalyzed reduction of sulfoxides (1 mmol) with crude glycerol (2.4 g, 5–8% purity), (b) recycling study of the Mo-catalyzed reduction of bis(p-tolyl) sulf-oxide with glycerol [18].

transesterification of dimethyl carbonate with glycerol in the presence of tetra-*n*-butylammonium bromide at 120°C leads to glyceryl carbonate, which is employed as a solvent, additive, and chemical intermediate in the synthesis of polyurethane and glycidol [17].

Recently, a new application for glycerol has been found that can be used as a reducing agent and solvent in Mo-catalyzed deoxygenation of sulfoxides, which conventionally usually used phosphorous(III) reagents or silanes [18]. This green reaction medium allows high yields, easy product isolation, and catalyst recycling at least five times with negligible change in its activity (see Figure 2.5).

Glycerol has also been investigated to be a solvent for separation, a solvent for biocatalysis, a solvent for enhancing reaction selectivity, and a promoting solvent for organic synthesis water due to its low toxicity, low price, large availability, renewability high boiling point, and low vapor pressure. The author claims that glycerol is an available green solvent that affords innovative solutions to the substitution of the conventionally used volatile organic solvents [19].

2.2.4 Ester Derivatives

Vegetable oils, esters by itself formed between glycerin and different fatty acids, are one of the most important renewable raw materials for a sustainable chemistry. To meet

Table 2.4 Viscosity of Various Vegetable Oils Compared to Diesel Fuel [25]

Oil	Diesel (#2)	Soybean	Sunflower	Coconut	Peanut	Palm
Viscosity (mPa·s, 21°C)	3.8	57.2	60.0	51.9	67.1	88.6

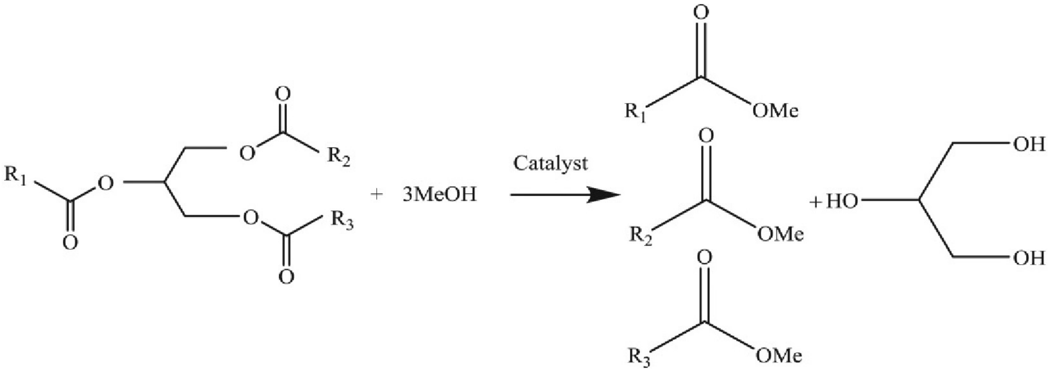


Figure 2.6 Transesterification of triglycerides to produce fatty acid methyl esters.

need for specific application, several ester derivatives have been obtained from vegetable oils. For example, fatty acid monoglycerides and diglycerides are obtained by glycerinolysis of triglycerides with an excess of glycerol at temperatures of 200–250°C in the presence of base catalysts, such as KOH or $Ca(OH)_2$ under an inert gas atmosphere [20]. The final products are usually mixture of 35–60% of monoglycerides and 35–50% of diglycerides. The separation can be achieved by distillation due to different emulsifying ability, but it is very expensive. Thus, these mixtures of monoglyceride and diglyceride are used as emulsifiers in the foodstuffs industry and cosmetics [21,22].

With the depleting of petroleum resources, there is increased interest in developing vegetable oil-based alternative fuel for diesel engines. However, due to the higher viscosity (see Table 2.4) and tendency to polymerize of vegetable oil, it does not atomize properly for combustion during injection into the cylinder, leading to failure of the lubricating oil, and may ruin the engine [25]. Transesterfication of vegetable oils into methyl and ethyl esters (Figure 2.6) or blending with diesel fuels reduces the problems encountered to produce biodiesel with several outstanding advantages among other new renewable and clean engine fuel alternatives. The structure of vegetable oil-based ester can be tailored by transesterification variables, such as ratio of glycerides to alcohol, the catalyst-type concentration, reaction temperature and pressure, the reaction time and the free fatty acids, and purity of the reactants [24,25]. For example, Clark has employed starbons-based catalysts (S400-SO_3H) to convert waste oils containing high free fatty acid into fatty acid methyl esters, a biodiesel-like fuel under both conventional and microwave heating (Figure 2.7) [23]. It is found that the Starbons acids initiate both esterification of fatty acids with methanol and triglyceride transesterification. The yield of fatty acid methyl esters was reported >95% (Figure 2.7a–c). Reactions rates could be increased by employing microwave, reducing reaction times from >12 h (using conventional heating) to <45 min, without a reduction in

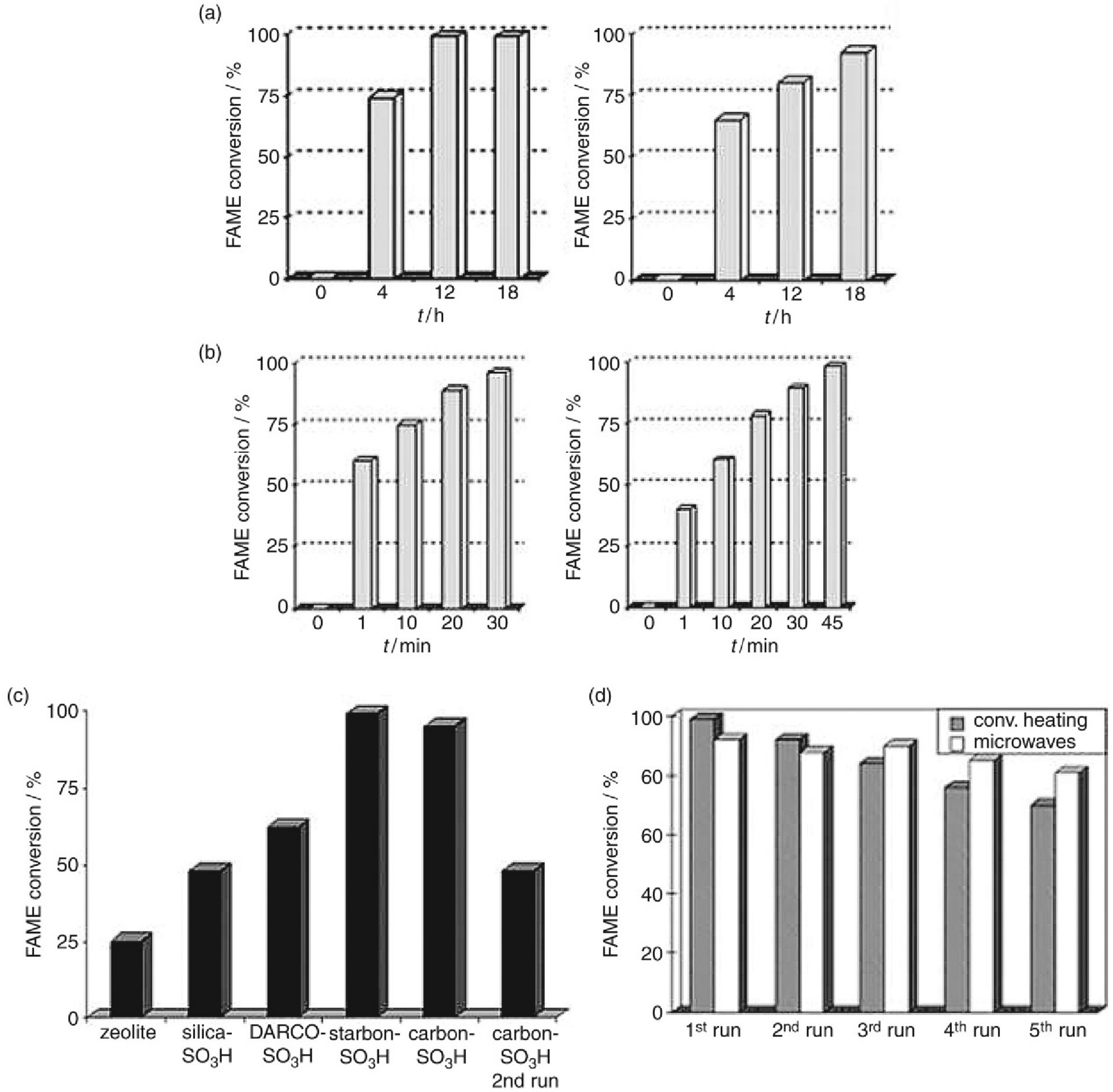


Figure 2.7 Activity of starbon-400SO$_3$H in the esterification/transesterification of waste oils rapeseed waste frying oil (10 wt% free fatty acids) (left); sunflower + olive waste frying oil (17 wt% free fatty acids) (right). (a) Under conventional heating at 80°C. (b) Under 300 W microwave irradiation at 80–85°C. (c) Activity comparison of different solid acids in the production of fatty acid methyl esters. (d) Comparison of recycle uses of starbons acid under conventional heating and MW [23].

activity. The Starbons-based catalyst maintained high fatty acid methyl esters conversions even after five recycle runs (>70 mol%), with the use of MW heating proving to be beneficial in terms of prolonging the high activity of the catalyst over a high number of catalytic runs (Figure 2.7) [25].

The transesterification of fatty acid esters with sucrose produces fatty acid derivative as surfactants that are used in applications such as cosmetics, cleaning, and washing [26]. Similar surfactants can be prepared by the condensation of glycosides with a fatty alcohol and esterification of sorbitol with fatty acid [27].

The transesterification of the vegetable oil with other polyols, such as trimethylolpropane, neopentyl glycol, or pentaerythritol polyols, produces a new generation of hydraulic fluids with many advantages and provides longevity comparable to that of petroleum-based fuel at moderate temperature [28,29].

2.2.5 *Epoxy Derivatives*

Epoxidation can be considered a common and useful method to transform the nature feedstock to significant industry compounds. The carbon–carbon double bonds on the fatty acid chains provide the reactive sites for epoxidation by chemical routine and enzymatic routine [30,31].

The most preferred epoxidation of vegetable oils is Prileschajew reaction, which is conducted in the presence of peracids (peracetic or performic acid) due to ready availability and low price [30,32]. The degree of epoxidation can be controlled by reaction ratios of starting materials, reaction time, and reaction temperatures. Acetic/peracetic acid is largely used because it leads to lower ring-opening than formic/performic acid. However, this method is not selective and the acid used would cause corrosion of the equipment as well as residue issue.

Thus, the heterogenization of such processes using solid catalysts is of great interest from industrial and environmental points of view (see Figure 2.8). Transition metal complexes such as Mo (VI), rhenium, oxomolybdenum are among the options. Maritana investigated the epoxidation of soybean oil with bis(acetyl-acetonato)dioxomolybdenum (VI) [$MoO_2(acac)_2$] as a catalyst in the presence of *tert*-butyl hydroperoxide as an oxidizing agent. The highest yield of epoxidation was 54.1 ± 0.9% at 110°C for 2 h. It also found that the unsaturation in the middle fatty acids chains was less susceptible to epoxidation in comparison with terminal double bonds of short chain alkenes [33,34].

Chemo-enzymatic epoxidation is another interesting route for the synthesis of epoxidized fatty acid derivatives because it avoids the ring-opening of epoxide [31]. Warwel reported that an immobilized lipase from *Candida antarctica* (Novozym 435) first converts unsaturated carboxylic acids to percarboxylic acids, followed by epoxidation themselves by intermolecular oxygen transfer (see Figure 2.9)

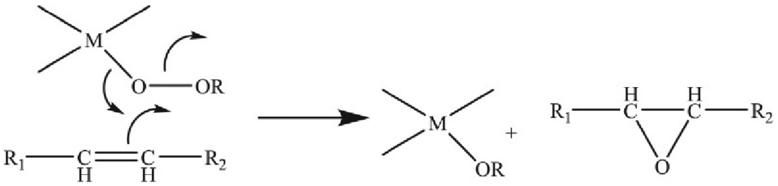


Figure 2.8 Mechanism of epoxidation of carbon double bonds by hydroperoxide in the presence of a transition metal catalyst.

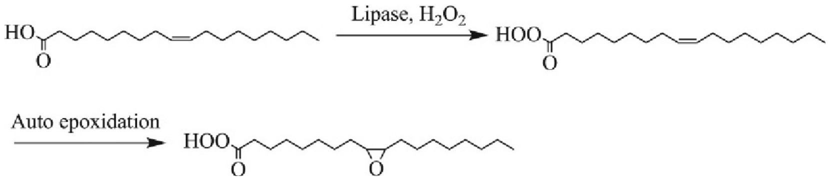


Figure 2.9 Epoxidation of fatty acids by lipase.

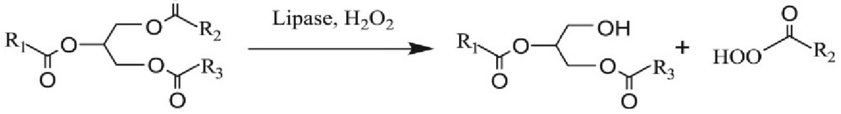


Figure 2.10 Perhydrolysis of plant oils.

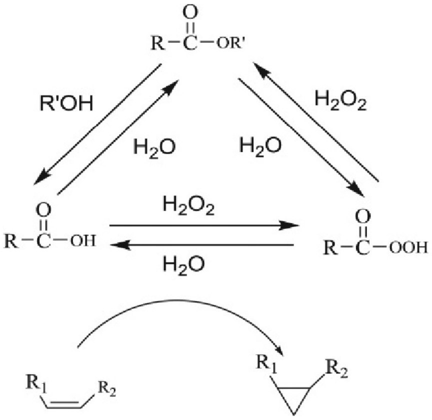


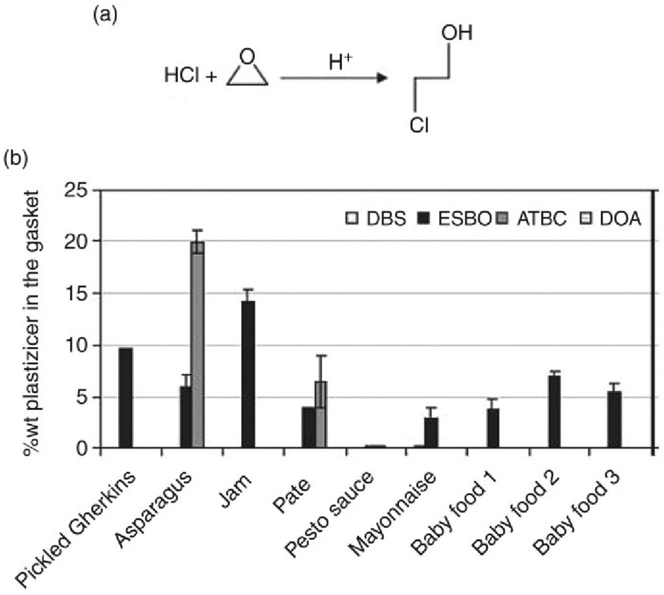
Figure 2.11 Three interconnected equilibria in epoxidation of plant oils by lipase [36].

with high yields of 72–91% after 16 h. Furthermore, the lipase is recovered and reused 15 times to produce epoxy-stearic acid on a multigram scale [35].

When a triglyceride is treated with hydrogen peroxide in the presence of Novozym 435, perfatty acids are formed by the perhydrolysis of plant oils (see Figure 2.10) and three interconnected equilibria (see Figure 2.11) existed in reaction mixture, resulting in epoxidized triglycerides containing small amounts of epoxidized free fatty acids and mono- and diglycerides. The formation of these side products could be avoided by simply adding a small amount of free fatty acids before reaction, and high yields can be obtained (rapeseed oil: 91%, sunflower oil: 88%, linseed oil: 80%) [36].

Epoxidized vegetable oils and epoxidized fatty acid are largely used as plasticizers, nonmetallic stabilizer, and antioxidants for PVC as they offer ease of processing and improve flexibility [37]. The epoxides react with hydrogen chloride released from the PVC resins under the prolonged action of light and heat, restoring the labile chlorine atoms back into the polymer chains (see Figure 2.12) [38]. Also, the epoxides might act as a polyene blocker, opening by reaction at a labile hydrogen site in the PVC to form an ether linkage with the chlorinated epoxy [39]. These reactions prevent PVC from further dehydrochlorination, preserving its color and limiting loss in plasticized PVC properties at high temperatures. Bouchareb found that the tensile strength of PVC decreases gradually with the content of epoxidized sunflower oil, whereas the elongation at break increases. However, increasing the degree of epoxidation of epoxidized sunflower oil will increase in tensile strength and decrease in elongation at break. The authors also pointed out that the plasticizing effect of epoxidized sunflower oil was higher than that of epoxidized soybean oil because of its higher compatibility with PVC [39]. Bueno-Ferrer evaluated the use of epoxidized soybean oil for PVC stabilization in commercial lids, and found that the thermal stability of PVC was highly dependent on the plasticizer concentration and a significant increase in thermal degradation temperature with increased content of epoxidized soybean oil, permitting their use in food processing at high temperatures [38].

Epoxy vegetable oils are also preferred lubricants, not only because they acquire most of the properties required for lubricants (such as high index viscosity, low volatility, and good lubricity), but also because they overcome the disadvantage of poor



(c)

Samples	$T_{95\%}$ (°C)
Raw materials	
PVC resin	271
Pure ESBO plasticizer	352
Cured plastisols	
30 wt% ESBO	280
40 wt% ESBO	282
50 wt% ESBO	291
Real samples (gaskets)	
Pickled gherkins	268
Asparagus	249
Jam	267
Pate	261
Pesto sauce	242
Mayonnaise	267
Baby food 1	258
Baby food 2	258
Baby food 3	260

Figure 2.12 (a) Scheme of the reaction of the oxirane ring in epoxidized soybean oil with HCl (PVC) inhibiting the thermal degradation process of PVC. (b) Plasticizers found in the gaskets of commercial lids, DBS-dibutyl sebacate, DOA-dioctyl adipate, ATBC-acetyl tributyl citrate. (c) Initial degradation temperatures (95%) of raw materials, cured plastiso, and gaskets for commercial lids [38].

oxidative and thermal stability of raw vegetable oils. For example, Wu reported that the epoxidized rapeseed oil has good friction-reducing and extreme pressure abilities, because the three-member ring of oxirane could form polyester or polyether material due to tribo-polymerization, which is tribologically effective to reduce friction [40].

2.2.6 Conjugates

Vegetable oils that contain fatty acids with conjugated double bonds are valuable drying agents in paints, varnishes, and inks. In conjugated fatty acids, cross-linking reactions occur by the action of atmospheric oxygen in room temperature when oxygen directly attacks the conjugated double bonds and forms free radicals. Although the fatty acid chains in triglyceride molecules contain a varied number of carbon–carbon double bonds, only few vegetable oils naturally contain conjugated carbon double bonds, such as Tung oil, which were of the prime interest to fine wood finishes. Most of these double bonds in fatty acid chains are not reactive enough to produce viable materials by free radical or cationic polymerization, in which double bonds are separated by methylene group, commonly referred to as being "methylene interrupted." Castor oil has only one carbon–carbon double bond in each fatty acid chain, and thus is cataloged as nondrying oil. However, it can be dehydrated at about 250°C and in the presence of catalysts (e.g., concentrated sulphuric acid, activated earth) and under an inert atmosphere or vacuum, forming chemicals containing conjugated double for making semidrying or drying oil resembling Tung oil, which is used extensively in paints and varnishes [41].

Isomerization of nonconjugated double bonds in fatty acid into conjugated counterparts has been regarded as a useful method to render vegetable oils new application for coating and paints application. Krompiec investigated the effect of different ruthenium complexes ($[RuHCl(CO)(PPh_3)_3]$) as catalyst on the isomerization of rapeseed, soybean, sunflower, and linseed oils. The conversions of conjugation were 30, 54, 54, and 50 wt% for rapeseed, soybean, sunflower, and linseed oils. However, high isomerization temperature (212–226°C) leads to 10 wt% polymerization of triglyceride oils [42]. Sleeter reduced isomerization temperature to 180°C for linseed and soybean oils with ruthenium catalysts in the presence of formic acid [43]. Larock found that the yields of homogeneous isomerization of vegetable oils can be increased to high yields (95%) using $[RhCl(C_8H_{14})_2]_2$ as catalyst in 60°C for 24 h [44].

2.2.7 Other Derivatives

Vegetable oil is a preferred carbon precursor with a low H content for the production of high-quality CNT production. Spray pyrolysis-assisted CVD is often used for the synthesis of CTN for these liquid bio-resources, in which vegetable oils are vaporized at low temperature on a furnace, and then transported by a carrier gas into a second furnace for pyrolysis and deposition at higher temperature with Fe/Co zeolite catalysts. The typical spray pyrolysis setup is shown in Figure 2.13.

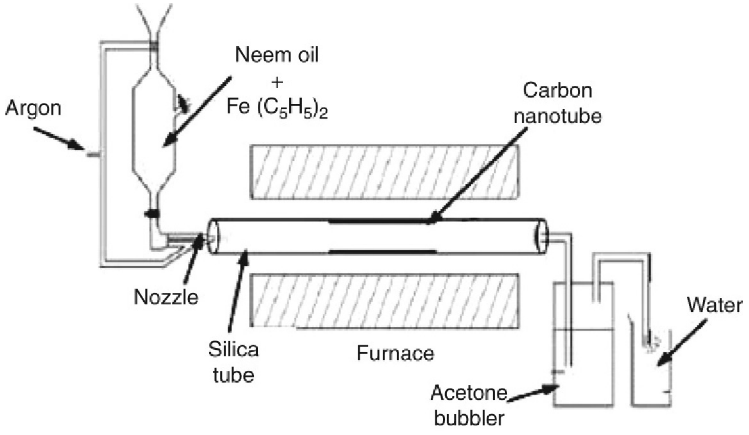


Figure 2.13 Spray pyrolysis setup for the synthesis of aligned CNTs [46].

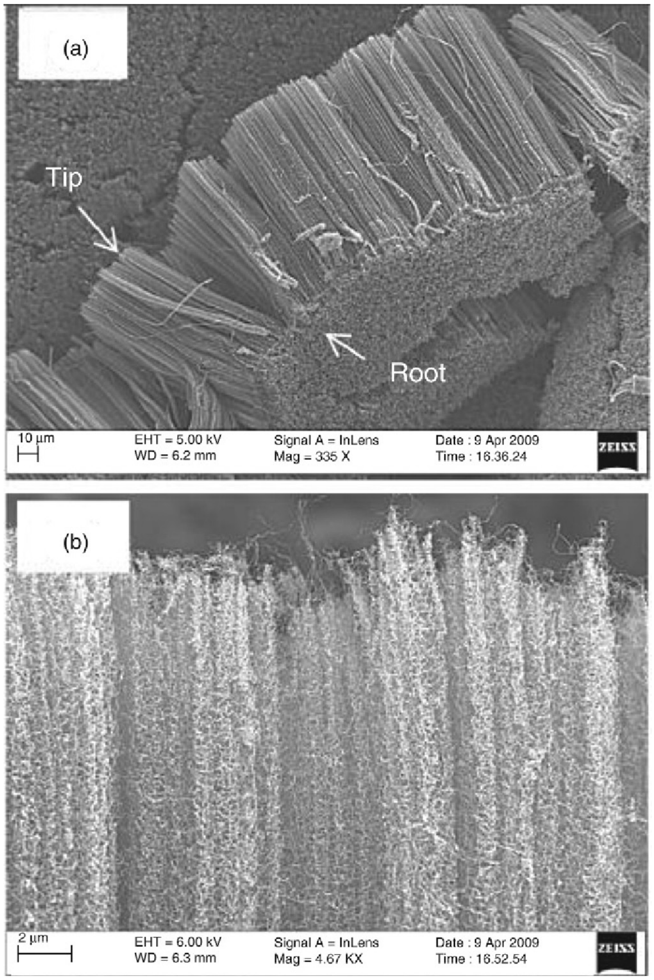


Figure 2.14 SEM images of CNT from palm oil on a Si substrate: (a) peeled off bundle of CNT, (b) side view of the aligned CNTs [49].

Turpentine oil [45], neem oil [46], coconut oil [47], eucalyptus oil [48], and palm oil [49] have been used as the carbon source for CNTs production with variable amorphous and diameters. In a spray pyrolysis process with carefully designed Fe zeolite catalysts and palm oil as carbon source, Suriani synthesized a bundle of mixed multiwalled and single-walled carbon nanotubes (CNTs) of about 90% purity, in which diameters of the single-walled carbon nanotubes were estimated to be 0.6–1.2 nm as shown in Figure 2.14 [49]. By controlling the growth temperature and concentration of catalyst, Paul prepared multiwalled carbon nanotubes with diameters in the range of 80–90 nm [47]. Tiwari reported a scalable synthesis of aligned multiwalled carbon nanotubes bundles with length in the range of 20–50 µm from neem oils by spray pyrolysis at 825°C. The diameters of multiwalled CNTs were found to be 15–30 nm [46].

2.3 Conclusions

With the advance of science and technology in the last decade, many important chemical compounds have been developed by modern synthetic methods, enzymatic and microbiological methods. Some of them have been employed as substitution of petroleum-based counterparts to benefit the whole society. And others are still in the laboratory due to the higher price or lower properties. However, with the breeding of new oil plants including the use of gene technology, more and new oil plants containing fatty acids with interesting desired properties and high yields will be introduced and cultivated for chemical utilization. Also, academia and industry are struggling to develop novel technology to improve conversion, and especially selectivity, low the coast to make possible a commercial application of those processes. In the coming years, the utilization of plant oils as renewable raw materials in the chemical industry is continued to be a challenge and direction for research and development.

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3 Plant Oil-Based Polyurethanes

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This chapter provides a brief overview of polyurethane chemistry and plant oil-based polyols. For some readers, this may be their first introduction to plant oil-based polyurethanes, while for others, this will be a review of the current literature. The primary objective of this chapter is to highlight the newest developments on plant oil-based polyurethanes rather than provide a comprehensive account of the field.

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In the past several years, a number of excellent reviews focused on this subject have been published. In 2008, Petrovic wrote a comprehensive review on vegetable oil-based polyurethanes [1]. Three years later, Pfister et al. reviewed recent progress in the field [2]. More recently, Desroches et al. wrote a comprehensive review on industrial products made from vegetable oil-based polyurethanes [3]. Many of the references in this chapter will highlight current research trends in plant oil-based polyurethanes since these reviews were published.

3.1 Polyurethane Chemistry

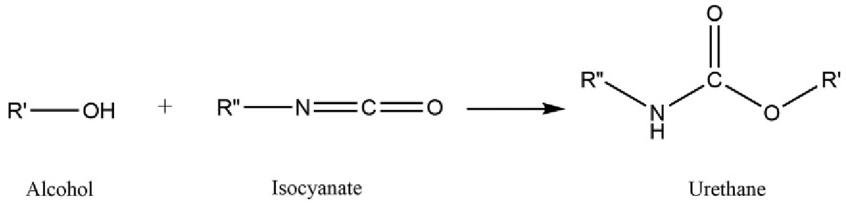
Polyurethanes are polymers which are typically made by reacting isocyanate groups from polyisocyanates with hydroxyl groups from polyols to form urethane bonds (see Scheme 3.1). Polymer chain extension occurs when polyols and isocyanates with a functionality of two (e.g., diols and diisocyanates) are reacted together. It should be noted that functionalities greater than two generate polymer crosslinking. Typically, polyurethanes are formulated with a slight excess of isocyanate groups due to the reactivity of isocyanates with water [4].

Isocyanates are highly reactive functional groups, which can react with a number of other functional groups including amines, carboxylic acids, ureas, and other isocyanate groups. Reactions of isocyanates with water and amines are discussed later in the section on polyurethane foams, while the other reactions are outside the scope of this chapter. Delebecq et al. wrote an excellent review on isocyanate chemistry, which also covers the development of blocked isocyanates [5].

Polyurethanes are versatile materials because the chemical structure of the isocyanate and polyol starting materials can be readily changed. Isocyanates can either be aromatic or aliphatic. Aromatic isocyanates have better thermal and flame retardant properties due to the stability of the aromatic rings and are used extensively in polyurethane foams. Common aromatic isocyanates used industrially include toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), and polymeric MDI. In contrast, aliphatic isocyanates are often used in coatings applications because they are more resistant to yellowing under UV exposure [6]. Examples of aliphatic diisocyanates include isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), and bis(4-isocyanatocyclohexyl)methane (H_{12}MDI) (Figure 3.1). Pentamethylene diisocyanate (PDI), a new bio-based aliphatic isocyanate designed for polyurethane coatings, is expected to be made commercially available in 2015 [7].

3.2 Plant Oil-Based Polyurethanes

In recent years, considerable research has focused on the replacement of petroleum-based starting materials for polyurethanes



Scheme 3.1 Urethane reaction of polyurethanes.

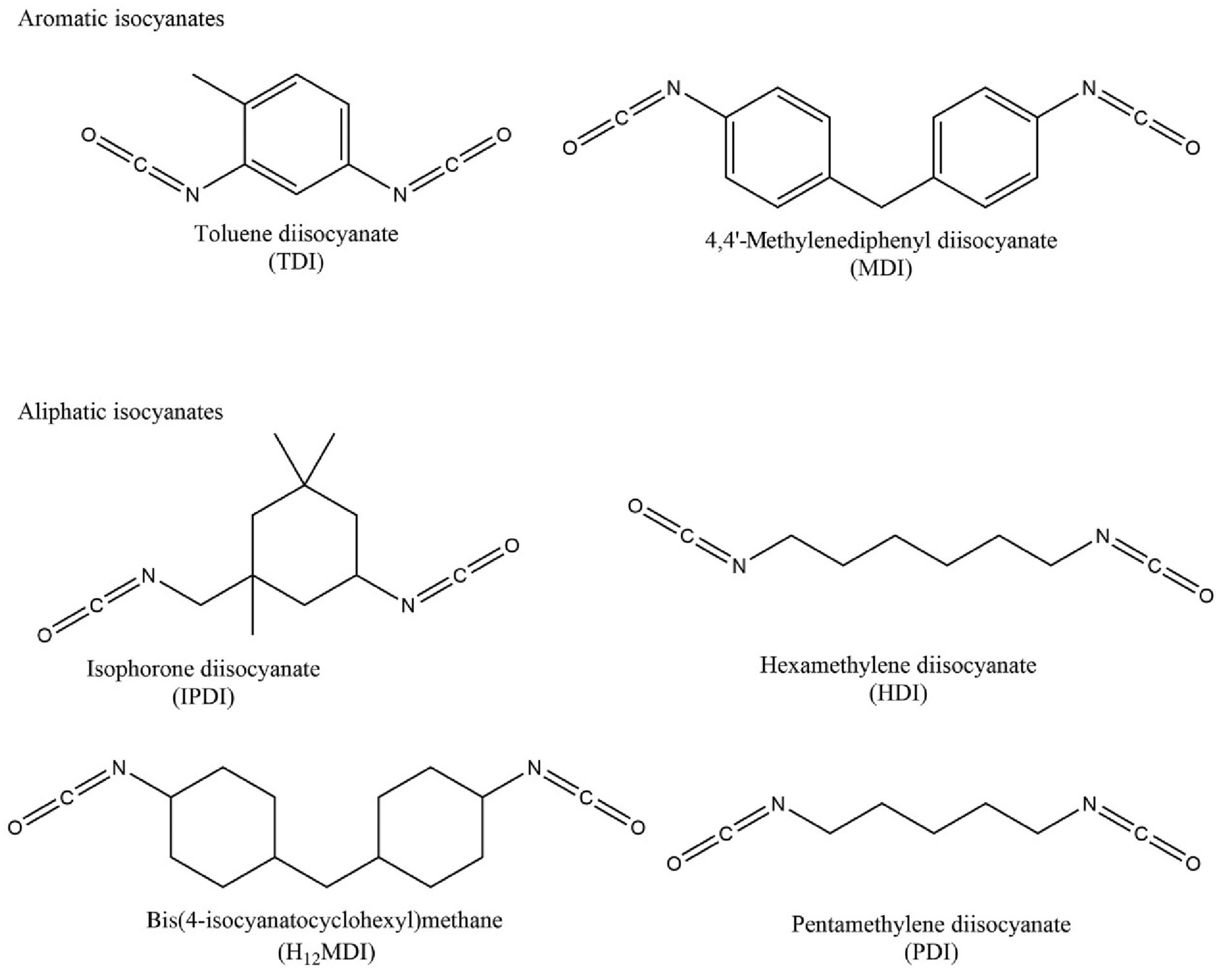


Figure 3.1 Structures of common diisocyanates.

with plant oil-based polyols [8]. Most plant oil-based polyols are made from triglycerides, although fatty acids and fatty acid derivatives can be used to make polyols. Triglycerides consist of three fatty acid chains connected to a glycerin backbone via ester linkages (see Figure 3.2). The most common fatty acids range in length from 16 to 20 carbons and vary in unsaturation from 0 to 3 double bonds (see Figure 3.3) [9]. Examples of saturated fatty acids include palmitic acid (C16:0)[1], and stearic acid (C18:0). Common unsaturated acids include oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3). Overall unsaturation of triglycerides is determined by the relative composition of fatty acids and is typically measured by iodine values[2]. Table 3.1 lists typical compositions for common plant oils.

---

[1] The convention for naming fatty acids is to list the number of carbons in the fatty acid chain followed by the number of double bonds. For example, palmitic acid (C16:0) has 16 carbon atoms and 0 double bonds.

[2] Iodine value (IV) or iodine number is a measure of the degree of unsaturation and is determined by the amount of iodine absorbed per gram of sample. Iodine values are typically expressed in terms of centigrams of iodine per gram of sample (weight percent of absorbed iodine) [10]. Higher iodine values indicate a greater amount of unsaturation.

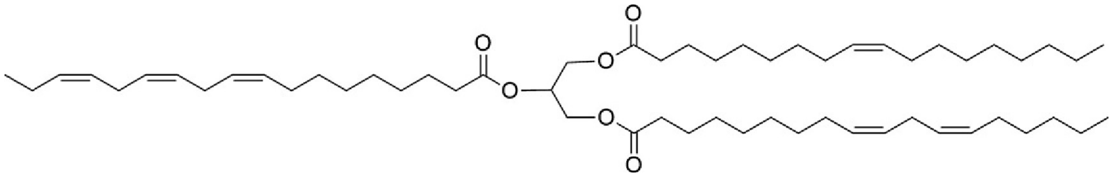


Figure 3.2 Structure of a typical triglyceride.

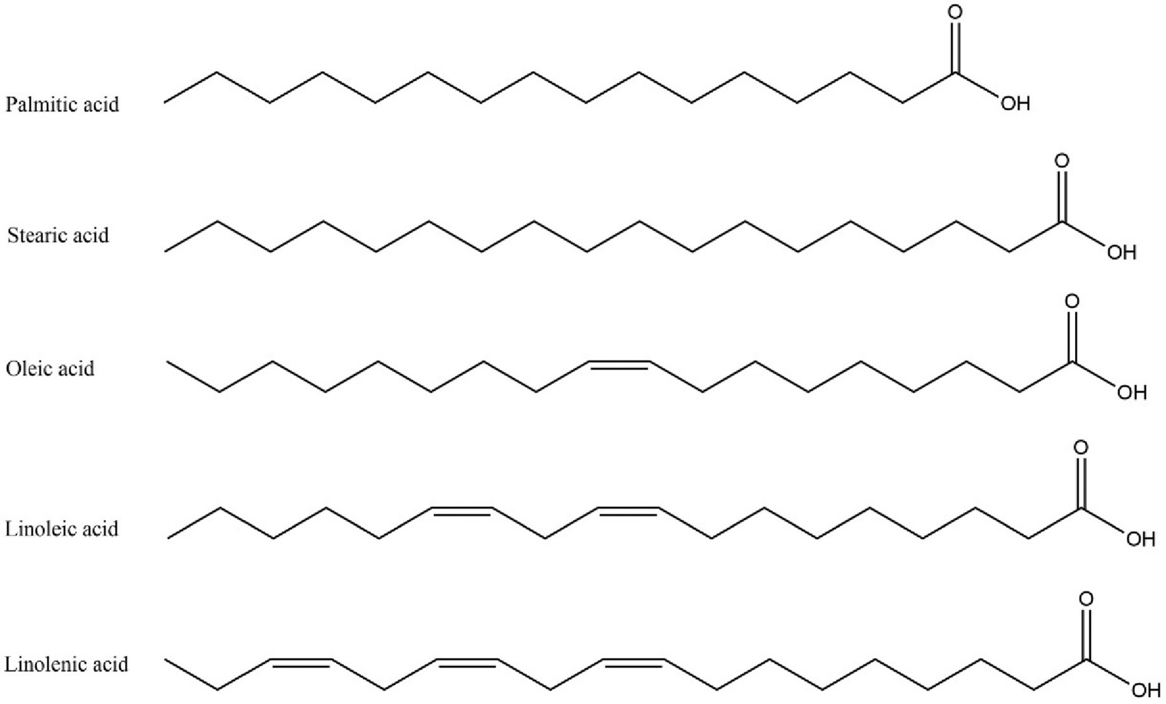


Figure 3.3 Most common fatty acids found in plant oils.

In fatty acids found in most plant oils, carboxylic acid groups and unsaturated carbon–carbon double bonds are the only naturally occurring functional groups. Three notable exceptions are ricinoleic acid, lesquerolic acid, and vernolic acid (see Figure 3.4). Ricinoleic acid, which makes up about 87% of castor oil, contains a hydroxyl group on the C12 position and a carbon–carbon double bond between C9 and C10. Lesquerolic acid, a component of lesquerella oil, is similar to castor oil because it has a hydroxyl group (C14) and a carbon–carbon double bond (between C11 and C12). With 20 carbons, lesquerella acid is slightly longer than the 18 carbon ricinoleic acid. Vernolic acid, the major component of vernonia oil, contains an oxirane (epoxy group) between the C12 and C13 carbon atoms and a double bond between C9 and C10.

3.3 Developing New Sources of Vegetable Oils

Abundant vegetable oils such as soybean oil, castor oil, and corn oil have already found widespread use in plant oil-based polyurethanes. Palm oil, despite is abundance, has found relatively limited use in making polyols

Table 3.1 Fatty Acid Composition and Iodine Values of Common Plant Oils[a]

Oil	Fatty Acid Composition (%)							Iodine Value
	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	
Castor[b]	–	–	1–2	0.9–2	2.9–6	3–5	0–0.5	81–91
Corn	0–0.3	0–0.3	9.2–16.5	0–3.3	20–42.2	39.4–65.6	0.5–1.5	107–135
Linseed	–	–	5.7–7	3–4	20–20.3	17–17.3	52–54	170–203
Olive	–	0–0.1	7.5–20	0.5–5.0	55–83	3.5–21	0–1.5	75–94
Palm[c]	0–0.4	0.5–2.0	40–48	3.5–6.5	36–44	6.5 – 12.0	0–0.5	49–55
Palm Kernal[c]	40–55	14–18	6.5–0.3	1.3–3	12–21	1–3.5	0–0.7	14–21
Peanut	0–0.1	0–0.1	8.3–4.0	1.9–4.4	36.4–67.1	14.0–43.0	0–0.1	83–107
Rapeseed	0.1	0.2	1.5–6	0.5–3.1	8–60	11–23	5–13	94–120
Soybean	0–0.1	0–0.2	9.7–13.3	3.0–5.4	17.7–28.5	49.8–57.1	5.5–9.5	118–139

[a] *Compiled information from* Physical and Chemical Characteristics of Oils, Fats, and Waxes*.*
[b] *Castor oil is composed of 88% ricinoleic acid.*
[c] *Elaeis guineensis.*

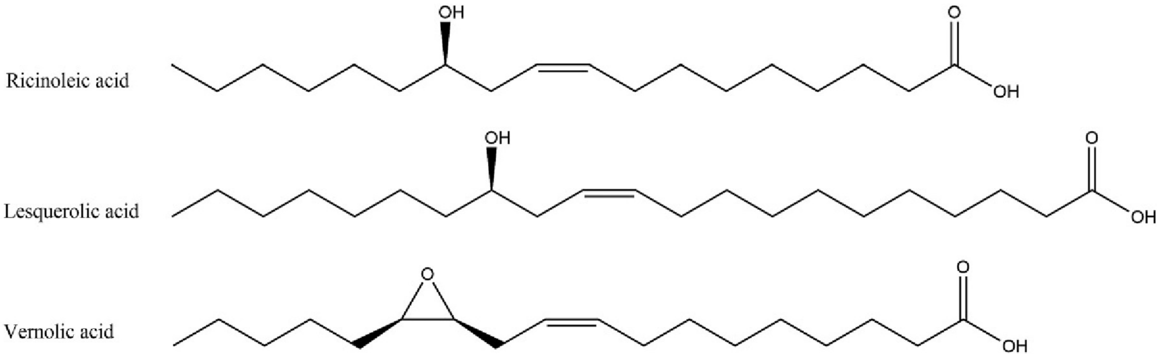


Figure 3.4 Structures of naturally occurring hydroxylated and epoxidized fatty acids.

for polyurethanes due to low unsaturation [2]. Seed oil from flowering plants such as rapeseed [11], sunflower (*Helianthus annuus* L.) [12], and *Camelina sativa* (a member of the mustard family) [13] is all being explored as sustainable sources of plant oil-based polyols. Algal oils are also a potential source of plant oil-based polyols, although there have been relatively few studies on using algal oil to make polymers [14].

There is significant interest in using a wide variety of underutilized plant oils from tree nuts and fruit seeds found in developing regions of the world as sustainable local or regional sources of polyols. For example, *Mesua ferrea* L., commonly known as nahar, is a tree found in India and other parts of Asia that has seeds with triglyceride contents of up to 70%. Nahar seed oil has been used to make polyols via transesterification with glycerol [15]. Jatropha (*Jatropha curcas* L.), which originated in the Americas, is now being grown globally for its seed oil as a source of biodiesel [16]. Jatropha oil-based polyols have been prepared from crude jatropha oil using conventional epoxidation and ring opening [17]. There was also a recent study that used seed oil from *Prosopis juliflora*, a shrub or small tree also known as mesquite, to make polyols for polyurethanes [18]. Yellow passion fruit (*Passiflora edulis* Sims *f. flavicarpa* Degener), a native plant in South America, is widely cultivated for its juice that generates large amounts of seeds as waste by-products. Passion fruit seed oil contains high amounts of unsaturated linoleic acid (73%) that can be used to make plant oil-based polyols [19]. Recent studies have investigated the synthesis of passion fruit oil-based polyols for making polyurethane foams [20].

3.4 Polyol Methods

Castor oil can be used to make polyurethanes without additional processing because it has an average hydroxyl functionality of 2.7 per triglyceride due to its high content of ricinoleic acid. Lesquerella oil naturally contains hydroxyl groups, but its potential for commercial applications is hampered by limited cultivation. All other plant oils require conversion of either carbon–carbon double bonds or the ester groups into hydroxyls. Polyols can be formed from double bonds by epoxidation/oxirane ring opening, ozonolysis/reduction, and hydroformylation/reduction (see Scheme 3.2). Examples of ester group modifications include transesterification with a polyol and amidation with an amine polyol (see Scheme 3.2). Recent developments for several of these methods are discussed further below.

Polyol structures formed by the different methods can play a significant role in determining reactivity of the polyols, as well as the material properties of the resulting polyurethanes. For example, primary hydroxyl groups are more reactive with isocyanates than secondary hydroxyls. Ozonolyis/reduction, hydroformylation/reduction, transesterification, and amidation are routes that form primary hydroxyls, whereas epoxidation/oxirane ring opening generates secondary hydroxyls. Hydroformylation inserts an additional carbon atom into the polyol structure, while ozonolysis yields polyols with decreased molecular weights. With the exception of polyols formed by ozonolysis, most plant oil-based polyols contain dangling chains that can act as internal plasticizers. The hydroxyl functionality of plant oil-based polyols – the average number of hydroxyl groups per molecule – can vary based on the route of polyol formation, the unsaturation of the plant oil, and the extent of reaction.

Molecular weight and hydroxyl functionality are two of the most important factors that control the overall properties of polyurethanes. In practice, hydroxyl (OH) numbers are more commonly used by formulators than functionalities because hydroxyl numbers correlate the hydroxyl content per mass of polyol sample. Hydroxyl numbers are easily determined by wet analytical techniques[3]. Equivalent weight of polyol,

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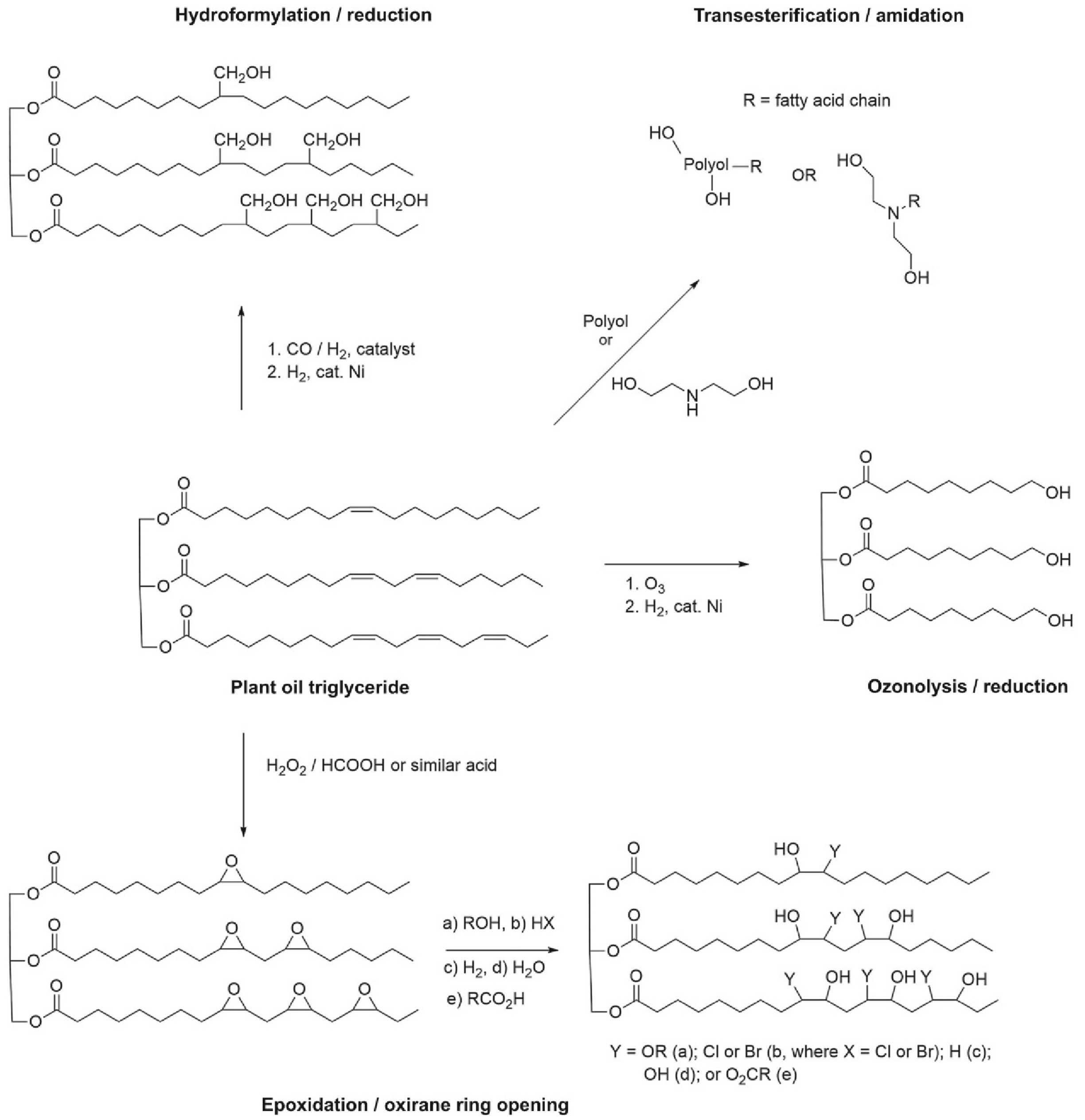
[3] Hydroxyl numbers are determined by following a standard analytical procedure, such as ASTM D1957. In these procedures, the hydroxyl groups are first acetylated and then titrated with potassium hydroxide. The units are given by milligrams KOH per gram polyol.



Scheme 3.2 Common routes to vegetable oil-based polyols.[4]

another important term, is the average molecular weight of the polyol divided by the average hydroxyl functionality. Relationships between molecular weight, functionality, hydroxyl number, and equivalent weights[5] are shown in the following equations [21]:

$$\text{Functionality} = \frac{\text{Molecular Weight}}{\text{Equivalent Weight}}$$

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[4] Adapted from a reaction scheme by Pfister et al. [2].

[5] In these equations, 56.1 is the molecular weight of potassium hydroxide, while 1000 is the conversion between milligrams and grams.

$$\text{Equivalent Weight} = \frac{56.1*1000}{\text{OH Number}}$$

$$\text{Functionality} = \frac{\text{Molecular Weight*OH Number}}{56.1*1000}$$

3.4.1 Epoxidation/Ring-Opening

Most widely available plant oil polyols are produced by some variation of epoxidation of double bonds, followed by nucleophilic ring opening. The most common method of epoxidizing plant oils uses peracids, which are often formed *in situ* with hydrogen peroxide and an acid, such as formic acid, acetic acid, or propionic acid [22]. Recyclable heterogeneous catalysts for ring opening oxiranes, such as sulfamic acid-functionalized iron nanoparticles, are being developed as sustainable alternatives to homogenous acid catalysts [23].

Ring opening of oxiranes is typically performed with alcohols, water, acids, or by hydrogenation [17]. In some cases, ring opening can be used to introduce additional functionality to plant oil-based polyols. For example, methacrylic acid has been used to ring open epoxidized plant oils to produce methacrylated plant oil-based polyols that can be further functionalized [13]. Zhang et al. recently reported a novel two-step approach for making plant oil-based polyols consisting of epoxidation of plant oils, followed by reduction of the epoxides and esters. In this study, epoxidized soybean oil and epoxidized linseed oil were reduced with lithium aluminum hydride ($LiAlH_4$) to form fatty acid-based polyols [24].

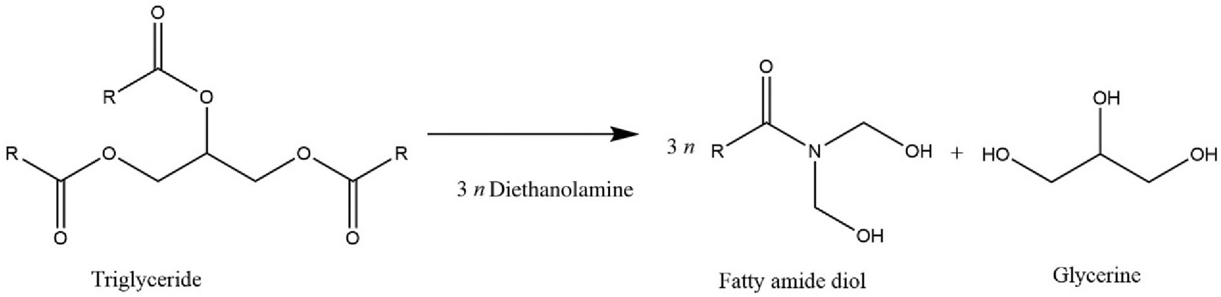
3.4.2 Ozonolysis

During ozonolysis, ozone reacts with double bonds to form an unstable ozonide ring. Aldehydes are formed upon decomposition of the ozonide rings. These carbonyls are subsequently reduced via hydrogenation to form primary hydroxyl groups [25]. Alternatively, polyols can be formed by reacting the unstable ozonides with diols (e.g., ethylene glycol) to form polyols with ester linkages [26]. A drawback of the ozonolysis/hydrogenation route is that the cleavage of double bonds during the ozonolysis step causes a reduction in molecular weight [27]. Furthermore, ozonolysis/hydrogenation of plant oils generates a mixture of products (alcohols, diols, and triols). Solvent selection is an important factor in determining the products and yields of ozonolysis. Mixtures of protic and aprotic solvents have been reported to maximize the yields of aldehydes, while minimizing the production of carboxylic acids [28].

3.4.3 Amidation

The amidation of fatty acid esters using diethanolamine to make amide polyols is an interesting approach for making plant oil-based polyols (see Scheme 3.3). This approach is particularly useful for feedstock with high free fatty acid contents. Tall oil, a by-product of Kraft pulping, is known for its high amounts of free fatty acids. Recently, tall oil fatty acids (TOFA) were used to make fatty acid-based amide polyols [29].

Amidation is also useful for nondrying oils, such as palm oil, which have high amounts of saturated fatty acids. Epoxidation and ring opening of nondrying oils tends to result in polyols with low hydroxyl functionalities. Amide polyols made from palm tree (*Elaeis guineensis*) oil have been used to make polyurethane coatings [30]. Likewise, seed oil from neem (*Azadiriachta indica juss*), a tree found in the Indian subcontinent, has been reacted with diethanolamine to make amide diols [31].



Scheme 3.3 Reaction scheme for making fatty acid-based amide polyols.

The composition of neem seed oil contains approximately 45% saturated fatty acids (palmitic, stearic, and arachidic). Other plant oils that have been used to make amide polyols include cottonseed oil [32] and olive oil [33].

Amide diols can be further functionalized into polyetheramides. Neem oil-based amide diols were further functionalized by reacting with bisphenol-A to make polyetheramides [31]. The thermal and mechanical properties of polyurethanes made from neem oil-based polyetheramides indicate that these materials have strong potential as resins in surface coatings. Polyetheramides have been synthesized from olive oil-based amide diols [33]. One drawback of amide diols is the high temperature necessary for making the reaction proceed. Recently, it has been shown that microwave assisted techniques are a more sustainable way to make amide diols and polyetheramides [33].

3.5 Flame Retardant Polyols

Polyurethanes, especially those made from plant oil-based polyols, require the use of flame retardants in their formulations. Flame retardants often contain phosphorus, halogen, boron, metal hydroxides, or nitrogen-based functional groups [34]. However, the use of halogenated (i.e., brominated or chlorinated) flame retardants is declining due to the potential release of toxic and corrosive combustion products [35]. As a result, many efforts to make bio-based flame retardants have focused on modifying plant oils with phosphorus-containing functional groups [36]. Boron-modified plant oil polyols have been prepared from castor oil [37] and linseed oil [38], but the flame retardant properties of these polyols were not reported.

Phosphorylated polyols with flame retardant properties have been synthesized from epoxidized soybean oil and phosphoric acid [39]. Rigid polyurethane foams made with phosphorylated polyols having phosphorus contents ranging from 0.4 wt% to 0.8 wt% displayed comparable flame retardant effects as commercial flame retardants based on limiting oxygen indexes (LOI) [40]. In another recent study, castor oil-based flame retardant polyols were prepared with diethyl phosphate [24]. The synthesis of these castor oil-based polyols followed a three-step process consisting of alcoholysis with glycerin, epoxidation with formic acid/hydrogen peroxide, and ring opening with diethyl phosphate. Resulting foams with 3 wt% phosphorus made with the flame retardant polyols showed a 24.3% improvement in LOI compared to foams made with gylcerolysis castor oil.

3.6 Alternative Routes for Making Polyurethanes

While the vast majority of research in bio-based polyurethanes has focused on using vegetable oil-based polyols, other routes for making renewable polyurethanes are being explored. Aliphatic vegetable oil-based isocyanates have been investigated [2]. The price of aliphatic amines has been a major factor limiting the development of renewable isocyanates [5].

Extensive research efforts have been made to find safer routes for making polyurethanes because isocyanates are toxic and can cause significant respiratory problems [41]. Furthermore, phosgene precursors of isocyanates are even more dangerous to the environment and to human health [42]. Phosgene-free methods of making isocyanates from fatty acids are a potential path for making more environmentally friendly isocyanates [43]. Polyurethane that avoids the use of isocyanate groups altogether has been prepared by reacting cyclo-carbonate functionalized soybean oil with diamines [41].

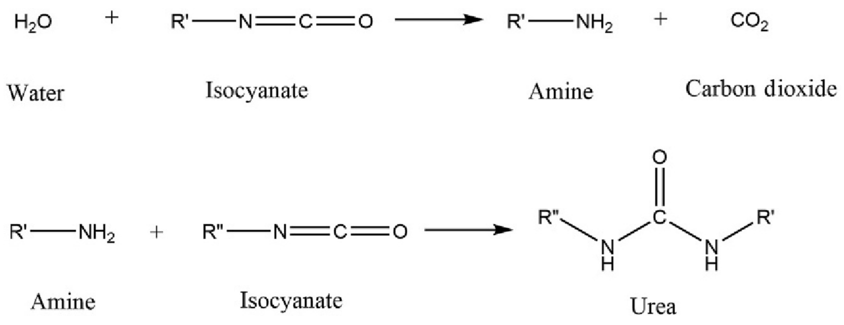
3.7 Applications of Plant Oil-Based Polyurethanes

Polyurethanes make up one of the most widely used and most versatile classes of polymers. However, the vast majority of polyurethanes are made from petrochemical-based feedstock. Applications of bio-based polyurethanes from plant oils include flexible foams [44], rigid foams [45], coatings [21], elastomers [46], and adhesives [47]. A few applications of plant oil-based polyurethanes, including foams, coatings, and shape memory polymers, will be discussed in greater detail below.

3.8 Foams

Foam materials, including polyurethane foams, are lightweight, resilient, energy absorbent materials with a range of thermal and mechanical properties that can be readily tailored to meet the application requirements [48]. The polyurethane foam industry in the United States generates $9.5 billion dollars a year and is expected to continue to grow at an annual growth rate of 2.6% over the next 5 years [49]. Downstream demand from new construction, furniture manufacturing, and automobile manufacturing are all expected to grow over the next few years as the economy recovers from the recession.

As described previously, urethane bonds are formed when isocyanate groups react with hydroxyl groups (see Scheme 3.1). The urethane reaction is sometimes referred to as the “gel” reaction. In polyurethane foams, a second chemical reaction, the urea reaction, occurs when an isocyanate reacts with water (see Scheme 3.4). The urea reaction is a two-step process that begins with an isocyanate



Scheme 3.4 Urea formation in polyurethane foams.

group reacting with water to yield an amine and a carbon dioxide molecule. In the second step, the amine subsequently reacts with a second isocyanate group to form a urea linkage. The urea reaction is sometimes called the "blow" reaction because CO_2 gas is generated, which causes the formation of the cell structures in polyurethane foams.

Foams that are made with CO_2 generated by water reacting with isocyanates are called "water blown." In certain applications, additional blowing agents are added to improve the thermal insulation properties or performance at extreme temperatures. In recent years, many of the conventional blowing agents that caused ozone depletion have been replaced with more environmentally friendly blowing agents [50]. Examples of environmentally friendly blowing agents include HFC-365mc, HFC-245fa, and pentane isomers [51].

3.8.1 Flexible Foams

Flexible foams are used in automotive, furniture, packaging, and bedding applications.

In the United States, polyurethane flexible foams make up 37.6% of the revenues in the foam industry [49]. TDI is the most common isocyanate used in manufacturing flexible foams [52]. Although overexposure to TDI can cause respiratory sensitization, industry sponsored studies have shown that PU flexible foam mattresses do not pose a health risk to consumers [53]. Flexible foams require low crosslink densities, which can be achieved by using polyols with either low functionalities or high molecular weights [54].

Palm oil is a good source of plant oil-based polyols for replacing conventional polyether polyols in polyurethane flexible foams because it has low levels of unsaturation. Palm oil-based polyols with low hydroxyl functionalities and minimal amounts of residual double bonds have been synthesized by epoxidizing and ring opening palm triglycerides [55]. However, the amount of polyether polyols that can be replaced with significant changes to the formulation is limited. In one reported study, significant shrinkage was observed when more than 15 wt% palm oil-based polyols were used [55].

3.8.2 Rigid Foams

Rigid foams are used in a wider range of applications including construction, appliances, packaging, industrial, and transportation. Rigid foams typically have heavier densities than flexible foams. MDI and polymeric MDI are the most common isocyanates used in rigid foams. Rigid foam products make up 23.6% of the revenues generated by foams domestically [49]. Soybean oil-based polyols have been investigated extensively in recent years for developing rigid polyurethane foams [56].

3.9 Coatings

Polyurethane coatings are widely used in applications such as construction, transportation, furniture, textile and fibers, and electronics. There has been a move in recent years to develop sustainable polymeric coatings that reduce the use of petrochemical-based polymers, as well as the emission of volatile organic compounds (VOCs). Spray-applied VOC-free polyurethane coatings with high solid contents have been made with rapeseed oil-based polyols [57]. Hyperbranched plant oil-based polyurethanes have potential for use as thin film materials in packaging applications [12]. Water repellant polyurethane coatings have been made using alkoxysilane castor oil synthesized from thiol-ene coupling of 3-mercaptopropyl trimethoxysilane [58].

3.9.1 Waterborne Dispersions

Waterborne polyurethane dispersions (PUDs) are widely used polymers with a diverse range of applications, including paints, inks, coatings, adhesives, paper, and textiles [59]. PUDs offer various advantages, including low viscosity, high molecular weights, and good film forming properties [60]. PUDs are excellent choice of materials for reducing the emission of volatile organic compounds (VOC) generated by organic solvents [61]. Recently, a plant oil-based ionic segment for dispersing polyurethanes was synthesized as a substitute for dimethylol propionic acid (DMPA) by ring-opening epoxidized linseed oil with glycol followed by saponification [62]. A fully bio-based PUD was synthesized from castor oil and castor oil-based derivatives [63]. In this study, a linear castor oil-based diisocyanate was made using a Curtiss rearrangement, while the castor oil-based hydrophilic chain extender was prepared though a thiol-ene coupling of 3-mercaptopropionic acid.

3.9.2 Antimicrobial Coatings

There has been growing interest in developing plant oil-based cationic polyurethane coatings with antimicrobial properties in biomedical applications and food packaging. Quaternary ammonium compounds are well known for their antimicrobial properties [64]. Xia et al. examined the effects of different amine polyols on the antimicrobial, mechanical, and thermal properties of soybean oil-based cationic polyurethane coatings [65]. This study reported that *N*-methyl diethanolamine provided a good balance of properties, including the best thermal stability compared to the other amine polyols tested. In a related study, polyurethanes with higher relative ratios of *N*-methyl diethanolamine and lower crosslink densities showed increased antimicrobial activity [66]. In a different study, polyurethanes made from soybean oil-based polyols functionalized with quaternary ammonium salts used alkylating agents (methyl iodide and benzyl chloride) as an alternative to using an acid [67]. Boron-modified linseed oil polyurethanes have shown moderate antimicrobial activity against *E. coli* and high antimicrobial activity against *S. aureus* [38]. Metallohybrid plant oil-based polyols containing copper have been used to make polyurethane coatings with antimicrobial activity against *S. aureus* and *E. coli* [68].

3.10 Shape Memory Polymers

Shape-memory polymers are an important class of polymers that are being used in a wide range of applications. Shape memory polymers retain a shape upon deformation, but will respond to a stimulus, such as temperature above a certain threshold, and return to its original predeformed shape [69]. Hyperbranched polyurethanes with shape memory properties have been prepared using monoglyceride polyols synthesized from transesterification of plant oils with glycerin [15]. Castor oil-based monoglyceride polyols demonstrated better shape memory properties due to higher crosslinking, while monoglyceride polyols with lower levels of unsaturation showed better thermal stability [70]. Another recent study using different soybean oil-based polyols confirmed the importance of glycerol crosslinking in shape recovery [71].

3.11 Conclusions

Plant oils and fatty acids are an important industrial feedstock for making sustainable polyurethanes. In recent years, there has been much work on developing regional sources of polyols from currently underutilized sources of plant oils. The goals of these efforts are to reduce dependence on petrochemicals, minimize environmental impacts, and improve local economies. There is also considerable interest in synthesizing multifunctional plant oil-based polyols to improve their performance in a wide range of applications. For example, phosphorus-modified plant oil-based polyols can impart fire resistance in polyurethane foams, while methacrylic acid-modified polyols provide graft sites for acrylic chains in hybrid polymers. Polyurethane coatings with antimicrobial properties can be synthesized using modified polyols. Although most of the attention has focused on developing plant oil-based polyols, new advances in bio-based isocyanates are expected to make an impact. Plant oil-based polyurethanes are already being used in major applications such as foams and coatings.

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4 Plant Oil-Based Polyhydroxyurethanes

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4.1 Introduction

The development of novel bio-based polymers from inexpensive and renewable materials has the potential to greatly impact our current economy, the environment, and our energy matrix. Due to the commercial importance of the plastics and coatings industries, and the uncertainty of the oil market, the replacement of petroleum-based materials with bio-based counterparts can be greatly advantageous. The advantages of bio-based materials are the ready availability of large quantities of renewable starting materials at insignificant costs, the potential of producing more bio-degradable materials than the virtually indestructible petroleum-based polymers, the possibility of obtaining properties not currently available in commercial petroleum-based products, and their overall intrinsic low toxicity. The current legislation and the frequent dramatic fluctuations in the price of oil also create an urgent need, from an industrial point of view, for renewable starting materials and bio-based products that have the potential to replace petroleum-based materials.

Vegetable oils are amongst the most widely used renewable raw materials [1]. They find use in paints [2], biocoatings [3–7], biofuels [8], and as building blocks for bio-based polymers [9–11]. Traditional polyurethanes with promising properties for use as coatings and adhesives

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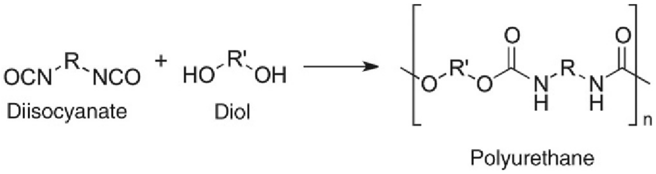


Figure 4.1 Generic chemical structure of polyurethanes.

have been obtained from vegetable oil-based polyols, and have been successfully used in the preparation of anionic [4], and cationic dispersions [5]. Hybrid emulsion systems have also been proposed [6,7]. The technology involved in these vegetable oil-based polyurethane systems is remarkably simple, and although it represents a step in the right direction, it does not address one of the major points of concern on the polyurethane production, which is the use of toxic chemicals such as diisocyanates.

This chapter presents the reader with an overview of the major accomplishments in bio-based polyurethane research, with a special focus on polyhydroxyurethanes (PHUs). The discussion starts with a brief description of the chemistry involved in polyurethanes (PUs), and then transitions into the advancements reported by select research groups on plant oil-based PUs and related systems. The last section of this manuscript addresses the chemistry involved in PHUs and the various proposed bio-based starting materials investigated to date, with an entire subsection dedicated to plant oil-based PHUs. Alternative PU systems from nonisocyanate sources are briefly described in this chapter, and concluding remarks give a perspective on the future of bio-based PHUs.

4.2 Petroleum-Based Polyurethanes

Polyurethanes are a class of polymers composed of repeating subunits linked together by urethane groups (R′-O-CO-NH-R) (Figure 4.1). Polyurethanes can be employed in a variety of applications due to the variety of subunits that can be used in their preparation. The subunits' structure determines bulk properties, such as flexibility, thermal stability, and mechanical strength. The range of applications for polyurethanes includes insulating foams, hard plastic parts, sealants, coatings, and durable flexible lining or tubes for the construction Industry.

The starting materials for most polyurethanes are diisocyanates and polyols. Typically, a diol is used, and occasionally a catalyst. Each monomer has at least two reactive functional groups, allowing the reaction to continue at the termini of the chains as the polymer grows [12]. Regardless of the exact starting material, the reaction proceeds to form polymer chains with repeating urethane groups as depicted in Figure 4.1. In that transformation, the hydroxyl group of the polyol acts as a nucleophile attacking the carbon of the isocyanate group as the pi electrons between C and O are pushed onto the oxygen. The re-establishment of the carbon–oxygen double bond pushes the electron density onto the nitrogen atom. A final proton transfer completes the mechanism, resulting in a urethane functional group. The reaction can be catalyzed by the addition of a base, which enhances the nucleophilicity of the polyol through deprotonation. The catalyst is regenerated during the final proton transfer step. This mechanism is widely accepted and therefore will not be explicitly presented in this chapter.

The structure of the polyol used in the preparation of a polyurethane significantly affects the properties of the resulting polymer [13]. The longer the carbon chain of the polyol is, the more ductile and flexible the resulting polymer. Reversely, shorter carbon chains in the polyol result in more rigid and durable polymers. The functionality of the polyol influences the crosslink density of the final material and therefore has a direct impact on the properties of the resulting polyurethane [14].

The structure of the diisocyanate used in the synthesis of polyurethanes is also crucial for the final properties of the polymer. Aromatic diisocyanates, such as toluene diisocyanate (TDI), or methylene diphenyl diisocyanate (MDI), are traditionally used for their high reactivity and stiffness conferred to the final material, most likely associated with pi-stacking interactions of the polymer chains. Polyurethanes made with TDI are usually more flexible than those made with MDI [15].

Recent research efforts have been targeted at replacing traditionally used polyols and diisocyanates with eco-friendly derivatives in the synthesis of polyurethanes. The use of diisocyanates represents a potential toxicity hazard in the manufacturing of polyurethanes as any unreacted isocyanate group left in the final product constitutes a risk that limits the applications of the final polymer. Additionally, bio-based polyols have been investigated as substitutes for petroleum-derived polyols commonly used in the synthesis of polyurethanes [16]. Another approach consists of the preparation of polymers containing repeating urethane linkages formed by alternative functional groups. One such example is the preparation of hydroxyurethanes from cyclic carbonates and amines. Such approach leads to polymers with properties very similar to traditional polyurethanes, with the added advantage of avoiding the use of diisocyanates and helping to mitigate toxicity and environmental concerns [17].

4.3 Polyurethanes from Bio-Based Polyols

Plant oils consist of triglycerides with fatty acid chains of varying length and degree of unsaturation depending on the plant from which the oil is extracted. These structural variations directly affect the physical and chemical properties of the oil, such as its reactivity toward other reagents. Thus, different plant oils can be classified as drying, semidrying, and nondrying oils, depending on their ability to auto-oxidize in the presence of O_2 from air. Some plant oils bear functional groups, like castor oil, which contains a hydroxyl (–OH) group attached to Carbon 12 (C_{12}) of the fatty acid chain. For illustration purposes, the accepted chemical structure of soybean oil is provided in Figure 4.2.

The carbon–carbon double bonds in plant oils can be reacted in many different ways to form bio-based polymers. The direct polymerization of carbon–carbon double bonds in triglycerides through thermal, cationic, and/or free radical processes, as well as ROMP and ADMET, is discussed in detail elsewhere [18]. Alternatively, the carbon–carbon double bonds in the fatty acid chains of vegetable oils can be epoxidized to form epoxidized triglycerides with various degrees of epoxidation [19]. Epoxidized oils can then be reacted with a variety of nucleophiles to append different functional groups to the triglyceride and therefore increase its reactivity. Acrylated epoxidized soybean oil (AESO), the product of the reaction of acrylic acid with epoxidized soybean oil (ESO), has been extensively studied

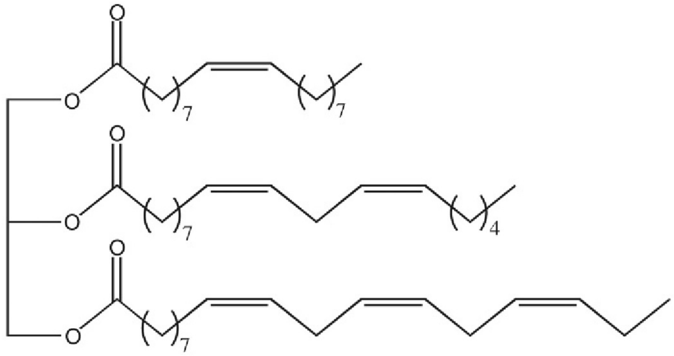
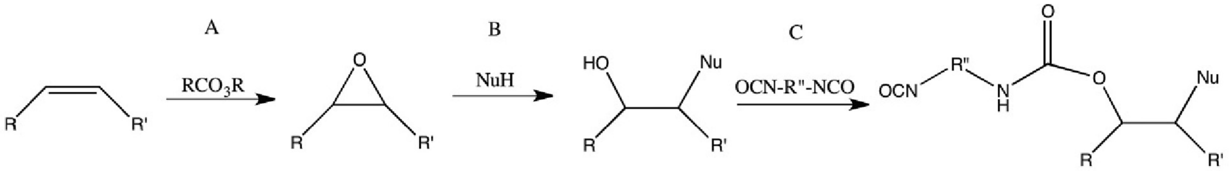


Figure 4.2 Accepted chemical structure of soybean oil.



where R, R', and R" are aliphatic alkyl chains, and Nu is a nucleophile

Figure 4.3 Steps involved in the conversion of plant oils into polyols for the preparation of polyurethanes. (a) epoxidation, (b) ring opening, (c) condensation.

and is currently commercially available [20]. Recently, AESO has been used to produce semirigid thermosetting foams with a high bio-based content and desirable mechanical properties for industrial uses [21]. Besides soybean oil, epoxidized methyl oleate has also been acrylated and polymerized to afford pressure-sensitive adhesives [22].

The ring opening reaction of the epoxide groups in epoxidized vegetable oils results in bio-based polyols. Such polyols can react with diisocyanates to give vegetable oil-based polyurethanes (Figure 4.3). Castor oil and ricinoleic acid, both of which are natural polyols, have been directly used in the preparation of polyurethanes [23–25]. Polyols based on a variety of epoxidized oils (sunflower, canola, soybean, corn, linseed [26], and passion fruit oils) (Rodrigues et al., unpublished work) have been polymerized with methylene diphenyl diisocyanate (MDI) to give polyurethanes. It has been found that the differences in the properties of these polyurethane networks result primarily from different crosslink densities, and are independent of the position of the reactive sites in the fatty acids.

Anionic waterborne polyurethane dispersions (PUDs) with no volatile organic compounds (VOCs) and uniform particle sizes have been prepared with 50–60 wt% methoxylated soybean oil polyols (MSOLs) [4]. These soybean oil-based polyurethanes have been obtained by the reaction of MSOLs with isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA), followed by neutralization with triethylamine and dispersion in water [4]. It was found that, besides the expected crosslink density dependence, the structure and the properties of the resulting materials greatly depend on the hard segment content of the PUs [4]. Along the same lines, vegetable oil-based cationic PUDs with uniform particle sizes have been prepared from castor oil, MSOLs, and AESO-based polyols [5]. The cocondensation of these plant oil-based polyols with *N*-methyl diethanol amine (MDEA) and MDI resulted in polyurethanes baring tertiary amines that were finally protonated to yield the desired waterborne, plant oil-based, cationic PUDs with improved adhesion to anionic substrates, such as leather and glass [5].

Polyurethane-acrylic hybrid systems have also been designed from soybean oil-based polyols [27]. In these systems, AESO has been condensed with toluene 2,4-diisocyanate, and DMPA, resulting in anionic PUDs with unreacted carbon–carbon double bonds. The subsequent free radical emulsion copolymerization of such PUDs with acrylic comonomers, such as butyl acrylate or methyl methacrylate, resulted in hybrid latexes with 15–60 wt% bio-based content [6,27]. The resulting plant oil-based hybrid latexes exhibit properties comparable to those of known polypropylene glycol-based polyurethane–acrylic hybrid latex films. Improved thermo-mechanical properties have been obtained by performing a seeded emulsion polymerization of 10–60 wt% of styrene or butyl acrylate in the presence of an anionic MSOL-based PUD as seed particles [7]. In that core-shell hybrid system, the PUD forms the latex shell, and serves as a high molecular weight emulsifier, while the vinyl polymers form the core [7].

4.4 Polyhydroxyurethanes (PHUs)

4.4.1 Introduction to PHUs

With a chemical structure very similar to that of regular polyurethanes, polyhydroxyurethanes have monomers connected through urethane linkages, with additional hydroxyl functional groups present on the polymer backbone (Figure 4.4). The presence of additional hydroxyl groups on PHUs allows for more possibilities of functionalization

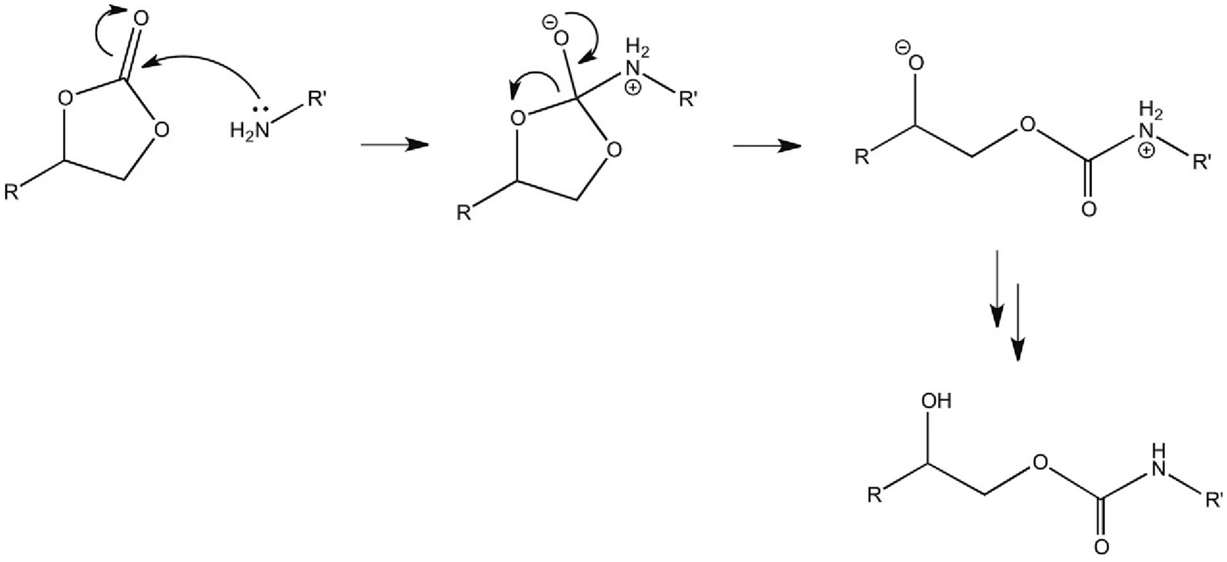


Figure 4.4 Simplified mechanism showing the synthesis of a hydroxyurethane from a cyclic carbonate and a primary amine.

and crosslinking in comparison to regular PUs. This leads to materials that have a wide range of applications, including tissue engineering [28], and polymer coatings [29]. In comparison to PUs, PHUs exhibit similar bulk properties with the added advantage of being more environmentally friendly. Indeed, in most cases, the production of PHUs does not involve the use of hazardous compounds, such as the diisocyanates frequently used in the synthesis of PUs. Due to the absence of isocyanates in their formulation, PHUs are also referred to as nonisocyanate polyurethanes (NIPU). The use of more environmentally friendly, and more cost-effective starting materials, including byproducts from other industrial processes has lately made PHUs an appealing alternative to regular PUs.

Several different starting materials can be used for the synthesis of PHUs. Petroleum-based, as well as biorenewable molecules, have been successfully used for the preparation of nonisocyanate polyurethanes. The most notable sources for the synthesis of bio-based PHUs include vegetable oils, glycerol carbonates, and terpenes [17]. Each one of these topics will be covered in more detail in the upcoming subsections. One of the most promising bio-based PHU systems is obtained by the nucleophilic polyaddition of polyamines to polycyclic carbonates prepared from vegetable oils or their derivatives [17]. PHUs can also be prepared from glycerol carbonate-based intermediates using a step growth polyaddition synthesis [30]. A simplified mechanism for the addition of amines and cyclic carbonates is presented in Figure 4.4 [31]. As detailed later in the text, depending on the structure of the starting cyclic carbonate used in the synthesis (5-membered versus 6-membered), PHUs containing either a primary or a secondary alcohol group may result.

4.4.2 Petroleum-Based PHUs

Polyhydroxyurethanes can be synthesized from petroleum-based molecules, as investigated, for example, by Endo et al. with the use of a five-membered cyclic carbonate, resulting in PHUs with both primary and secondary hydroxyl groups, with molecular weights of approximately 15,000 g/mol [32]. In the synthesis of PHUs from seven-membered cyclic carbonates, two different diamines were used, 4,9-dioxa-1,12-dodecanediamine (DODDA), and *p*-xylylenediamine (*p*-XDA) [34]. Endo found that using DODDA with a 6-h reaction time yielded complete conversion of the cyclic carbonates at temperatures ranging from 30°C to 70°C [33]. Increasing the reaction temperature resulted in an increase of the final polymer molecular weights, which ranged from 32,800 g/mol to 35,700 g/mol [34]. *p*-XDA was found to be less reactive than DODDA, causing both lower reaction yields and lower molecular weights [33].

In a similar system, the preparation of PHUs from the reaction between terephthaloyl dicyclocarbonate (DCter) and 1,10-diaminodecane (DA10) was optimized using rheometry [34]. The ideal temperature leading to high molecular weight chains was found to be 90°C [35]. Recently, Endo et al. synthesized PHUs with a silicone backbone [35]. Polyaddition synthesis was used substituting the diamine with silicone diamine [35]. This change resulted in a lower glass transition temperature, as well as an increased hydrophobicity [35]. Possible applications of this silicone backbone PHU include antifouling, anticorrosion, and water-repellent coatings [35]. Typically, PHUs are prepared from bio-based resources in an effort to move away from dependence on petroleum products and into materials with a more limited carbon footprint.

4.4.3 Bio-Based PHUs

Nonisocyanate polyurethanes can be successfully prepared from bio-based resources leading to environmentally friendly products with great appeal due to their intrinsic low toxicity. Among the different bio-based PHUs investigated to date, the ones prepared from cyclic carbonates derived from triglycerides, glycerol, and terpenes stand out due to the abundance and low cost of the starting materials. Following a different approach, organic/inorganic hybrid PHUs have been prepared from the reaction of cyclic carbonates with amino-modified silica nanoparticles, leading to materials with very interesting mechanical properties [36]. Each one of these topics is covered in more detail next.

4.4.3.1 Triglycerides

Triglycerides can be easily converted into reactive monomers by modification of their chemical structure. Functional group transformations can potentially convert unsaturated triglycerides or fatty acids into polymerizable moieties. Polyurethanes from triglyceride-based polyols are one of the most common bio-based polymers for coating applications [37]. As discussed earlier, the preparation of nonisocyanate polyurethanes from triglycerides can be successfully achieved, and such materials have proven to be very promising. Recently, soybean, sunflower, and palm oils have served as starting materials for the preparation of bio-based PHUs [38]. Triglyceride-based cyclic carbonates can be obtained by epoxidation of unsaturated vegetable oils with hydrogen peroxide in acetic or formic acid [39], followed by carbonation, carried out in the presence of carbon dioxide and a catalyst [40]. The polyaddition reaction is then carried out through ring-opening polymerization of the di- and polyfunctional cyclic carbonates with di- or polyamines [38,41,42].

When supercritical carbon dioxide is used in the preparation of cyclic carbonates from vegetable oils, decreases of approximately 66% in reaction time have been detected in comparison to reactions carried out under regular conditions. In general, supercritical conditions yield preferentially five-membered ring carbonates over their six-membered ring counterparts [17]. Catalysts such as quaternary ammonium halides, polystyrene-bound quaternary ammonium salts, and alkali metal halides have been shown to work most effectively in these reactions [38].

Cyclic carbonates have been shown to produce hydroxyurethanes upon aminolysis with a primary amine. Multiple procedures have been reported for the synthesis of five- and six-membered cyclic carbonates at the terminus of aliphatic chains [17]. Overall, when five-membered cyclic carbonates are attacked by a primary amine, two possible isomers can be obtained, with selectivity favoring the product containing a secondary hydroxyl group. The more symmetrical six-membered cyclic carbonates can only produce a single hydroxyurethane [17,38,43]. For the synthesis of polyhydroxyurethanes, a polyaddition reaction must occur between bifunctional cyclic carbonates and aliphatic diamines [38].

The synthesis of plant oil-based polyhydroxyurethanes has been carried out under various conditions. Wilkes reported the preparation of PHUs with tensile strength of 0.2–1.5 MPa and 70–170% elongation at break through the heating of carbonated soybean oil with various amines [44]. Such mixtures were heated at 70°C for 10 h, followed by a 3 h stage at 100°C [44]. In a related study, a cyclic carbonate was developed from cashew nut shell liquid and reacted with hexamethylene diamine and isophorone diamine at 120 and 150°C for various time intervals. The resulting materials held potential application in coatings formulations [45].

Tamami et al. reported the synthesis of novel triglyceride-based PHUs through the use of soybean oil. The reaction of epoxidized soybean oil with carbon dioxide was catalyzed by tetrabutylammonium bromide (TBAB) at 110°C. The carbonated soybean oil was then reacted with primary di- and triamines, resulting in products with mechanical and thermal properties that vary according to the type of amine used [39]. Carbonated soybean oil was also shown to react with *n*-butylamine to produce β-hydroxyurethane systems [39].

In another study, Bahr et al. prepared PHUs from soybean and linseed oils [42]. Both TBAB and silica-supported 4-pyrrolidinopyridinium iodide were used as catalysts in the conversion of epoxidized oils into their carbonated equivalents [42]. The conversion rates were monitored, and TBAB was determined to be the most efficient catalyst [42]. The cyclic carbonates were cured with 1,2-ethane diamine (EDA), 1,4-butane diamine (BDA), and isophorone diamine (IPDA) [42]. Compared with the previous literature, Bahr reported increased glass transition temperatures as well as improved stiffness for the systems prepared [42].

Hybrid PHUs, as opposed to their linear counterparts derived from the reaction of bifunctional cyclic carbonates with diamines [17], have been prepared by a four-step method consisting in: (i) carbonation of epoxidized unsaturated fatty acid triglycerides with conversion rates ranging from 35% to 85%, (ii) stoichiometric ring opening of the carbonate groups with primary mono-amines, (iii) followed by subsequent ring-opening of the remaining epoxide groups with primary diamines, and finally (iv) crosslinking this intermediate with difunctional comonomers bearing amino-reactive groups [40]. The usage of this method can lessen the time required for synthesis and potentially increase the properties of the resulting products [40].

Numerous other polymeric networks have been reported, with soybean and linseed oil-based systems being the most extensively studied. Bio-based PHUs have also been prepared from other nontriglyceride-based, biorenewable derivatives, such as cashew nut shell liquid [40]. Overall, the use of triglycerides holds much potential for the future as a safe and environmentally friendly route for the production of polyhydroxyurethanes [17].

4.4.3.2 Glycerol

Glycerol is a widely available bio-based resource that can be used in the synthesis of polyhydroxyurethanes without an intermediate isocyanate. Often obtained as the byproduct of industrial processes involving vegetable oils, such as soap manufacturing or biodiesel production, glycerol holds potential for PHU preparation due to its easy conversion to glycerol carbonate. A variety of cyclic carbonates can be synthesized from glycerol and subsequently reacted with a range of amines to produce polyhydroxyurethanes through ring-opening polymerization [17].

Several reaction conditions have been studied for the conversion of glycerol to glycerol carbonate, as well as the reaction of the resulting carbonate with amines to form PHU networks. The reaction of glycerol with compounds such as carbon dioxide, urea, dimethyl carbonate, ethylene carbonate, and propylene carbonate leads to the formation

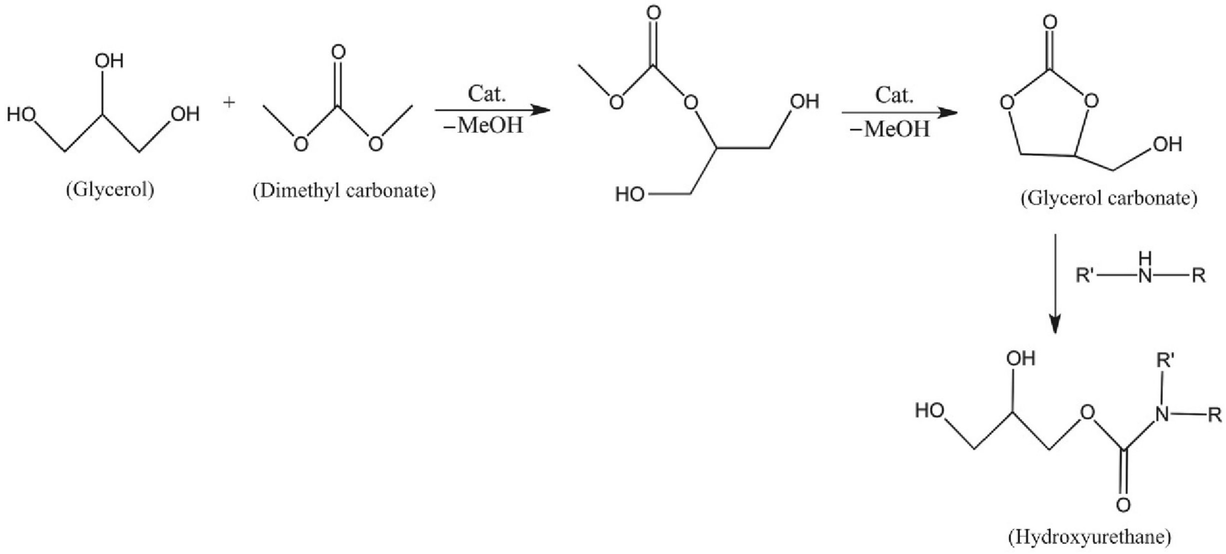


Figure 4.5 Example of the step-wise synthesis of hydroxyurethanes from glycerol.

of glycerol carbonate [46–49]. The synthetic approach is illustrated in Figure 4.5 for dimethyl carbonate. Glycerol carbonate may be further modified to form larger carbonate compounds, altering the structure of the final PHU product. Likewise, the structure and substitution pattern of the amine used in the ring-opening polymerization step has an impact on the final product.

Nohra et al. reported a PHU yield of 87% when the ring opening was carried out using amines with up to 12 carbon atoms in the alkyl chain [46]. A decrease in the yield was observed for amines with alkyl chains bearing more than 12 carbon atoms [46]. It was also observed that the yield increases with temperature and amine/carbonate ratio [46]. For an amine/carbonate ratio of 1:1.4, a 98% PHU yield is obtained when the reaction mixture is heated at 90°C for 4 h [46]. The use of additional catalysts during the synthesis of PHUs has also been investigated. Addition of catalytic amounts of 1,4-diazabicyclo[2.2.2]octane (DABCO) has been shown to allow curing to occur at room temperature [50]. Along the same lines, it has been observed that addition of 5 mol% of LiBr enhances the ring opening polymerization reaction [51].

In 2012, Raether et al. found that both linear and branched polyhydroxyurethanes can be prepared from glycerol carbonate [52]. Raether stated that the polymerization of glycerol carbonate, an amine, and an alkylene oxide could result in either branched or linear PHUs [52]. As expected, the structure of the networks was a direct result of the reaction conditions, the temperature employed, and the reagents used [52]. Furthermore, control over the degree of branching was achieved by controlling the number of resulting hydroxyl groups on the PHU, as each additional hydroxyl group increases crosslinking [52].

PHU systems have been successfully formed through the use of 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (AGC), a derivative of glycerol carbonate that can be easily obtained from the reaction of glycerol with allylic acid chlorides under basic conditions [30]. Without the use of a photoinitiator or solvent, AGC can be coupled

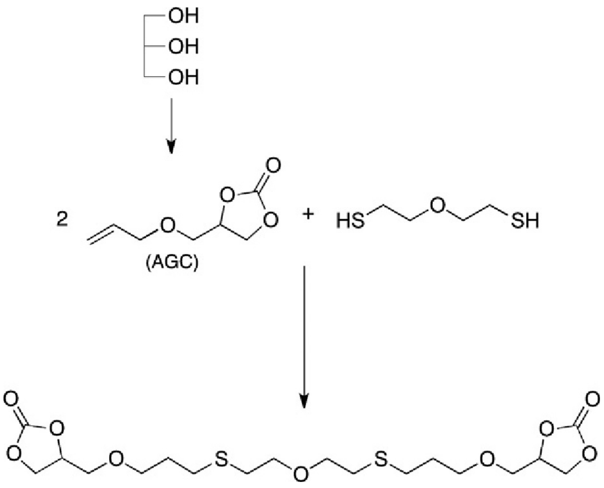


Figure 4.6 Synthesis of a difunctional cyclic carbonate from glycerol.

with 2,20-oxidiethanethiol, leading to the formation of difunctional cyclic carbonates [30]. This process is illustrated in Figure 4.6. The polyaddition of these difunctional cyclic carbonates with 1,10-diaminodecane results in polymers with molecular weights between 7000 g/mol and 9000 g/mol, and glass transition temperatures ranging from 14°C to 31°C [30].

In another report, phenoxycarbonyloxymethyl ethylene carbonate was prepared from glycerol carbonate and phenyl chloroformate [53]. The synthesis of this dicarbonate is shown in Figure 4.7. Both carbonate groups on the ethylene carbonate undergo polycondensation with diamines to produce amorphous PHUs with primary and secondary pendant hydroxyl groups [53]. It was observed that the glass transition temperatures of these systems decrease with increasing alkyl chain lengths of the diamines [53].

Cyclic carbonates derived from triglycerides often exhibit unclear functionality due to the complexity and variability of the triglyceride structure in vegetable oils. When cyclic carbonates are prepared from glycerol, a definite structure is obtained, and the preparation of monomers with known functionality becomes possible. Three different types of difunctional cyclic carbonate monomers have been recently prepared from glycerol carbonate [54]. In the synthesis of five-membered difunctional cyclic glyceryl carbonate diesters, fatty acids or diesters are added to glycerol carbonate through esterification or transesterification [54]. Since all materials involved in the synthesis of such difunctional carbonates are obtained from

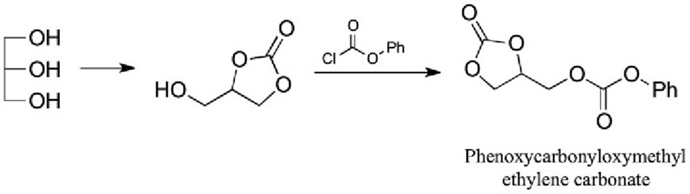


Figure 4.7 Preparation of phenoxycarbonyloxymethyl ethylene carbonate from glycerol carbonate.

renewable resources, this process holds much potential as an alternative in the production of PHUs.

Ultimately, the importance of glycerol and glycerol carbonate may increase in the future due to the range of possible applications, availability, and low toxicity. The incorporation of glycerol into polyhydroxyurethanes presents a pathway for isocyanate-free synthesis of PHUs.

4.4.3.3 Terpenes

Terpenes consist of a wide variety of naturally occurring organic compounds biosynthesized primarily by plants from isoprene. These highly odorous compounds are well known for giving different plants their distinct scents and have been utilized as agents for aromatherapy. Overall, terpenes are characterized by a variety of differing carbon skeletons with little or no functional groups (Figure 4.8) [55]. These carbon skeletons typically include one or more carbon–carbon double bonds that have been shown to be highly reactive toward free-radical initiators for the synthesis of bio-based polymers and copolymers [56]. Terpenes also show potential as starting materials in the production of cyclic carbonates [41]. Because of the wide abundance and low cost of this environmentally friendly, carbon-rich biomass [41,56], terpenes are promising candidates for the isocyanate-free production of polyhydroxyurethanes.

The use of terpenes for the preparation of polyurethanes has been reported recently [57]. In that instance, an anionic polyol dispersion has been prepared by modifying a terpene-based epoxy resin with *p*-aminobenzoic acid [57]. The dispersion was then crosslinked with a hexamethylene diisocyanate tripolymer to create a waterborne polyurethane/epoxy resin hybrid coating [57].

Unsaturated terpenes, along with unsaturated plant oils and natural polyols, have also

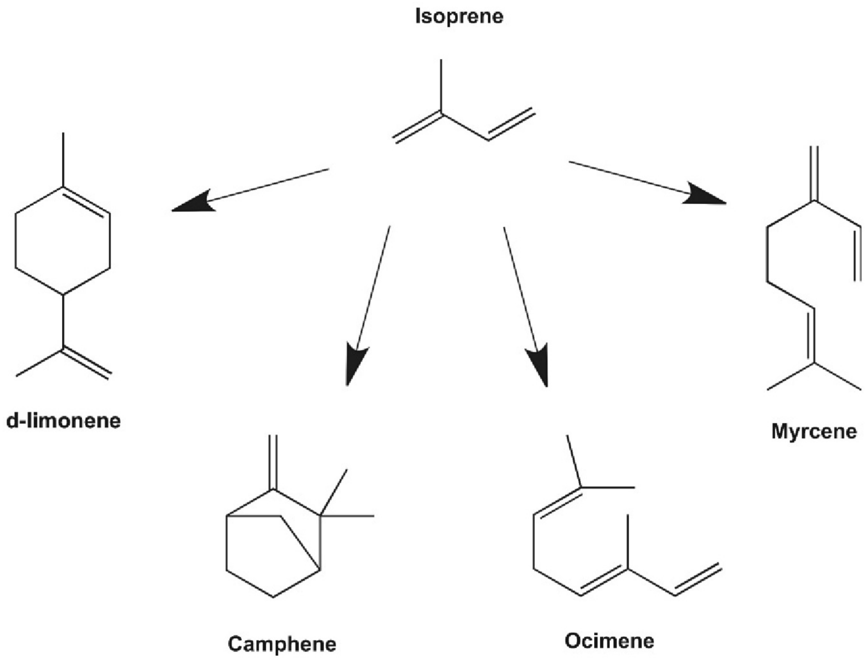


Figure 4.8 Isoprene-derived terpenes.

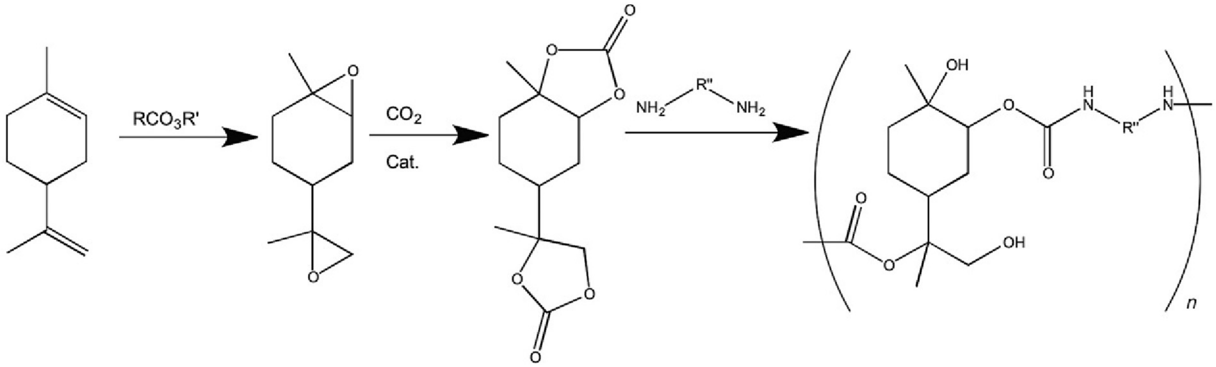


Figure 4.9 Step-wise synthesis of a PHU from limonene.

played a role in carbon dioxide fixation in the synthesis of nonisocyanate polyurethanes [41]. They have been used as intermediates along with bio-based amine curing agents in the production of PHUs from cyclic carbonates [41]. Along the same lines, linear and crosslinked terpene-based PHUs have been prepared by curing carbonated terpenes, such as limonene dicarbonate, with different diamines [58]. The step-wise synthesis is illustrated in Figure 4.9. It has been shown that terpene-based cyclic carbonates afford much higher CO_2 fixation and do not contain ester groups, which makes them stand out from conventional plant oil-based cyclic carbonates. The absence of ester groups prevents problems, such as ester cleavage and amide formation, during the amine curing step. Such problems are notorious for impairing network formation, as well as leading to low molecular weight polyol emissions, which can plastify nonisocyanate polyurethanes, and therefore compromise mechanical performance [58].

4.4.3.4 Hybrid PHUs and Composites

Organosiliconic polymers incorporate silicon-containing monomers into organic polymers and utilize silicon's unique properties to yield materials that combine high temperature stability and excellent low temperature elastomeric properties [59]. In that context, polysiloxane-modified polyhydroxyurethanes have been prepared from the reaction of five-membered cyclic carbonate polysiloxane compounds with amines, as illustrated in Figure 4.10 [60,61]. These hybrid polymers find potential applications in the production of thermal recording media, imitation leather, thermoplastic polyolefin coatings, and weather strips [60].

One issue associated with the use of polyhydroxyurethanes involves their poor water resistance due to their extended hydroxyl group functionality. To address this problem, some formulations of PHUs have been developed to confer materials with water-resistant properties. Along these lines, cyclic carbonates have been recently prepared from acrylic epoxy oligomers for the subsequent preparation of PHUs with high water and weather stabilities [58].

Bifunctional cyclic carbonates were reacted with amines to quantitatively yield PHUs that were then reacted with isophorone diisocyanate and end-capped with acrylate to form prepolymers [62]. These prepolymers were mixed with reactive diluents and liquid crystals (LCs), and subjected to UV cure

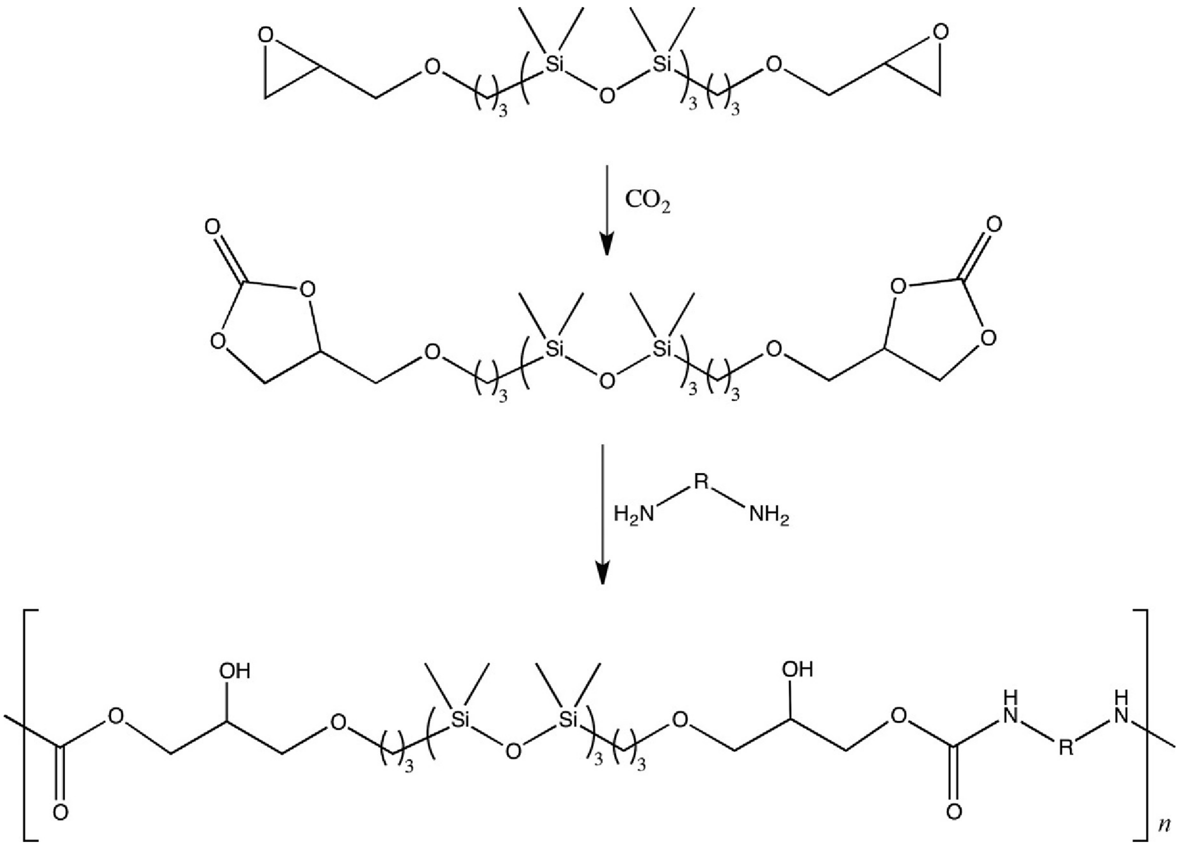


Figure 4.10 Step-wise synthesis of a PHU–polysiloxane hybrid material.

to form transparent hybrid PHU-acrylic/LC composite films [62].

PHU/attapulgite nanocomposites (PHU/ATP) have been prepared by the *in-situ* surface-initiated polymerization of a five-membered cyclic carbonate, 2,2-bis[*p*-(1,3-dioxolan-2-one-4-yl-methoxy)phenyl] propane (B5CC), and hexamethylene diamine [63]. In this case, amino-modified attapulgite nanoparticles served as the reactive surface for the synthesis of the composite [63]. A similar technology has been employed in the preparation of PHUs reinforced with silica nanoparticles [36]. It has been proven that grafting significantly enhances the stability of the nanoparticles in the polymer matrix by increasing the affinity of its surface with organic substrates [36].

4.5 Alternative Systems

Alternative systems with a chemical structure very similar to PHUs can be obtained in an environmentally benign way from sources other than cyclic carbonates. For example, polyurethanes have been efficiently synthesized in aqueous solution by a polymerization process that is free of isocyanates and catalysts [64]. This method has been shown to be effective and environmentally friendly [64]. In the procedure, *bis*(pentafluorophenyl) carbonate was first activated by reaction with 1,6-hexanediol and polyethylene glycol at various ratios [64]. Subsequent condensation polymerization of the activated carbonates with polyetheramines under aqueous conditions resulted in polyurethanes [64]. Despite exhibiting very similar properties in comparison to PUs and PHUs, this system differs from the traditional PHUs described earlier in the text by the absence of hydroxyl groups along the final polymer backbone.

Likewise, polyurethanes with no additional hydroxyl groups can be generated from the reaction of vegetable oil-derived carbamates and diols [65]. In fact, it was recently reported that dimethyl dicarbamates can be prepared from dicarboxylic acids obtained from plant oils [65]. The carbamate precursors prepared from vegetable oils already contain urethane functional groups that are modified to yield the desired PUs. These two approaches represent interesting and sustainable alternatives for the preparation of polyurethanes from nonisocyanate sources.

4.6 Conclusions

As mentioned initially, polyurethanes are very versatile polymers that are currently used in a wide variety of industrial and large-scale applications. Extensive research efforts surrounding the chemistry of polyurethanes have resulted, over the years, in various materials with different properties, designed for specific applications. Despite its widespread use and solid chemistry background, PUs are typically synthesized from diisocyanates, which exhibit a strong bioincompatibility. For that reason, the production of PUs has raised environmental and health concerns that limit its applications to some extent.

In an effort to make PUs more environmentally friendly, an intense effort has been put into the preparation and use of bio-based polyols. Among the many options, polyols obtained from plant oils became very popular due to the availability of the starting materials and the simple chemistry involved. Although appealing, the use of bio-based polyols for the preparation of PUs does not address the main concern, i.e., the use of hazardous diisocyanates.

More recently, a new class of polymers (polyhydroxyurethanes) consisting of monomers connected by urethane linkages and additional hydroxyl groups sparked the interest of many researchers. Due to their structural similarities, such polymers exhibit properties comparable to those of regular PUs, with the added advantage of not requiring the use of diisocyanates for their synthesis. Indeed, PHUs are typically prepared by the ring-opening polymerization of multifunctional cyclic carbonates and amines. Over the past few years, PHU-related research has focused mainly on the investigation of possible bio-based cyclic carbonate components. Initially, the most obvious options were cyclic carbonates obtained from plant oils, due to the same reasons plant oil-based polyols are so popular in PU production.

A growing interest in alternative bio-based cyclic carbonates currently arises from the need to prevent undesirable ester cleavages and low molecular weight products that are normally formed when plant oil-based cyclic carbonates are used in the synthesis of PHUs. The most current trends in alternative sources of bio-based cyclic carbonates are glycerol, which is also, to some extent, derived from plant oils, and terpenes. Current trends also point to an increased interest in hybrid PHU systems, in which PHU networks are simultaneously formed along other polymers, such as acrylics, polyolefins, epoxy, and/or polysiloxanes. It is expected that research in this area will continue to grow as novel materials with improved properties may potentially address the issues associated with the currently known systems.

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5 Plant Oil-Based Polyester

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5.1 Introduction

Alternatives to replace chemicals from petroleum, silicate minerals, pure metals, wood, etc., have been searched to attend the necessities of Earth's growing population. By 2040, we will have to feed 9–10 billion people and provide them with energy and materials [1]. Important features in this search involve aspects associated with the primary source, processing and final product such as, price, shipping, weight, recycling, biocompatibility, and chemical, physical-chemical, mechanical, and thermal properties [2].

Plant oil is an environmentally friendly resource [3]. Diverse new materials derived from plant oil have been invented and innovated to attend the worldwide demands with perspective to avoid environmental problems.

The success of using plant oil in various fields of science is mainly associated with the type of reaction methodology used to obtain an addressed material. In particular, reactions from plant oil are currently recognized and largely employed in polymer science [4].

The diversity of application and advantages of plant oil compared with the usual chemicals from petroleum in classical polymerization methods have led many researchers to initiate developments to obtain new polymeric materials from plant oil in the last three decades. Furthermore, many polymerization procedures have been reformulated considering that the use of plant oil

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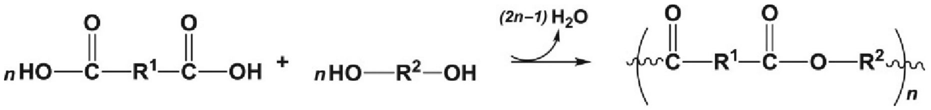


Figure 5.1 Polycondensation reaction to obtain polyester.

follows the Green Chemical Principles, with a valuable gain over the use of harmful reagents [5].

Plant oil is an important source that can be used as a precursor for different industrial applications. In the field of polymeric material, plant oils are interesting because the functional groups present in triglyceride molecules, such as double bond, hydroxyl, epoxy, ester, acid, etc., can provide a great variety of polymers, with different structures and functionalities, via a desired chemical reaction. Considering their availability and/or possible biodegradability, there is particular interest of the industry in biobased polymers, and scientific research on this type of carbon source has also increased [6,7]. This advance in biobased polymers may use this valuable natural source from oils that are not used as food or without impacts in this purpose.

Plant oil-based polymers can generate:

- *polyolefins,*
- *polyamides,*
- *polyethers,*
- *polyesters, among others.*

As it is well known, esters are produced from the condensation of a carboxylic acid with an alcohol. Thus, esters are functional groups derived from carboxylic acid, where the hydroxyl (OH) group is replaced with an alkoxy (OR) group. Natural triglycerides from plant oils present this functional group in their molecular compositions, as well as mono and diglycerides, and fatty acid methyl ester (FAME) from transesterification reactions of plant oils. The presence of the ester group in these molecules could already induce the production of a type of macromolecule containing the functional ester group via modifications of other functional groups present in the chains to be polymerized. In this type of structure, the ester group is part of the pendant unit in the main chain. This does not characterize a polyester. Differently, polyesters are defined as polymers containing at least one ester group per repeating unit (R—COO—R’) in the main chain that was involved in the polymerization reaction. Thus, generally, polyesters are formed by a condensation reaction between a diacid and a dialcohol, with elimination of one water molecule (Figure 5.1). The polycondensation reaction occurs through step growth polymerization. The *mers* units R^1 and R^2 are the repeating units in the polyester main chain, and they can drive the applications depending on the used monomers.

Polyesters are one of the most important classes of polymers in the world and the demand for biobased polyester has increased in the past years aiming a more sustainable chemistry. In addition, the versatility of the ester linkage has increased the development of novel polyesters and copolyesters from plant oil, as well as their applications [8,9].

5.2 Processes and Monomers

There are many procedures for the syntheses of plant oil-modified polyesters. For example:

- *monoglyceride process,*
- *fatty acid process,*
- *fatty acid-oil process.*

The monoglyceride process obtained from monopolyol can occur with or without a catalyst. Without a catalyst, a temperature of at least 280°C is necessary [10]. Catalysts can be acids or bases, but acid catalysts are more efficient. Therefore, plant oil-based polyester resins can be obtained using enzyme as a catalyst. In the fatty acid process, polyesters are obtained at ca. 260°C when reacting with polyol, dibasic acid, and fatty acid, simultaneously [10]. This process is faster, more controlled, and more reproducible than the monoglyceride acid process [11,12]. The fatty acid-oil process involves fatty acid, oil, polyol, and dibasic acid, producing polyester with high viscosity, which is an advantage compared with the monoglyceride process [10].

The type of monomer, aliphatic (saturated/unsaturated) or aromatic, is essential to define the polyester obtained from plant oils. Fatty acids can be utilized as monomers in polycondensation reactions because the carboxyl group at the end of the chain, the hydroxyl groups, occasionally present in the chain and functionalized double bonds. The characteristics of the fatty acids, such as degree of unsaturation, number of carbons, and functional group, provide different properties to the biopolymer synthesized.

If the monomer is bifunctional ($f = 2$) (diacid and dialcohol), a linear polyester is obtained. If the monomer has functionality greater than 2 ($f > 2$), in other words, more than two reactive sites on a monomer, branched polymers are obtained, and there is the possibility of forming a polymer network.

Soybean, linseed, tung, and castor oil are interesting triglycerides applied in polymer chemistry, because of the occurrence of many reactions by using the double bond or the hydroxyl group present in the fatty acids (Figure 5.2) from these oils. Thus, plant oil can also be an effective approach to reduce petrochemical compounds.

Castor oil has been a feedstock of great demand by the pharmaceutical and chemical

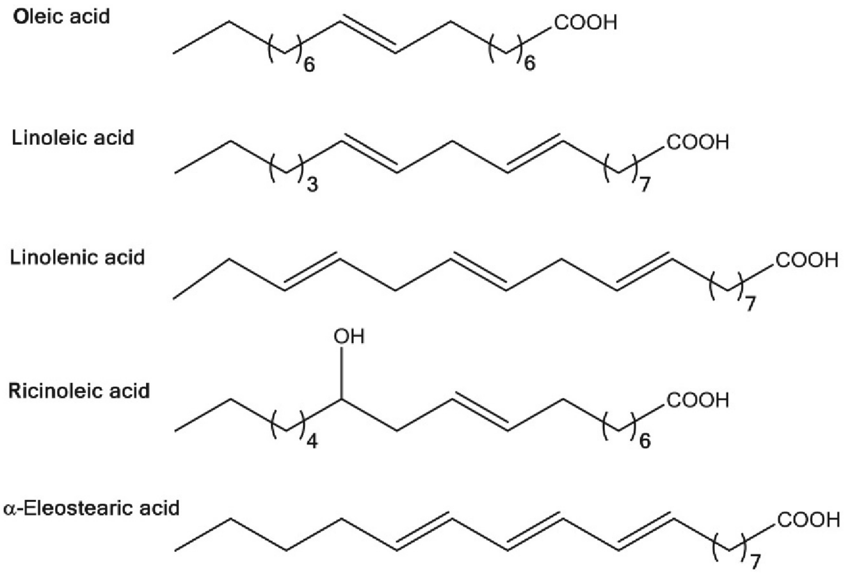


Figure 5.2 Structure of fatty acids.

Table 5.1 Fatty Acid Composition of Vegetable Oils

	Oleic Acid (C18:1)	Linoleic Acid (C18:2)	Linolenic Acid (C18:3)	Any Special Fatty Acid
Castor oil	7.0	5.0	–	86–90 (ricinoleic acid)
Linseed oil	12.0–34.0	17–24	35–60	–
Soybean oil	22–34	43–56	5–11	–
Tung oil	8.0	4.0	3.0	80 (α-eleostearic acid)

industry [13,14]. The high content of ricinoleic acid (Table 5.1) is the reason for the versatile value of castor oil in technology because of functionalization at either the double bond or the hydroxyl group. Soybean, linseed, and tung oil present highly unsaturated chains (Table 5.1) that are reactive in free radical or cationic polymerization.

5.3 Thermoplastic Polyesters

Different combinations of aliphatic and aromatic monomers in the principal polymeric chain can determine different types of thermoplastic polyesters for different purposes [15]. The units R^1 and R^2 (Figure 5.1) can be combined in three different ways:

- *When R^1 and R^2 are aliphatic groups,* the polyester can be used in the medical field as biomaterials for implants, drug delivery, prosthesis, etc. Further, the obtained polyester can present features such as biodegradability.
- *When R^1 and R^2 are aromatic groups*, the polyester presents superior mechanical properties and heat resistance, which are applied in high-performance thermoplastics.
- *When R^1 is aliphatic and R^2 is aromatic,* the polyesters are considered engineering thermoplastics.

Amorphous aliphatic polyesters usually present low T_g values, while amorphous aromatic polyesters present high T_g values [15]. The thermal stability is influenced by the aromatic group content, because the rings bring rigidity to the polymer chain. Hence, molecular mobility is affected by the aromatic ring sits in a plane [15].

Linear polyesters without or with pendant groups are typical thermoplastics (Figure 5.3), which are widely used because of their mechanical strength, low cost, easy

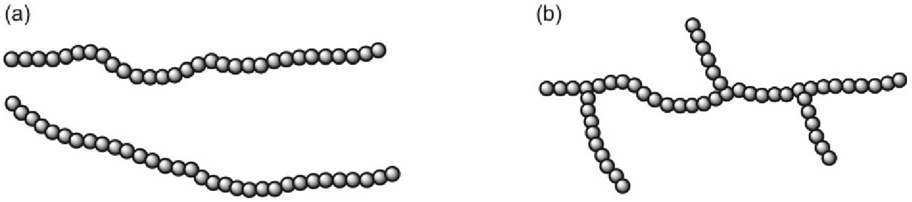


Figure 5.3 Illustration of linear polymer without (a) or with (b) pendant groups.

processability, and resistance to chemical and biological attack.

The chain length in linear polyesters can affect their properties [16–20]. One common way to obtain linear long-chain polyesters is by polycondensation of monomers synthesized from plant oil via three steps: self-metathesis, hydrogenation, and reduction. Aliphatic polyesters are usually semicrystalline materials with low melting point owing to the absence of cross-linking.

Chain length shows a tendency to increase the melting point, as example, in the polyester (—OC—R^1—COO—R^2—), in which R^1 and R^2 are CH_2 groups [18]. When the number of CH_2 groups for R^1 is 21, the increasing number of CH_2 groups for R^2 changes the T_m values in the following order describing a saturation profile: $R^2 = 6$ ($T_m = 92°C$); $R^2 = 12$ ($T_m = 100°C$); $R^2 = 19$ ($T_m = 106°C$); $R^2 = 23$ ($T_m = 108°C$); $R^2 = 38$ ($T_m = 109°C$); $R^2 = 44$ ($T_m = 111°C$). These values are comparable with the T_m value of low-density polyethylene.

Random and block copolyesters with pendant chains were synthesized from lauric and stearic acid to obtain bifunctional compounds selectively and to promote the syntheses of linear polymers [21]. Longe side-chains increased the crystallinity and raised the melting temperature because of the side-chain crystallization. In all the cases, block copolyesters showed higher melting temperature than random copolyesters.

5.4 Biodegradable Polyesters

Since plastic waste has accumulated in the environment, leading to long-term environmental and waste management problems, much concern has been placed on pollution. As biobased polymers are possible candidates to reduce pollution problems caused by plastic wastes, their biodegradability has been extensively investigated.

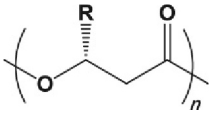


Figure 5.4 Structure of PHAs.

In response to problems with plastic waste and harmful effects to the environment, there has been considerable interest in the development of materials that could be more biodegradable than petroleum-based plastics. As a result, polymers such as polylactides, polysaccharides, and polyhydroxyalkanoates have been considered substitutes for conventional plastics, beside aliphatic polyesters.

Polyhydroxyalkanoates (PHAs) are linear polyesters of hydroxyalkanoates (HAs) produced in nature by bacterial fermentation of sugar or lipids (Figure 5.4). They can behave either as thermoplastic or as elastomeric materials, with melting points ranging from 40°C to 180°C [22]. They present useful mechanical properties and excellent biodegradability under various conditions by a multiplicity of microorganisms within a period of 1 year [22,23].

So far, PHAs have been recognized as good candidates for biodegradable plastics; unfortunately, their high price compared with conventional plastics has limited their use in a wide range of applications [22]. This occurs because of the high synthesis costs of PHAs, which limits their production on a large scale [22]. Therefore, there is a need for the development of novel processes using inexpensive carbon substrates as plant oils. The use of waste plant oils generated from the food industry and food

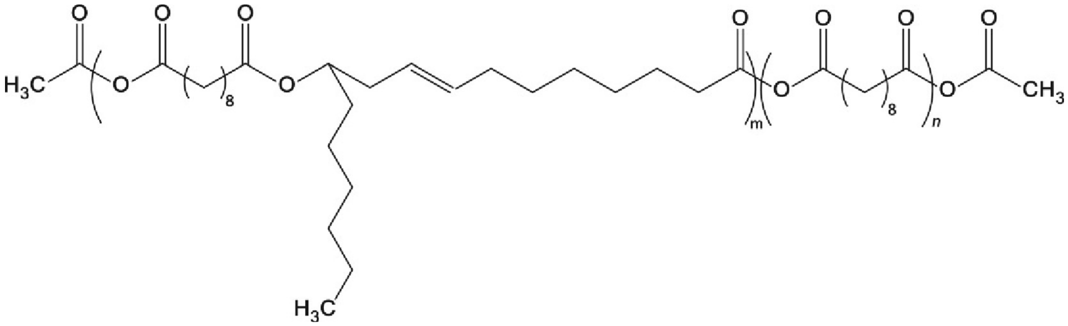


Figure 5.5 Structure of poly(sebacic acid-*co*-ricinoleic acid).

service could be reasonable from the economic and environmental point of view. The conversion of these residues into new biomaterials is an eco-innovative approach. Soybean oil, palm oil, and corn oil are desirable carbon sources for PHA production as they are relatively cheaper than most sugars [22].

Various plant oils have been tested and proved to be effective carbon sources to PHA biosynthesis with interesting material properties. The physical and material properties of PHAs depend on their monomer composition and chemical structure, such as the length of the pendent groups in the polymer backbone, the chemical nature, or the distance between the ester linkages [24]. PHAs synthesized from fatty acids depend on the synthesis procedure, as well as the degradation pathway [25]. The microorganism used and the culture conditions depend on the monomer incorporated in the polymer chain.

It has been reported that the theoretical yield of PHA production from fatty acids is 0.65 g/g, whereas the theoretical yield of PHA production from glucose ranges from 0.30 g/g to 0.40 g/g [26]. This is an advantage for plant oil.

Methyl ester of 9-hydoxynonanoic acid from castor oil produced high molecular weight linear polyester (62,200 g/mol) by self-transesterification [27]. Polyester presented higher melting point (70°C) and glass transition (−31°C) than polycaprolactone. The new polymer is potentially biodegradable and more thermally and hydrolytically stable than PHAs, with shorter methylene chains between ester groups. This may have some interesting applications in industry and medicine in substitution to polycaprolactone (PCL).

Poly(sebacic acid-*co*-ricinoleic acid) is a linear polyester with pendant aliphatic chains (Figure 5.5). It has been studied as a biodegradable polymer to act as drug delivery systems by insertion of ricinoleic acid into poly(sebatic acid). Ester bonds are more stable toward hydrolysis than anhydride bonds [28,29].

5.5 Unsaturated Polyester Resin (UPR)

Thermoset plastics present cross linked chains by covalent bonds produced during the curing process, resulting in a stable material because of the chemical bond type involved (Figure 5.6) [30].

Thermoset polyesters have been denominated as unsaturated polyester resins (UPRs), which are obtained from a typical free-radical polymerization. The chain

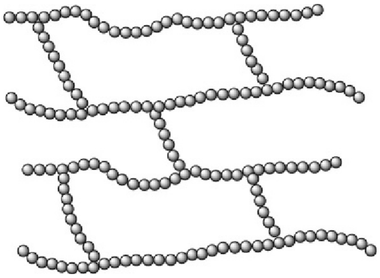


Figure 5.6 Illustration of cross linked polymer.

growth polymerization occurs via an unsaturated monomer and a vinyl monomer. The vinyl monomer acts as a solvent for the unsaturated polyester, decreasing the viscosity, and as an agent of cure.

UPRs are currently the most largely utilized thermosetting polymers because of their low cost, easy handling, and good balance of mechanical, electrical, and chemical properties [31]. Their room temperature cure capability, good mechanical properties, and transparency make these materials popular thermosets. Curing of unsaturated polyesters occurs through a polymerization reaction that causes cross-linking among individual linear polymer chains. In the past decade, there has been a growing trend to incorporate plant oils and/or their derivatives into UPR to produce novel biobased materials to reduce petroleum consumption [32]. The reinforced composite materials and nonreinforced materials of UPRs have been broadly employed in the aerospace, automotive, maritime, infra-structure, military, sports, and industrial fields [31].

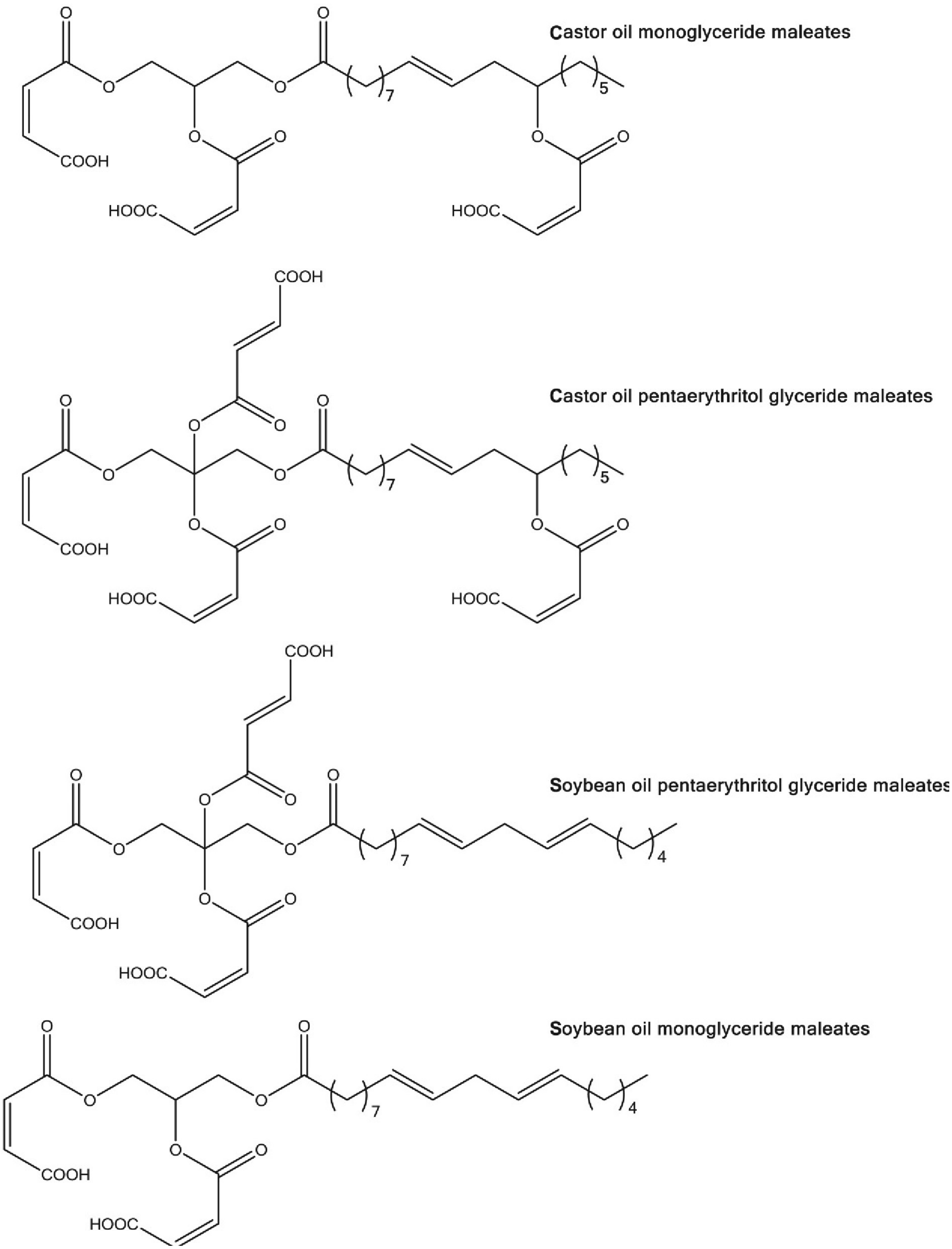
Maleates alcoholyzed triglyceride resins from castor and soybean oils were synthesized to obtain partial biobased UPRs (Figure 5.7) [32–34]. The alcoholysis reaction can be performed with aliphatic alcohols, such as pentaerythritol and glycerol, and an aromatic alcohol, such as bisphenol A propoxylate. The resulting alcoholysis product can be maleated and cured in the presence of styrene to obtain thermoset polymers.

There is an extra hydroxyl group on each fatty acid chain of castor oil that is expected to have a maleate C = C functionality of 3–4. It was copolymerized with styrene to produce rigid plastics with high performance. This polymeric matrix showed a high crosslink density (4400 mol/m^3) which was comparable with that of petroleum-derived UPRs [33,35,36]. The high functionality of the castor oil did not reduce the crosslink density of the resulting material.

Maleates are unreactive in homopolymerization, but are very reactive in copolymerization with styrene. Styrene is the typical vinyl monomer utilized in UPR synthesis because of its low viscosity, low cost, and reactivity with the unsaturated sites of polyesters [34]. Maleates alcoholyzed triglycerides resins were solids at room temperature. Thus, styrene is used in the formulations to make the resins more processable and ensure the polymerization of maleate reactive groups.

Maleates castor oil (MACO) was used as a biomodifier in UPR at different proportions (5, 10, and 15 wt%), and fly ash was used as a filler [37]. With the incorporation of 5 wt% MACO, the impact strength of the UPR matrix increased by 52% without any loss in modulus [37]. It was evident that the storage modulus (*E*') value gradually decreased with the addition of MACO [37]. These results indicate that brittleness of UPR-based composites can be improved by introducing MACO [37].

Epoxidized plant oils can be used in substitution to polyester resins. Methyl ester of soybean oil (EMS) and epoxidized methyl linseedate (EML) were employed to toughen UPR and biocomposites prepared from the modified UPRs [35]. Biobased resins were



Castor oil monoglyceride maleates

Castor oil pentaerythritol glyceride maleates

Soybean oil pentaerythritol glyceride maleates

Soybean oil monoglyceride maleates

Figure 5.7 Structures of maleates alcoholyzed triglycerides resins from castor and soybean oil.

prepared by a partial substitution of UPR by EMS or EML, and reinforced with natural fibers, nano clays, or layered silicates [35]. Toughness of the biobased resins was improved by the incorporation of EMS or EML. The biobased UPRs containing more than 20 wt% EML were not transparent because of the creation of EML-rich rubbery phases. The behavior of neat UPRs with 0–10 wt% EML was elastic [35].

Novel biomaterials were the blending of an unsaturated polyester resin/styrene mix with tung oil, which offered improved impact strength at a very low content of oil [38]. The principal compound of tung oil is a glyceride based on α-elaeostearic acid, a highly unsaturated conjugated system. Dicyclopentadiene was inserted in UPR, and then it was modified with tung oil via the intermolecular Diels–Alder reaction. The oil was incorporated into UPR via the intermolecular Diels–Alder reaction between double ($C=C$) bonds of the polyester chain and conjugated triene groups of the oil [31]. The thermal stability (T_{10} and T_{50}) and toughness were improved when the UPR content tung oil was equal to or greater than 10%. The mechanical and thermal properties of the polymer matrices were influenced by the synergistic effects of phase separation and crosslink density. The mechanical properties are benefit to modify the petroleum-based materials with soft bioresources. These biomaterials, including renewable resources, are very promising in the application of fiber-reinforced composite materials.

5.6 Other Applications

The production of polyester from ricinoleic acid with and without *in situ* insertion of magnetic Fe_3O_4 nanoparticles with their surface modified by ricinoleic acid has been obtained [39]. It was observed that the magnetic Fe_3O_4 nanoparticles act as Lewis acid catalysts during the polymerization. Using the Fe_3O_4 nanoparticles modified by ricinoleic acid, the final polymeric material had an increase in the reaction rate, exhibiting good thermal stability and behaving as superparamagnetic material.

There is an enormous demand for lightweight materials for use in the transportation and construction sectors [40]. Natural fibers exhibit many advantageous properties. They are low-density materials yielding relatively lightweight composites with high specific properties [41]. Oil palm fiber is a good reinforcement in the polyester matrix. It is hard and tough, and its porous surface morphology is useful for better mechanical interlocking with matrix resin for composite production [40,42]. Thermal stability, strength, dielectric constant, and electrical conductivity were improved in the presence of oil palm fiber.

Another application related to oil palm was the development of polymer biocomposites from unsaturated isophethalic polyester resin containing powdered oil palm shell as a function of powder particle size, increasing thermal stability, and improving mechanical properties [43].

Polymeric biomaterials are currently dominated by thermoplastic polyesters such as poly(lactic acid) (PLA), poly(glycolic acid) (PGA), polycaprolactone (PCL), and their blends or copolymers [44]. Many esters, such as fatty acids, are endogenous to human metabolism, and therefore biocompatible. A biomaterial is designed to be used in intimate contact with living tissue; then, it is essential that the implanted material not causes any harmful effects to host tissues and organs [45]. In spite of the fact that many polyesters can break down to natural metabolic products by simple hydrolysis, they did not present adverse effects [44]. Although these biomaterials have been well characterized and fabricated to match the biochemical properties of soft tissues, there is generally a lack of mechanical compatibility between thermoplastic polymer implants and living tissues [45].

Some biopolymers obtained from natural oils are flexible and rubbery [46]. Generally, they are prepared as cross-linked copolymers [46].

The cross-linking process for unsaturated polyester from soybean oil fatty acid was performed by thermal and UV irradiation with 365 nm wavelength. Cross-linking was observed in at least two polyester chain double bonds [47]. The polymerization with the fatty acid from soybean oil (linoleic acid) is more reactive than the reaction with the pure soybean oil by free radical [47]. The cationic polymerization with soybean oil was difficult to occur [47]. As the cross-linking increases, the ultimate strength increases and the elongation at break decreases, obtaining very good damping and shape-memory properties over a wide temperature range [46]. The fatty acid ester groups directly attached to the polymer backbone are presumed to be responsible for damping properties [46].

Damping materials have numerous applications in the aircraft, automobile, and machinery industry, being used in noise reduction as well as in the prevention of vibrational fatigue failure [46]. Shape-memory materials have applications in civil construction, mechanics and manufacturing, electronics and communications, printing and packaging, medical equipment, recreation and sports, and household items [46].

5.7 Applications of Plant Oil-Based Polyester as an Alternative for Petroleum-Based Polyester

A straight relationship of data comparing polyester obtained from different sources is still vague in the literature [2]. However, the replacement of petroleum-based polyesters by biobased polyester from plant oil has motivated the academia and industry to obtain new materials with similar or better proprieties.

For example, methyl ester of tung oil was synthesized as comonomer to replace the more frequently used styrene in UPRs because of conjugated double bonds that are reactive in cationic polymerizations [48]. Alternatively, the incorporation of a green modifier, a commercial acrylated epoxidized soybean oil, was also considered. The use of any of these modifiers allowed preparing materials with high contents of bioderived components. All the materials obtained presented good mechanical damping capacity, as well as dynamic mechanical properties comparable to those of analogous materials obtained by copolymerization with styrene. One of the formulations prepared by copolymerization with tung oil methyl ester presented shape memory behavior.

Tartaric and phthalic acid were used individually to prepare polyesters by a reaction with glycerin, but the polyesters were found to be brittle and inflexible, whereas fatty acids with glycerin showed good film-forming properties [49].

Biofoam composites from acrylated epoxidized soybean oil resin were prepared to replace the traditional unsaturated polyester foams. The plant oil-based foam showed similar compressive stress to commercial UP foam [50].

New biobased resins for use in sheet-molding compound (SMC) applications were synthesized from soybean and linseed oil [51]. The new biobased resin from soybean oil showed mechanical properties inferior to those of commercial unsaturated polyesters [52]. However, the new biobased resin from linseed oil had properties very comparable to those of the commercial unsaturated polyesters, and they showed promise as replacement petroleum-based polymers in the SMC industry [51].

As a new material, novel approaches are in constant drive to develop new biobased monomers from plant oil to discovery different polymers for diverse applications, as well as to improve the properties of known polyesters.

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6 Plant Oil-Based Polyether

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6.1 Background

6.1.1 Introduction

Plant oils are mainly triglycerides comprising a variety of different fatty acids. The fatty acid composition differs on the basis of the type of the plant and the plant's growing environment. These differences could be in chain length, composition, distribution, and location [1,2]. Historically, fossil oils have been used as the main source of polymers; however, the use of plant oils for the production of polymers has been increasing each year. Using plant oils as a source for polymers has many advantages over using petroleum as a polymer source. Their advantage over fossil-based polymers is shown by the following facts [3–9]:

- Plant oil-based polymers, such as vegetable oil-based polymers, are environmentally safer compared to the fossil oil-based alternative; this is due to the fact that plant oil-based polymers are at worst partially, and sometimes fully, biodegradable.
- Compared to petroleum-based polymer, plant oils are cheaper to extract. They also have a more environmentally friendly extraction process.

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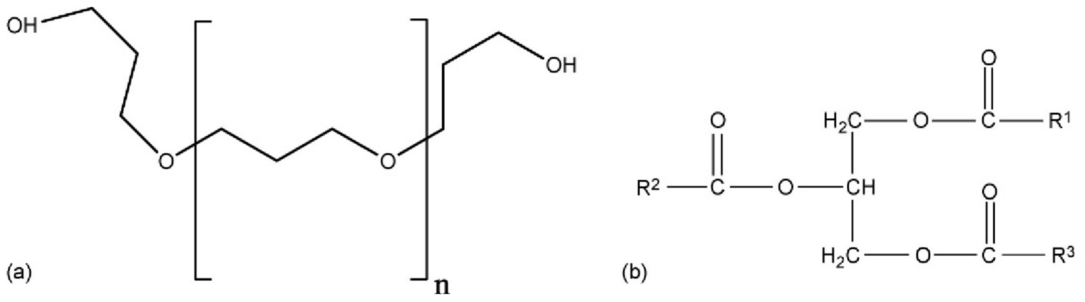

Figure 6.1 (a) Generic repeat unit of a polyether. (b) General form of triglyceride which will be processed and monomerized for the polymerization of polyether.

Plant oils are more abundant than fossil oil. This abundance – combined with the low cost of extraction, as noted previously – makes them an attractive choice for industrial use. According to Cargill's estimation, 2200 barrels of crude oil could be saved by replacing 1 million pounds of traditional polyol with soybean-oil-based polyols [2]. The current development of synthetic, enzymatic, and microbiological methods is realizing such replacements progressively [10,11].

Extraction of plant oils from these sources has been going on since distant past, but commercialization on larger scale has been following the advancement of polymer science. Plant oil seeds, such as soybean and corn, can be genetically modified to influence the extraction process. More research is needed in this area; however, research has shown that it is possible to modify the contents of the fatty acid for the oil seed with the product in consideration [2]. Significant parts of the vegetable oil production are from soybean, palm, rapeseed, sunflower, castor, tobacco, linseed oil, corn, Mesua ferrea, agremone, and canola oil [6]. Unsaturation can be measured by using iodine value (IV), which is used by measuring amount of iodine in milligram that reacts with carbon–carbon double bonds in 100 g of vegetable oil [12]. Vegetable oil is a source for 80% of oil and fat production globally, of which around 25% is soybean [10]. Refined soy oil consists of more than 99% triglycerides and a significant variety of fatty acids [2]. The chemical and physical properties of these oils significantly depend on the degree of unsaturation.

Polyethers are formed by creating ether links between monomers. Varying the amount of functional groups in the monomer will have a large impact on the properties of the polymer. Polyethers can be linear, branched, or cross-linked. Plant oil-based polyethers are derived from plant-oil based monomers. Figure 6.1 shows an example of a polyether-based plant-oil and triglyceride.

6.1.2 Molecular Weight and Networks

Polymer material properties are highly dependent upon the molecular weight; plant oil-based polyethers can vary from oligomers to very large polymers. Typically materials that have low molecular weights tend to be much softer than materials with higher molecular weights. Also, it is much easier to produce materials that are not cross-linked at lower molecular weights. This means that at lower molecular weights it is far simpler to produce melt-processable materials. Linear polyethers are very difficult to form from triglyceride-based monomers, owing to the intrinsically multifunctional nature of triglycerides. These monomers may, on average, have only one functional group; however, it is very difficult to have a material that has an absolute value of one functional group. Due to this, making linear polymers from plant-based sources is impractical. The exception to this is if the plant oil is cleaved (e.g., through transesterification), leaving behind monofunctional fatty acids and fatty esters. Formation of cross-linked polyethers can be controlled by manipulating the context of the mixer and the nature of cross-linking agent [11]. Polyether dendrimers have an advantage over linear polyethers due to their high surface area-to-volume ratios, flexibility in functionality, and low polydispersity index [4,13].

6.2 Methods

6.2.1 *Extraction Process from Natural Source*

Extraction of the oil from the oil seeds is mainly achieved using mechanical or solvent-based extraction methods. The extraction method used is dependent on the size of the industry and the requirement on efficiency. The cost of the extraction process may rise proportionally with the efficiency of extracting oils from the oil seeds [2]. During mechanical extraction, squeezing the oil out of the oilseeds by using mechanical means, the protein denaturation is also achieved due to the heat generated through the extraction.This process is mainly popular with industries with capital constriction but efficiency tolerance. This method has the advantage of being more environmentally friendly than solvent-based extraction. Solvent-based extraction is done by diffusing the oil out of the seed using solvents, such as hexane, as a carrier. The factors for diffusion rate are the characteristics of solvent, thickness, and size of the oil flakes. Since the extraction is diffusion dependent, the efficiency is tied with the choice of the solvent. The solvent choice is with the consideration of cost of the solvent and the efficiency; here, it will be the desired rate of oil diffusion from the oil seeds [14]. As shown by Othmer and Agarwal [15], the relationship between concentration of oil and of thickness of the flake is given as $-\frac{dC}{dt} = kF^{3.97}C^{3.5}$, where C is concentration of oil, F is the flake thickness, t is time, and k is the rate constant.

6.2.2 *Purifications after Extractions*

Additional extraction methods are introduced after the crude oil is extracted from the seed. The method chosen is tailored to the final product, but can include: removing phospholipids (degumming), removing free fatty acid, bleaching, and deodorizing. Phospholipids between 500 ppm and 900 ppm are not suitable for storage and transport due to the unwanted cake they form. This removal could be easily achieved by using warm water. For most applications, the fatty acid content will also need to be around 0.05% to improve the smoke point and foaming upon heating. Further bleaching is introduced to improve the appearance, especially for food-related products, and to remove more residual impurities. Deodorization is also used as needed in the final product [16,17].

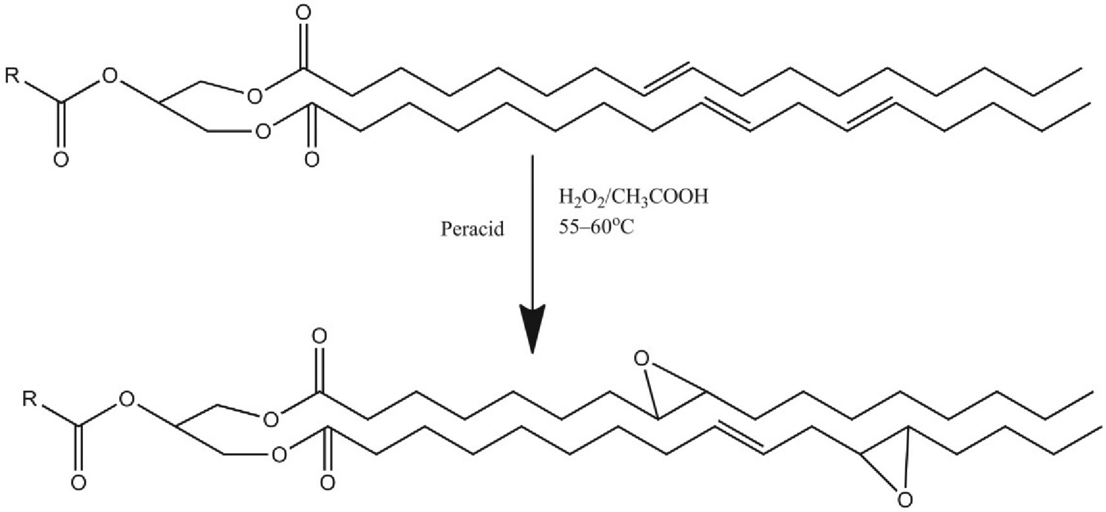

Figure 6.2 Epoxidization of triglyceride by the *in situ* peracid method as described in [4].

6.2.3 Modification from Oil to Polyether Monomers

If the triglyceride does not naturally contain epoxy or hydroxyl moieties, it is necessary to functionalize the triglyceride with chemical groups – such as maleates, hydroxyl, or epoxy – through the unsaturated double bond to use the triglyceride for either polycondensation or ring opening mechanism. An example for naturally occurring epoxidized triglyceride is vernonia oil. Additional functionalities for the natural epoxy or hydroxyl triglyceride can be attached as well, i.e., vinyl functionalities [2,14,18,19] (see Figure 6.2).

6.2.4 Polymerization from Oil Source to Polyether

Natural unsaturation in vegetable oils presents a number of possibilities for monomers with minimal chemical processing. For example, vegetable oil monomers can be used to create polyethers through manipulation of the reactive sites of the monomers [20]. Triglycerides, comprising fatty acid chains with 12–18 carbon bonds and less than four double bonds, can be used to create polyethers by manipulating the double bonds, allyic carbons, and carbon alpha to the ester groups [21]. Glycolysis or amidation could also be used to convert triglycerides into monoglycerides. This converted monoglyceride could also be manipulated with various attachments to prepare suitable monomers for polymerization [5]. For example, it is possible to prepare monomer that is ready for free-radical polymerization from triglyceride using maleic anhydride after hydroxylation [2,22,23]. The thiol–ene addition is used to functionalize triglycerides without a solvent in a single step to produce bio-based polyols from a vegetable oil [24].

The popular way of producing vegetable-oil-based polyethers is using cationic polymerization of epoxidized vegetable oils, which usually has higher reactivity compared to other oils [3,20]. Earlier practices of using epoxidized castor, soybean, and linseed oils to produce polyethers by photo-initiation did not have adequate mechanical properties. The desired mechanical properties are

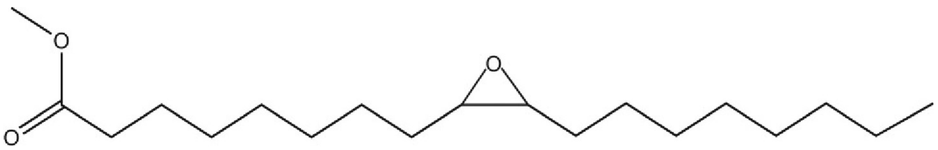

Figure 6.3 Epoxidized methyl oleate that is derived from the triglyceride [42].

achieved by increasing the degree of crosslinking, like with epoxidized soybean oil [20,25].

Epoxidation of a triglyceride can be achieved using conventional chemical treatment, acid ion exchange resin, using enzymes, using metal catalysts and other means. Such epoxidation methods can be briefly stated as follows:

- Conventional chemical treatment includes the use of carboxylic acid with concentrated hydrogen peroxide. Although use of H_2SO_4 as a catalyst for hydrogen peroxide has been proven to be most successful, works of Jai Lian Kun et al. showed that production of cottonseed oil-based polyether polyols through ring opening reaction after epoxidation while using H_2SO_4 as acid catalysis will lead to multiple undesired side reactions. The more stable way of producing epoxidized soybean oil is to use formic acid as the catalyst [26–31].
- Acid ion exchange resin methods (AIER) are the use of peroxy acid to fill the AIER pores to lower oxirane degradation by limiting the competition with triglyceride. This will also improve the selectivity and reduce undesired side reactions in the epoxidation process [2,26,32–36].
- Enzymatic methods are more environmentally friendly and less prone to side reactions. Despite low stability of lipase, usage of Immobilized Candida Antarctica lipase as a catalyst will improve the epoxidation reaction in temperature and enzyme load controlled environment. Lipase catalysis can be taken as an alternative of chemical treatment and they are recyclable. Warwel also showed that epoxidation of plant oils such as sunflower, soybean, linseed, and rapeseed can have high selectivity and more than 90% conversion [37–41].
- Metal catalysts usually have low selectivity, is difficult to separate, and is corrosive to reactors due to the strong acids. Titanium, molybdenum, and tungsten are commonly used metal catalysts. Such metal catalysts are usually used to improve the epoxidation by increasing oxirane content, such as significantly decreasing degradation of oxirane ring by using amorphous heterogeneous Ti/SiO_2 catalysis in *tert*-butyl alcohol as shown in Campanella et al. work [26, 42, 43] (see Figure 6.3).

6.3 Properties of Plant Oil-Based Polyethers

As shown by Lligadas et al., epoxidized methyl oleate (EMO), derivative from high oleic sunflower oil, can be used to prepare polyether polyols by ring-opening cationic polymerization of EMO oligomers and partial reduction of the carboxylate groups to hydroxyl moieties with a reducing agent of lithium aluminum hydride ($LiAlH_4$). Partial reduction of ester groups was used to increase the variety of polyols that also have different physical characteristics at room temperature [42–44]. Preparation of polyethers from EMO is also possible by using ionic-coordinative ring opening mechanisms, as shown by Del Rio et al. This work shows the use of a limited amount of THF to copolymerize the EMO to avoid the competitions of transesterification which formed branched ester groups. These approaches will be able to produce linear polyether polyols with 6–8 kDa with limited hydroxyls [43]. Both linear and dendritic glycerol can also be used to produce biobased polyethers by using alkoxide catalysis, which different types of epoxide monomers can be copolymerized with glycidol. It was shown that hyperbranched polyols with a well-defined polyether arrangement could be formed by controlling the monomer addition and cyclization [45].

As shown by Alam et al., Pongamia oil can be used to produce a polyether product that posses good chemical resistance and physio-mechanical performance, PEFA-BMF45. They used Pongamia oil to produce *N*,*N′*-bis(2-hydroxy ethyl) Pongamia glabra oil fatty amide (HEPFA) by mixing it with diethanolamine and using HEPFA and cyclohexanedimethanol mix to produce poly(ether fatty amide) (PEFA). Then, they mixed PEFA with butylated melamine formaldehyde (BMF) (45) in xylene solvent with phosphoric acid catalyst to produce PEFA-BMF45 [46]. Recent work of their group shows polyether fatty amide, modified with tannic acid, can be used as a coating with excellent corrosion protection properties for carbon steel, with stability up to 300°C [47].

BMF modified poly(ether fatty acid amide) that shows excellent chemical resistance and thermal stability can be prepared by modifying HEPFA with cyclohexanedimethanol Pongamia oil with Diethanolamine Manawwer. Alam et al. prepared poly(ether fatty acid amide) (PEFA) by mixing amine derivative of pongamia glabra oil and cyclohexanedimethanol. Photon initiated, radical mediated thiol–ene click reactions are used for the production of cross linked polymer network with various frameworks and functional groups. Such polymerization have fast reaction rate, better regioselectivity, and low polymerizations with limited oxygen inhibition [46,48,49]. A flame retardant bio oil-based polyether was synthesized by Hoffendahl et al. This material showed excellent resistance to flame and was remarkably stable up to 320°C with most of the degradation beginning at 455°C [50] (see Figure 6.4).

Plant oil-based polyethers have properties that can range depending on the type of material that is desired. In a paper by Lu and Larock, a polyurethane that was synthesized from methoxylated soybean oil was investigated. They discovered that these are materials that are amorphous having glass transitions anywhere from 8.9°C to 33.5°C depending on the number of hydroxyl groups present in the soybean molecule. These materials can also widely vary in mechanical properties depending on how the material is synthesized. The modulus, tensile strength, and elongation before breaking are highly dependent on the amount of soybean oil present in the preparation of these polyurethanes [51,52]. In a review article, Lu et al. talked about the synthesis of another soybean oil-based polyurethane. Depending on the molecular weight of the polyether, the final polyurethane will have very different properties. For example, plant oil-based

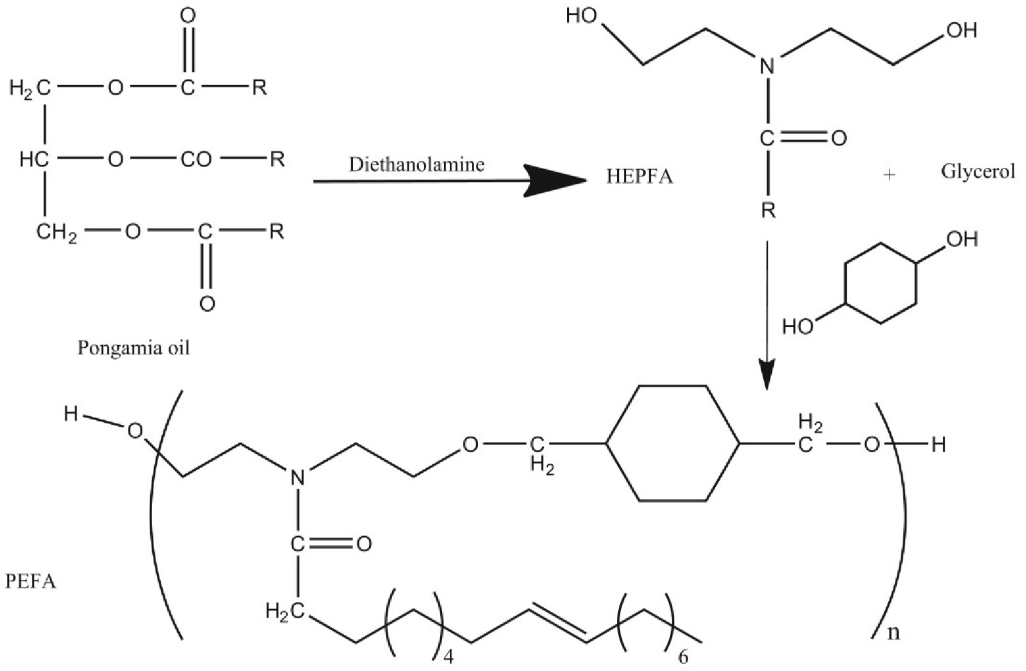

Figure 6.4 Preparation of poly(ether fatty amide) (PEFA). *Adapted from [46].*

polyethers that have molecular weights above 3000 g/mol tend to produce softer flexible polyurethanes, whereas plant-based polyethers that have molecular weights in the range of 200–1200 g/mol tend to make very stiff, rigid polymers [53]. Copolymerizing the monomer by using polyhedral oligomeric silsesquioxane (POSS) compounds to modify the epoxy networks can improve the temperature stability and mechanical properties. Also, during the processing of the polymeric material, it will lower flammability, heat evolution, and viscosity [3,19].

6.4 Applications

Polyethers based on plant-based oils properties are incredibly diverse depending on many factors. This leads to a great number of potential applications especially in the production of polyurethanes, which is thus far the most substantial application for plant oil-based polyethers. It has been demonstrated that plant oil based polyurethanes have a very wide range of mechanical and thermal properties and are very stable at temperatures below 300°C [51]. Silicon/plant oil-based polyurethanes have applications as a flame retardant [1]. Plant oil-based polyethers can also be used to synthesized waterborne dispersions [51,54]. The biomedical field has large potential for the use of plant oil-based polyurethanes. Zdrahala et al. published a review article with the potential uses of polyurethanes in the biomedical fields for materials. For example, they talk about the use of polyurethanes as an implant to support an artificial organ [55]. It is possible that plant oil-based polyurethanes might have potential in this field as they are materials that have little to no toxicity and their properties are very customizable.

Polyether polyols are usually produced by the anionic ring-opening polymerization of alkylene oxides such as ethylene oxide or propylene oxide. Polyether polyols with molecular weights of 200–10,000 g/mol can be used for the formation of polyurethane, whereas rigid polyurethanes can be produced from such polyols with molecular weight of 200–1200 g/mol and flexible polyurethanes can be produced from molecular weight of above 3000 g/mol [3,36,56]. Rigid polyurethane foams are widely used in thermal insulation and packaging. Due to the uniqueness castor oil, having both unsaturated and nonconjugated hydroxyl functions, can react with polyfunctional isocyanides to form polyurethanes with a wide range of physical characteristics. It is also used to improve polyether-based foam [57–59]. Polyurethanes are used for coatings, adhesives, medical devices, and in textile industries [60]. Wu et al. showed that epoxidized rapeseed can be used as a biodegradable lubricant due to the polyether material formation on the frictional surface through tribo-polymerization [61]. As the works of Miao et al. show, polyglycerol-derived hyperbranched dendritic polyether can be used as a flexible, highly interactive drug delivery means [20,45]. Gupta et al. showed the reasonable effectiveness of polyether as an injectable drug delivery system. Their study shows that standard –PEG demonstrated ideal biocompatibility [62]. Use of polyether derivative as a lubricant was also shown in the Zhang et al. work in which they have shown the use of aqueous amine-polyoxyethylene-polyoxypropylene-ether, KE-1, solution to reduce friction and wear. The antiwear property was reported improved and friction coefficient lowered for both steel–steel and steel–aluminum frictions [63]. Louie et al. showed that we can have smoother membrane surfaces by applying 1% of polyether–polyamide block copolymer (PEBAX) solution on polyamide reverse osmosis membranes. They found that such coating will improve the fouling resistance against a surfactant, water emulsion feed or model oil for both high and low flux reverse osmosis membranes [64]. Works by Zheng et al. showed that perfluoropolyether (PFPE) can also be used as a lubricant for very thin layer of PEEK coating [65]. Alam's work shows that urethane modified plyetheramide resins (UPEtA) that is derived from linseed oil can be used as anticorrosion lubricant. They showed that this resins showed good chemical resistance in acid, alkalie, and organic solvent where UPEtA-24 outperformed other variants. The synthesized resins decomposed only 5% at 190°C and were decomposed 75% at 500°C [66].

6.5 Challenges and Trends

More work is needed to increase the effectiveness of the monomerization of fatty acid with functional groups. Considering most of the petroleum-based polyethers can be replicated using the bio-based oil sources, improving this process is important to accelerating the use of bio-based oil as a substitute. More work is needed to understand the effect of protein structures, oil content, and fatty acid type in the final product. The current trend of genetic modification of oilseeds to lower the production cost as well as the extraction efficiency needs to be strengthened more.

Modification of existing catalyst and producing new catalyst are also an important means of reducing the cost, time needed, and improving conversion. Even if improvement of catalysts is a significant solution to current challenges, developing more efficient synthesis methods without catalyst or with a limited use of catalyst will remove or reduce the dependency of monomerization on catalyst. More work is also needed in terms of developing an assessment that will help the industry understand the challenges and opportunity of the academic research. More work on production of polyether or polyether-specific monomers by thiol–ene coupling reactions with fatty acid derivatives is also needed [67,68]. Finally, these materials have exciting properties, and developing further applications is a must to make these polymers scalable.

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7 Plant Oil-Based Epoxy Intermediates for Polymers

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7.1 Introduction

Epoxy resins are an important class of materials, which are used widely in electrical, automobile, and other applications because of their excellent chemical resistance, outstanding adhesion, high tensile and compressive strengths, electrical insulation properties, and superior fatigue strength [1–4]. Currently, the major components used in most epoxy-based thermoset polymer formulations originate from petroleum-based derivatives. However, resins and composites incorporating renewable resources are increasingly being used in diverse areas of manufacturing because of the heightened awareness of environmental issues. To date, these biobased resins have only represented a very small percentage of the entire plastics market, and the widespread application of biobased materials is still limited by the available materials plus their cost of production. Hence, the development of cost-effective biobased materials from abundantly available renewable sources is of great interest to prevent reliance on finite petroleum resources.

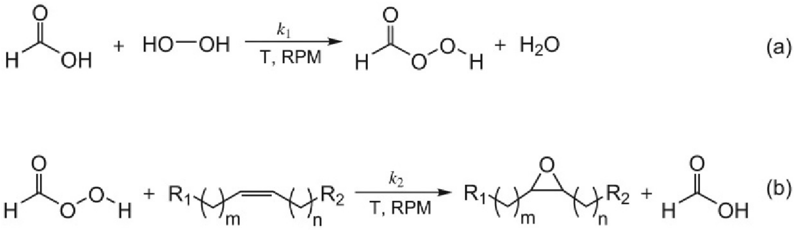
Unsaturated plant oils, such as palm oil, soybean, canola (rapeseed), camelina, flax, hemp, sunflower, safflower, cottonseed, and other oils, can be chemically modified to produce epoxidized plant oils. These epoxidized oils can, in turn, be further modified or cured into thermoset epoxy resins, in similar ways as used for their petroleum-based counterparts.

This chapter describes the materials and methods for making plant oil-based epoxides, and the use of these epoxides in making variety of the intermediate monomers, oligomers, and polymers.

7.2 Epoxidation of Plant Oils

Functionalization of the carbon–carbon double bonds ($\text{—C}=\text{C—}$) of unsaturated plant oils and oil derivatives is a commonly used process making use of a range of reactions. Some important examples of the modification of double bonds from unsaturated oils and fats include the use of environmentally friendly processes such as acid catalyzed chemical epoxidation [5–9] by hydrogen peroxide (H_2O_2), chemo-enzymatic epoxidation [10–20], or ozonolysis reactions [21–24]. These methods can produce a wide range of oil derivatives and products. Ozonolysis of the $C = C$ of plant oils leads to the formation of ozonides which can subsequently cleave to yield aldehydes, acids, or ketones, while the chemical and chemo-enzymatic oxidation of the double bonds lead to the formation of epoxides. Despite the use of variety of catalysts for the epoxidation of unsaturated oils and oil derivatives, the acid-catalyzed epoxidation methods of unsaturates have received much attention as the most cost-effective route. The most commonly used acids in the epoxidation processes of plant oils include aliphatic (such as formic, acetic, lauric, trifluoroacetic) and aromatic (such as benzoic, *m*-chlorobenzoic) species [25]. The use of microwaves as an accelerated method for making epoxidized fatty acid esters has been reported to produce a $>90\%$ yield of epoxides within 5 min [6].

Although there are several approaches available for the modification of double bonds of unsaturated oils and oil derivatives to make biobased epoxides, the most commercially viable method of epoxidation is the classic epoxidation reaction proposed by Prilezhaev (Prileschajew) [26]. Thus, our main focus will be put toward discussion of



Scheme 7.1 Formation of performic acid (a) and epoxidation of double bonds with this performic acid (b). Note that to reduce analytical complexities, epoxidized plant oil structure provided in Scheme 1 (b) is substituted with the monounsaturated single-chain platform such as methyl oleate. R_1 and R_2 are the mixture of hydrocarbon and ester parts of FAME; *m* and *n* are the numbers repeating hydrocarbon units in different parts of the chain; k_1 and k_2 are the performic acid and epoxide formation rates, respectively.

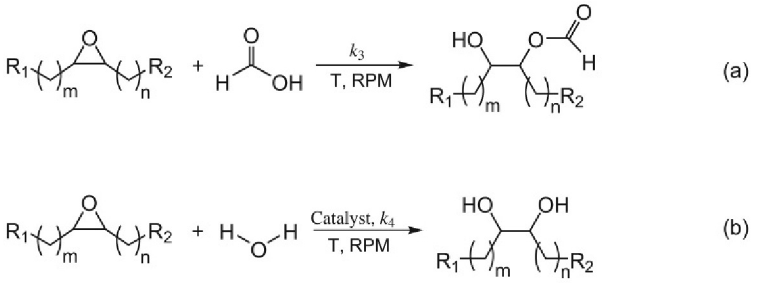
the aspects of the *in-situ* acid catalyzed epoxidation of double bonds of plant oils and oil derivatives using the H_2O_2.

Epoxidation of the plant oils and oil derivatives in an industrial scale are typically carried out using peroxy (performic or peracetic) acid generated *in-situ* from carboxylic acid and H_2O_2 [27]. The epoxidation reaction takes place in two stages: first the formation of a peroxy acid and subsequently the reaction of the peroxy acid with the unsaturates [26]. As an example, Scheme 7.1 demonstrates these two stages of epoxidation reaction of unsaturated fatty acid using formic acid as a catalyst (oxygen carrier).

Reaction of the formic acid with hydrogen peroxide leads to the formation of performic acid, which is the main oxidizing product of the double bonds of the oil (Scheme 7.1a). This reaction eventually consumes a stoichiometric amount of hydrogen peroxide. The performic acid so formed then reacts with double bonds of the oil by donating an oxygen atom to form the epoxide group. At the same time, formic acid is liberated to the bulk reaction mixture (Scheme 7.1b) [28]. Due to the regeneration of the formic acid, it is possible to use low molar amount of the formic acid in the epoxidation processes.

Since oil epoxides are fairly reactive they may readily undergo ring-opening reactions or participate in oligomerization processes. It was reported [29] that a high molar ratio of acid to hydrogen peroxide is deleterious to the survival of an epoxy group. The attack of epoxy groups by formic acid may lead to the formation of hydroxylated-formiated products [30,31] due to the acid catalyzed epoxy ring-opening reactions (protonation of epoxy oxygen), as shown in Scheme 7.2a.

It has been reported [31] that protons at the surface of catalysts can cause epoxy ring opening by reaction with a number of chemicals present (or formed) in the overall mixture. The epoxy ring opening can also be caused by water in the presence of a strong acid catalyst [32] to form di-hydroxy groups per epoxy site, as demonstrated in Scheme 7.2b. Note that the premature epoxy ring opening is considered at this stage to be an undesirable side reaction. In contrast, the controlled occurrence of this oxirane cleavage by nucleophiles is an important reaction route that is used in making biobased intermediates or polymers from epoxidized plant oils. Thus, it is critical to control the conditions used in manufacturing the epoxidized plant oils in order to minimize such side reactions. This is summarized in the following:



Scheme 7.2 Examples of possible epoxy ring opening: with formic acid (a) and water (b). k_3 and k_4 are the ring-opening reaction rates by carboxylic acid and water, respectively.

1. *In-situ* epoxidation of the plant oils needs to be carried out at a moderate temperature, usually below 70°C:
    a. high temperature epoxidation processes lead to the excessive epoxy ring-opening reactions;
    b. in addition, it was reported that the decomposition rate of H_2O_2 increases approximately 2.2 times for each 10°C rise in temperature in the range from 20°C to 100°C [33];
    c. peroxy acids are readily decomposed upon heating, and can explode upon rapid heating to 80–85°C.
2. Use of an excess of hydrogen peroxide is necessary to ensure complete epoxidation and to compensate for the loss/decomposition of hydrogen peroxide. Typically, 20–50% excess of H_2O_2 from the stoichiometric ratio to double bonds is sufficient.
3. The concentration of the carboxylic acid (homogeneous) catalyst should be significantly lower than its stoichiometric ratio to double bonds in order to avoid or minimize undesirable epoxy ring-opening reactions from occurring during epoxidation. The optimal concentration is about 0.2–0.3 moles of carboxylic acid per mole of double bonds of the unsaturated oil.

Using these methods, epoxidized plant oils can be manufactured with a range of oxirane contents, depending on the fatty acid profiles of the input oils. Usually, the conversion of double bounds of the unsaturated oils into epoxides is quantitative; however, it should be noted that small amount of epoxy ring opening may still take place.

Figure 7.1 shows the epoxidation kinetics for canola oil fatty acid methyl esters (FAME) at an epoxidation temperature of 60°C. As can be seen from Figure 7.1 (Omonov et al., unpublished work, 2015), the amount of unsaturated FAME decreases exponentially over the epoxidation time (diamond symbols), reaching a plateau region after 24 h. This indicates that complete epoxidation of FAME has been achieved, and no further change is expected as all unsaturated FAME have been converted into epoxidized derivatives. Meanwhile, the oxirane oxygen content (OOC) of the system increases in a similar way, i.e., exponentially, over epoxidation time (open-circle symbols) to approach maximum values. (Note that the term OOC is a characteristic of epoxides that describes the weight percentage of oxirane oxygen in 100 g of epoxidized product). After 24 h of epoxidation the OOC values start to decrease as a result of epoxy ring-opening reactions described in Scheme 7.2. This reaction in its turn will generate the secondary mono- or

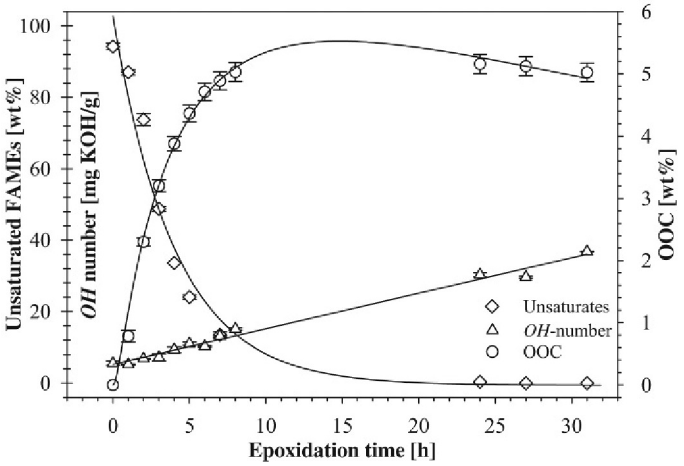
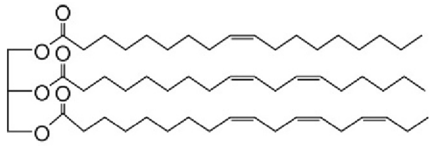


Figure 7.1 Epoxidation kinetics of canola oil FAMEs at 60°C using formic acid and hydrogen peroxide. The ratio of H_2O_2 and formic acid is 1.5 and 0.25 moles per double bond of the canola oil, respectively. Agitation speed is ~300 RPM.

di-hydroxyl groups on the fatty acid chain. The *in-situ* formation and increase of the hydroxyl groups during the epoxidation process can be monitored by measurement of the hydroxyl value of the partially epoxidized oil, as shown in Figure 7.1 (triangle symbols). It is clear from the figure that minimizing the epoxidation time will minimize the formation of secondary hydroxy-byproducts.

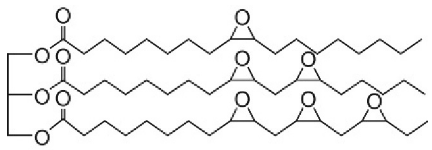
7.3 Derivatives of Epoxidized Plant Oils

Plant oils mainly contain triglycerides (TAG), which are the esters of glycerol and three fatty acids. The fatty acids of the majority of plant oil TAGs consist of unsaturated C_{16}–C_{22} aliphatic chains bearing double bonds (especially unsaturated C_{18} – oleic, linoleic, or linolenic) and saturated C_{16}–C_{22} fatty acids (mainly stearic or palmitic). The fatty acid profiles of the major oils are presented elsewhere in the literature [34–36]. Scheme 7.3 illustrates the structure of a hypothetical TAG containing unsaturated fatty acids.

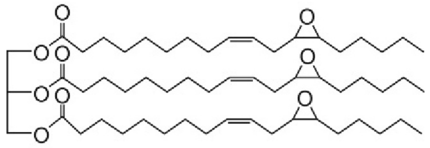


Scheme 7.3 Structure of the TAG, containing the oleic, linoleic, and linolenic fatty acids.

Plant oils with a high unsaturated fatty acid content, such as soybean, canola (rapeseed), camelina, flax, hemp, sunflower, safflower oils, have become attractive feedstocks for chemical modifications since numerous reactions, including epoxidation, could be performed at the site of their internal alkene-moieties. Epoxidation of the unsaturated TAG presented in Scheme 7.3, according to the reaction path in the Scheme 7.1b, leads to the formation of epoxidized TAG, as shown in Scheme 7.4.



Scheme 7.4 Structure of the epoxidized TAG, containing the oleic, linoleic, and linolenic fatty acids.



Scheme 7.5 Structure of the vernonia oil, containing three vernolic acids. *Adapted from [39]*

It should be noted that some naturally occurring epoxidized fatty acids have been found in certain plant oils [37]. Of these, vernonia oil extracted from the seeds of the tropical African plant *Vernonia galamensis* appears to have the best potential for commercial application. This is due to its high concentration of epoxidized fatty acid (vernolic acid, 75–80%), relatively low viscosity for its high epoxide equivalent weight (about 400 g/Eq) [37,38]. The conceptual structure of a vernonia oil TAG molecule containing three vernolic acids is given in Scheme 7.5.

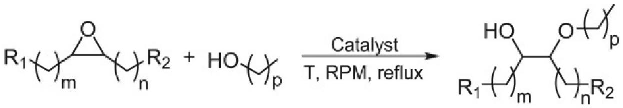
Usually, the oxirane groups of epoxidized plant oils are reactive and can easily be modified using a variety of procedures to tailor-make specific monomers that possess desirable functionalities for use in making polymers. Such reactions have included hydrolysis, acrylation, ethoxylation, propoxylation, hydroxylation, hydrogenation, carbonation, oligomerization, and many others resulting in a wide range of monomer functions. Note that in the following, only epoxides containing a single fatty acyl chain are used for illustration in order to simplify the discussion. However, the same general principles also apply to TAG epoxides.

7.3.1 Epoxy Ring Opening by Alcohols

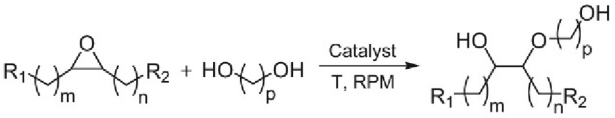
One of the most commonly used methods of modification of the epoxidized plant oils is the epoxy ring-opening reactions with alcohols. Hydroxylation (alcoholysis) of epoxidized plant oils and oil derivatives using mono-, di-, or poly-alcohols in the presence of a variety of acid catalysts is used to make biobased polyols. The concept of epoxy ring-opening reactions using monofunctional alcohols is given in Scheme 7.6. The product of epoxy ring-opening reactions of epoxidized plant oils via alcoholysis is lipid derivatives containing secondary hydroxyl groups along with an alkoxy dangling chain.

A great variety of homogenous and heterogeneous catalysts have been used to catalyze epoxy ring-opening reaction, including sulfuric acid [7–9,39,40], *p*-toluenesulfonic acid [41], fluoroboric acid, activated clay [42], strongly acidic ion exchange resins [43], fluoroantimonic acid ($HSbF_6$) [44], *m*-chloronbenzoic [5,6], and other acids.

Similarly, a diversity of monofunctional alcohols [39,40,45–55] have been used in epoxy ring-opening reactions of the biobased epoxides. Although some authors [7] have described the possible use of C_1–C_{12} linear chain monofunctional alcohols, secondary alcohols (such as isopropanol), or cyclic monofunctional alcohols (such as cyclohexanol or benzyl alcohol) in epoxy



Scheme 7.6 The concept of epoxy ring-opening reaction by monofunctional alcohols as nucleophiles in the presence of catalyst.



Scheme 7.7 The concept of epoxy ring-opening reaction by poly-functional alcohols as nucleophiles in the presence of catalyst.

ring-opening reactions, it is preferred to use short-chain monofunctional alcohols such as methanol, ethanol, and propanol.

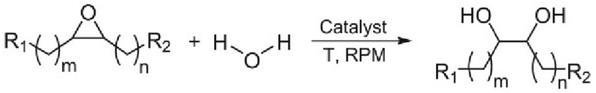
The process of making commercially available BiOH® series (Cargill, Inc.) polyols from different epoxidized plant oils with the hydroxyl number ranging between 56 and 225 mg KOH/g polyol is described in [56]. This polyol is prepared via epoxy ring-opening reaction (Scheme 7.6) by methanol in the presence of fluoroboric acid as a catalyst.

Epoxy ring-opening reactions of epoxidized plant oils and oil derivatives using di-alcohols have received considerable attention [7,57–61]. The use of 1,3-propanediol [60], 1,2-propanediol and ethylene glycol [60,61], or esters of ethylene glycol [7] is reported in nucleophilic ring-opening reactions in biobased epoxides in the presence of strong acids to make polyols. The concept of epoxy ring opening with poly-functional alcohols is similar to Scheme 7.2b. The resulting polyols have high hydroxyl numbers comprising a mixture of primary and secondary hydroxyl groups (Scheme 7.7).

The use of sulfuric acid [7,58,60], tetrafluoroboric acid [57,59,61], macroreticular ion exchange resin, and diethylether–trifuoride borate complexes [62] as catalysts of the alcoholysis reactions is reported at different reaction temperatures.

Alcohols including propanediol, butanediol, pentanediol, hexanediol, and polyoxyethylene have been used to make poly-hydroxylated fatty acid esters. These poly-hydroxylated fatty acid esters have further been used to make polyols from epoxidized plant oils with primary hydroxyl groups [63]. The authors [64] also used several di- and poly-alcohols in epoxy ring-opening reactions of epoxidized soybean, sunflower, and linseed oils to produce oleochemical polyols. The produced polyols had high primary and secondary hydroxyl functionality (between 370 mg KOH/g and 418 mg KOH/g) and controllable reactivity. These polyols were manufactured utilizing the hydroxylation concept described in Scheme 7.7.

Some commercial examples of this process include BASF's SOVERMOL® series of biobased polyols made from soybean oil for various applications such as solvent-free UV-stable coating, flexible coating and casting, and polyurethane production. The chemical pathway of some of these biobased polyols is based on the epoxidation of vegetable oils followed by ring opening of epoxides by nucleophilic attack of alcohols, then transesterification of poly-hydroxylated oils with the same alcohol [65]. Another example is from Hobum Oleochemicals who are producing their MERGINOL® series of biobased polyester and polyether–polyester polyols for low density polyurethane applications and as raw materials for polyesters, surfactants, and lubricants. These polyols are produced via epoxidation of plant oils followed by nucleophilic ring opening by water, mono-, or di-alcohols and alcoholamines.



Scheme 7.8 The epoxy ring-opening reaction by water in the presence of catalyst.

7.3.2 Epoxy Ring Opening by Water

One of the simplest methods of epoxy ring opening is the use of the water as a nucleophile in the presence of a strong acid [32,66–68]. This reaction yields a di-hydroxylated oil or oil derivative, containing secondary hydroxyl groups (Scheme 7.8). The use of sulphuric acid, formic acid, acetic acid, or various organometallic catalysts for this reaction has been reported. [69–74].

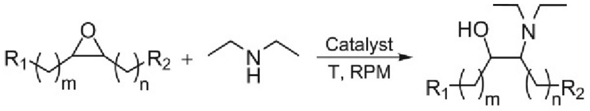
As an example, the Sofiproteol Group is manufacturing biobased polyols under tradename of RADIA®. Their polyester and polyether polyols are intended to be used for flexible and rigid PU applications respectively, while RADIA amorphous polyester polyols were developed for CASE (coatings, adhesives, sealants, and elastomers) and thermoplastic PU applications. The chemical routes for manufacturing these polyols are based on the epoxidation of oils and its derivatives by H_2O_2 with metal catalysts followed by nucleophilic ring opening of epoxides by water [75], as shown in Scheme 7.8. However, it should be noted that whilst the production of polyols with the secondary hydroxyl groups is simple and inexpensive, the demand for the use of these products is less due to the relatively low reactivity and high viscosity, compared to the other biobased polyols.

7.3.3 Amine-to-Epoxide Reactions

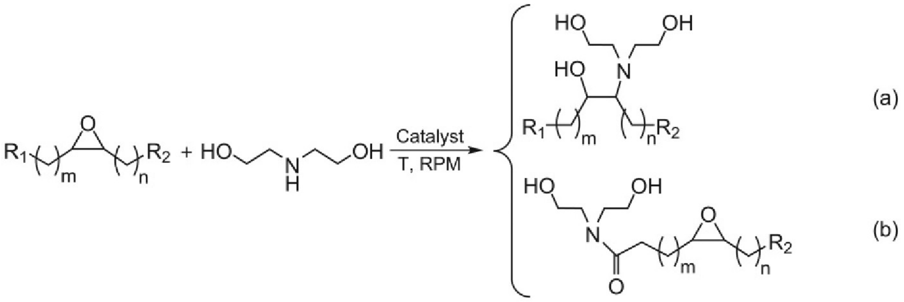
Monofunctional amines or alcoholamines could also directly be used as nucleophile to open epoxy ring of epoxidized plant oils. The use of monofunctional amines, such as diethylamine, *n*-propylamine, *tert*-butylamine, and isobutylamine, for the epoxide ring opening of epoxidized plant oil in the presence of zinc chloride ($ZnCl_2$) catalyst was reported [76]. The reaction conditions were optimized using a variety of parameters to favor epoxy ring-opening reaction for maximum aminolysis of epoxy group, without cross-linking and with little disruption of the ester linkage. The best results were achieved with diethylamine (Scheme 7.9).

These authors [76] describe that the use of epoxy ring opening by an amine is an effective way of introducing branching on the fatty acid chain of plant oils. The resulting products (defined as "aminol") possess significantly improved thermal, oxidative, and low-temperature stability compared to the equivalent unmodified oil, and can be used for antioxidant and antiwear specialty chemicals in automotive and industrial applications.

Other authors [64,77] described the formation of the mixture of biobased polyester polyols (from the amidification reaction) and



Scheme 7.9 The concept of epoxy ring-opening reaction with diethylamine. *Adapted from [77].*



Scheme 7.10 The concept of epoxy ring-opening reaction and amidification reaction with diethanolamine.

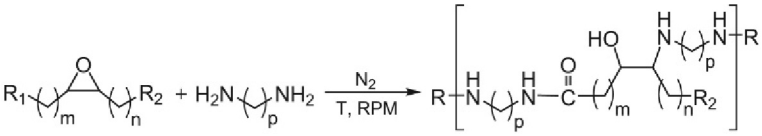
polyether polyols (from the oxirane ring-opening reaction) from the reaction of epoxidized triacylglycerol and alcoholamines. The concept of the epoxy ring opening with diethanolamine to produce fatty amide (a) and amine (b) polyols is presented in Scheme 7.10. It was demonstrated that high temperature reactions (130–180°C) and extended reaction times (from 2 up to 7 h) favored the epoxide ring opening by diethanolamine [77].

This knowledge of making polyols from epoxidized soybean oil and alkanolamines has been realized in commercial scale by Huntsman Petrochemical LLC [78] in manufacturing JEFFADD™ B650 biobased polyols. This autocatalytic polyol is described to comprise primary and secondary hydroxyl groups (400–600 meq KOH/g), tertiary amine groups (1.5–3.5 meq/g), free from odor and acidity, water soluble and intended to use as a replacement for all, or a portion of, petroleum-derived polyols generally used in the production of polyurethane materials.

The double hydroxylation procedure is used to make biobased polyols with increased hydroxyl numbers and moderate viscosities. First, the epoxide ring of an epoxidized plant oil is opened via the reaction shown in Scheme 7.2a to make polyols [79]. Then, the aminolysis process by hydroxyl alkylamines of the ester bond in polyols is carried out to increase the hydroxyl number and lower the viscosity [80]. This polyol is currently marketed by BioBased Technologies LLC as AGROL® Diamond polyol, with typical hydroxyl value of 340–370 mg KOH/g, viscosity 3300 cP, and a molecular weight of 510–560 g/mol.

The use of novel polyol synthetic routes starting from epoxidized plant oils and primary amines has been reported for coatings, adhesives, and foam applications [81]. Materials that contain mixed amino and/or hydroxyl poly functionality ("polyolamines") have been prepared by epoxy ring opening and amide formation reactions (Scheme 7.11).

The final poly-functionalized intermediate products were cross-linked with a variety of curing agents to form urethane-like polymeric materials [77,81,82].

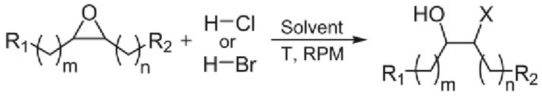


Scheme 7.11 The concept of direct epoxy ring opening and amidification reactions with polyamines. Note that R is H or fatty acid adduct.

7.3.4 Epoxy Ring Opening with Halogen Reagents

Hydrohalogenation methods have been used to analyze epoxy groups via halohydrin formation reactions [83] using HCl or HBr as the halide reagent. Halogenation via ring-opening reactions has been reported, using both hydrochloric (HCl) and hydrobromic (HBr) acids to prepare halogenated polyols from epoxidized plant oils (Scheme 7.12) [52,84,85]. It was anticipated that the polyurethanes made from these halogenated polyols would have enhanced fire resistant properties due to the incorporation of halogen atoms in the fatty acid chain along with the hydroxyl group [85].

The thermal stability and physical properties of these halogenated polyols were evaluated and compared with nonhalogenated polyols. Halogenated polyols exhibit higher densities and viscosities compared to their nonhalogenated counterparts. Polyurethanes incorporating halogenated polyols demonstrated higher glass transition temperatures and mechanical performance [52,84], as well as superior resistance to flammability [85].



Scheme 7.12 The concept of epoxy ring opening with hydrochloric and hydrobromic acids. Note X represents Cl– or Br–.

7.3.5 Epoxy Ring Opening by Lactic Acid

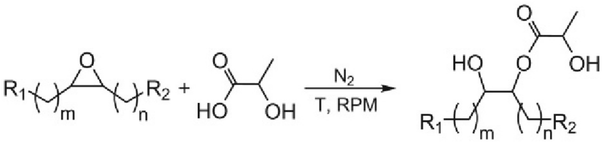
An attempt has been made to introduce two hydroxyl groups per epoxy site of the epoxidized plant oil via an epoxy ring-opening reaction with lactic acid (Scheme 7.13) [86].

A lactic acid-epoxidized soybean oil (LA-ESO) hybrid monomer has been synthesized with the 70% conversion of epoxide into dihydroxy groups. The product was claimed to be an intermediate for the production of partially biorenewable polyurethanes with a unique crosslinking structure. Polyurethane materials with the controllable, broad range of glass transition temperature (up to 96°C) were prepared from LA-ESO and MDI using different ratios of isocyanate to hydroxyl groups [86].

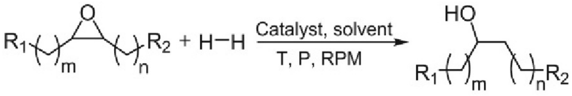
7.3.6 Hydrogenation of Epoxidized Oils

A modification of epoxide groups of bio-based epoxides using catalytic hydrogenation in the presence of a Raney nickel catalyst has been reported [52,84,87]. Epoxy ring opening by hydrogen addition leads to the formation of hydroxylated fatty acids with only secondary hydroxyl groups (Scheme 7.14).

It was reported that the hydrogenated soy polyols (Soy-H_2) demonstrated higher hydroxyl numbers (212 mg KOH/g) compared to the chlorinated (Soy-HCl), brominated (Soy-HBr), and methoxylated (Soy-Met)



Scheme 7.13 The concept of epoxy ring opening with lactic acid.



Scheme 7.14 The concept of catalytic epoxy ring-opening reaction. *Adapted from [66,85].*

polyols (below 200 mg KOH/g) [52,84]. However, the glass transition temperatures of polyurethanes from hydrogenated polyols were significantly lower (<40°C) compared to the polyurethanes from the other Soy-HCl, Soy-HBr, Soy-Met polyols (between 66°C and 88°C). These differing values of T_g were ascribed to differences in the crosslinking densities and in the free volumes of these substituent groups within the polyurethanes. In addition, the use of a variety of palladium-based catalysts [88] has been reported for the catalytic hydrogenation reactions that can selectively reduce aromatic epoxides to the corresponding alcohols in high yield and under mild conditions.

7.3.7 Acrylated Epoxidized Plant Oils

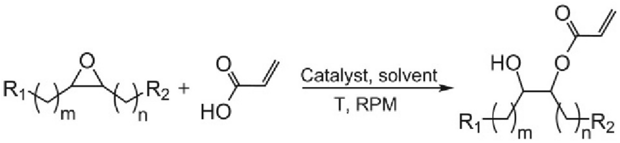
Epoxidized plant oils and their derivatives can be chemically modified through simple reactions to introduce readily polymerizable groups [89,90]. One such approach is to make a reactive acrylic polymer containing both hydroxyl and acidic functional groups (Scheme 7.15).

Acrylated epoxidized plant oils were prepared using epoxidized plant oils along with acrylic acid, an amine-type catalyst and hydroquinone as a gelling inhibitor [90,91]. This primary objective of these reports was to make UV radiation curable polymer precursors. Similar strategies have been applied to the synthesis of acrylated or methacrylated plant oils using epoxidized plant oils including soybean [36], canola oil [92], linseed [93,94] castor [95], palm [96], and vernonia [97].

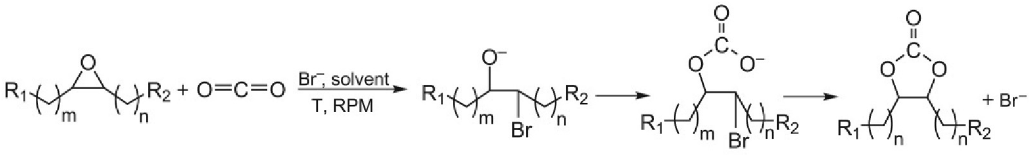
7.3.8 Carbonated Plant Oil and its Derivatives

Novel methods of producing carbonated plant oils have been described in the literature by several authors [98–102]. They have outlined the synthetic pathways for the modification of epoxidized oil which involves the reaction of oxirane of an epoxidized plant oil with the carbon dioxide (CO_2) to form a carbonated oil. It was claimed that they could successfully incorporate CO_2 into the fatty acids of epoxidized soybean oil in order to produce carbonated soybean oil with high yields (94% [102]), under moderate flow of CO_2 in the presence of tetrabutylammonium bromide (Scheme 7.16).

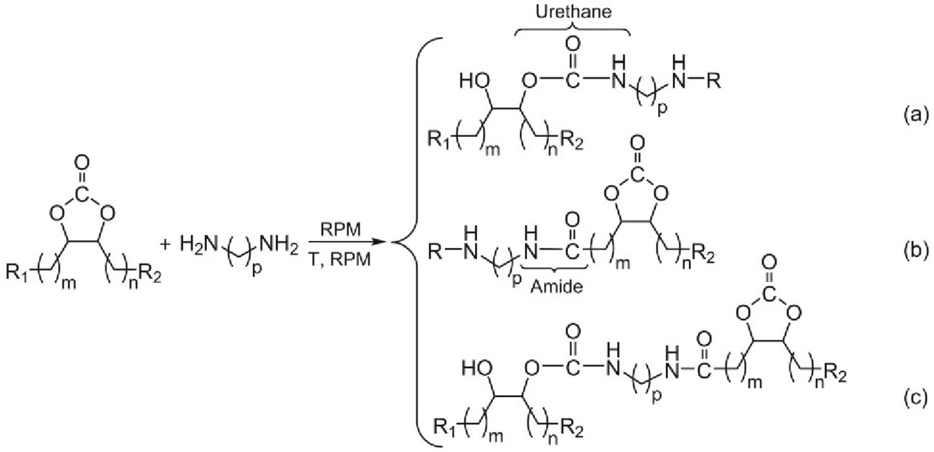
The carbonated oil produced as shown in Scheme 7.16 has been used in producing a variety of oil derivatives via cyclic carbonate ring-opening reactions with polyamines having two or more amine functionalities, under mild conditions [101–105]. A variety of polyamines, including



Scheme 7.15 The concept of epoxy ring-opening reaction by acrylates. *Adapted from [90,91].*



Scheme 7.16 The concept of epoxy ring opening reaction by CO_2 to form carbonated oil.



Scheme 7.17 The concept of cyclic carbonates ring opening by polyamines to form urethane (a), amide (b) or urethane–amide compounds (c). *Adapted from [103,106]*. Note that R is hydrogen or fatty acid adduct.

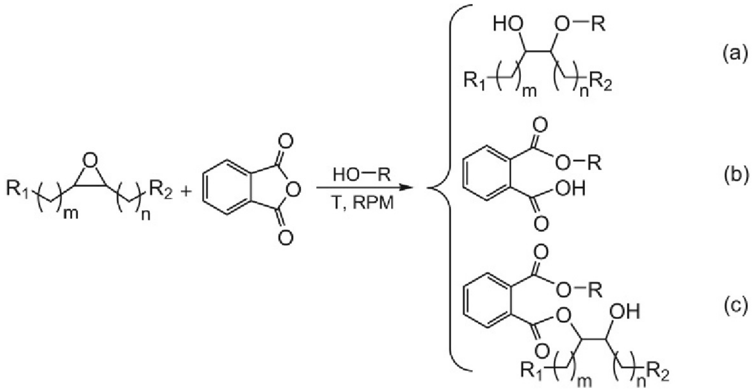
1,2-ethane diamine [102,103,105], isophorone diamine [101,103], 1,6-hexanediamine [101,102,105], triethylenetetraamine and diethylenetriamine [101], tris(2-aminoethyl) amine [102], have been used in carbonate ring-opening reactions at different carbonate-to-polyamine ratios. Depending on carbonate-to-polyamine ratio the final product may contain urethane, amide bonds or the simultaneous formation of both links can be favored (Scheme 7.17) [105].

Note that these carbonate ring-opening reactions with polyamines have mainly been used to produce nonisocyanate polyurethane (NIPU) networks [102,104,105]. The effects of the amine structure and carbonate to amine ratio on biobased NIPUs structure and mechanical, physical, and swelling properties were also studied. It was reported that the stoichiometric carbonate-to-amine ratio produced the polymer networks with the highest density and the highest T_g (between 35.3 °C and 40.1°C from DMA) and hardness (between 47 and 83 shore A), and tensile strengths (between 3.80 MPa and 5.77 MPa).

7.3.9 Epoxy Ring-Opening Reactions by Anhydrides

Epoxy ring-opening reactions by anhydrides and acid anhydrides have been reported to make biobased epoxy resins using different epoxidized oils, such as epoxidized canola (ECO) [106], [107], soybean (ESO), camelina (EcamO), linseed (ELO) [106,108,109] and hemp (EHO) oils [106]. Usually, the reaction of epoxides with anhydrides involves multistep reactions, and some important simple examples are given in Scheme 7.18.

In the presence of a nucleophile, the epoxide groups can produce hydroxylated fatty



Scheme 7.18 The concept of epoxy and phthalic anhydride ring-opening reactions in the presence of nucleophilic alcohol, and possible oligomerization of components. *Adapted from [108].*

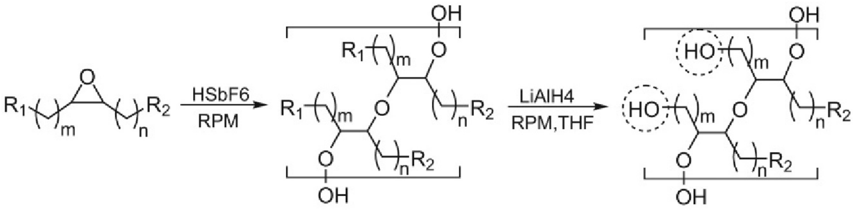
acid ethers (reaction A), while an anhydride can ring can be opened to form both monoester and carboxylic acid groups (reaction B). In these reactions, the nucleophiles or nucleophilic components could be those already existing or added or those formed via reaction (A) or (B). Hence, the hydroxyl and/or acid groups of the components formed in (A) and (B) give rise to oligomeric structures, an example of which is indicated in reaction (C). The use of these oligomeric prepolymers as aldehyde-free internal bonding adhesives in manufacturing lignocellulosic fiberboards and particleboards has been reported [106].

7.3.10 Epoxy Ring-Opening Polymerization

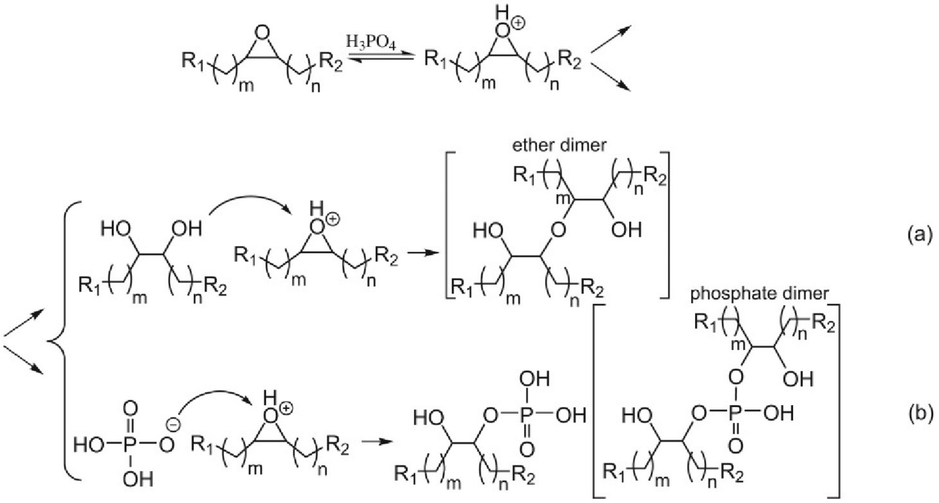
A method for producing oligomeric polyether polyols through acid-catalyzed ring-opening polymerization of epoxidized methyl oleate (EMO) in the presence of $HSbF_6$ has been described [44]. A subsequent partial reduction of the ester groups resulted in the formation of primary alcohols (Scheme 7.19).

This controlled reduction of the carboxylate groups to hydroxyl moieties was carried out in tetrahydrofuran using lithium aluminum hydride ($LiAlH_4$). Depending on the degree of reduction, the polyols with a broad range of hydroxyl functionalities (between 94 mg KOH/g and 298 mg KOH/g) were obtained, and these range from clear liquids to white, waxy solids at room temperature. These polyols were reacted with 4,4′-methylenebis(phenyl isocyanate) to make corresponding polyurethane networks. The T_g of the polyurethanes produced varied from –15°C to 80°C (determined by DSC) depending on hydroxyl functionality of the polyols.

A similar concept involving the epoxy ring-opening oligomerization of epoxidized



Scheme 7.19 The concept of cationic epoxy ring-opening oligomerization reaction and controlled reduction of carboxylates into hydroxyl groups. *Adapted from [45].*

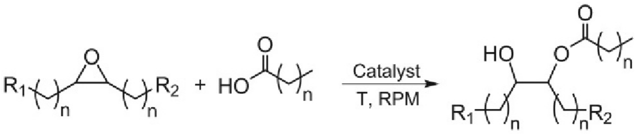


Scheme 7.20 The concept of epoxy ring opening by phosphoric acid and the mechanism of ether (a) and phosphate ester (b) cross-link formation. *Adapted from [111].*

plant oils has been suggested [56,110]. In this case, phosphoric acid (H_3PO_4) was used to make novel biobased pressure-sensitive adhesives (PSA) from epoxidized soybean oil (ESO). In this work, two key functions of phosphoric acid were reported: (i) acting as a general acid catalyst activating the epoxide toward nucleophilic attack by the diol (Scheme 7.20), thus generating an ether cross-linkage (reaction a); (ii) as a coreacting component in establishing phosphate ester linkages (reaction b). These reaction pathways have led to the formation of epoxidized and dihydroxylated soybean oils. Copolymerization of epoxidized and hydroxylated soybean oil in the presence of H_3PO_4 resulted in a product with the potential as a PSA. The biobased PSA showed similar peel adhesion strength properties as selected commercial PSAs.

7.3.11 Estolides of Epoxides

The estolides are a developing class of materials which can be synthesized by the condensation of a fatty acid with a second fatty acid or fatty acid alkyl ester. They have a great potential as base stocks for a wide range of lubricant applications due to their excellent cold temperature properties coupled with their good oxidative stability [111]. A variety of routes for estolide formation from fatty acids have been discussed extensively in the literature [111–113], including the epoxy ring-opening esterification reactions. The epoxy ring opening of epoxidized plant oil derivatives (FFA, FAMEs, etc.) catalyzed *in situ* by the FFAs lead to the subsequent condensation of fatty acid to form the hydroxyl estolide (Scheme 7.21).



Scheme 7.21 The concept of estolide formation from epoxide and fatty acid. *Adapted from [112].*

A range of short-chain fatty acids, including propanoic, 2-propanoic, octanoic, and 2-ethylhexanoic acids, have been used to form hydroxylated di-esters (estolides) from propyl and octyl epoxystearate esters [114]. The best cold temperature properties (pour point of –39°C) and oxidative stability was noticed for the propyl ester of a hydroxy, 2-ethylhexyl estolide. It has been reported that epoxidation of oleic acid is used to produce dihydroxystearic acid estolides via intermolecular esterification between the hydroxyl and carboxyl groups [115]. In that work, it was reported that the synthesis of oligomers with average estolide number (the average number of fatty acid units added to a base fatty acid) of 5 was achieved within 8 h of reaction at high temperature (180°C). The use of these types of estolides in cosmetics and personal care products is described [116].

7.4 Biobased Epoxy Resins

Epoxy groups react readily with many functional groups, including amines, anhydrides, phenols, mercaptans, imidazoles, isocyanates, acids, and others, as discussed above [2,3,117,118]. The mechanisms for the polymerization of epoxy monomers to form crosslinked polymers via step polymerization, chain homo- or copolymerization, or a combination of these mechanisms were reviewed earlier [2,119]. Linear or crosslinked epoxy polymers are obtained by the reaction of epoxy monomers with curing agents (hardeners) and/or initiators. In order to obtain a linear polymer, the epoxy resin precursor and (co)curing agent should have two coreacting sites, while the formation of the branched or cross-linked polymers requires the reactive functionality of one of the (co)reacting components to be more than two. Note that introducing monofunctional components is not desirable as their presence in the reaction medium will interrupt the growth of the polymer chain. The molar weight of linear polymers grows gradually with maximum of polydispersity of two, while the average molar mass of a crosslinked structure tends to be infinite at gelation. Thus, the amount and ratio of the reactive functional groups of (co)curing components are the key parameters to control the final polymer structure.

Although the formation of the epoxides from oil derivatives, and their curing with a variety of curing agents, have been reported in the literature, the use of epoxidized plant oils has received much attention due to the high functionally of the epoxidized triacylglycerols (TAG) compared to their epoxidized derivatives such as epoxidized fatty acid alkyl esters. For example, epoxidized canola oil has between two and seven epoxy groups per TAG molecule, while negligible amount of canola TAGs (~1 %) is expected to have zero to one oxirane group per molecule [107].

Epoxidized plant oils can be cured in similar ways as petroleum-based epoxy counterparts. Usually, the concentration of epoxy groups in the epoxy monomer used is approximately equal to the concentration of reactive groups in the hardener/initiators because, under these conditions, unwanted side reactions are minimized. A variety of curing agents or combinations of curing agents have been used to prepare biobased epoxy resins.

In Section 7.3, some possible epoxy ring-opening reactions in epoxidized plant oils to make polymer precursors have been described. In contrast, the aim of this section is to give examples of the polymers manufactured directly from epoxidized plant oils. Some of the thermo-mechanical and physical properties of these epoxy resins are also addressed.

7.4.1 Anhydride-Cured Epoxidized Oils

Thermoset epoxy resins from epoxidized canola oil (ECO) were formulated with phthalic anhydride (PA) as the curing agent for different ratios of ECO to PA (1:1, 1:1.5, and 1:2 mol/mol) at curing temperatures (T_{cure}) of 155, 170, 185, and 200°C [106]. The gelation process and the viscoelastic properties of the system during curing were studied. It was found that at a fixed ECO/PA ratio the thermo-mechanical properties of the resins were not strongly dependent on the curing temperature of the resin, although elevated temperatures significantly accelerated the curing process. However, an increase in the curing agent (PA) amount significantly altered both the reaction rate and the thermo-mechanical properties of the final resin. Depending on the curing conditions, thermosets with a wide range of properties were produced. At low T_{cure} and low PA content, clear and transparent rubberlike flexible thermosets with the T_g in the range of –3.3 to –4.4°C were produced. In contrast, at high T_{cure} and high PA contents, almost rigid, semiflexible plastics with T_g in the range of 37.8–40.4°C (at a) were formed. It was reported that the selective combination of the curing temperature and the molar ratios of the curing agent could be used to design the thermoset resins with selected properties. The authors of this work reported [106] the use of a variety of epoxidized plant oils, including epoxidized canola (ECO), camelina (ECamO), linseed (ELO), and soybean (ESO) in making biobased thermoset resins using anhydrides, acid anhydrides, biobased diacids, and food acids. The influence of the types of cocuring agents and epoxy functionality of epoxides oils to the dynamic-mechanical, thermal properties of the thermoset resins have been evaluated. The applicability of these thermoset resin precursors as aldehyde-free alternatives for aldehyde-containing internal bonding adhesives (melamine, urea, or phenol formaldehyde) to manufacture lignocellulosic fiberboard or particleboard has been demonstrated.

A variety of flexible rubbery and rigid crosslinked polymers were prepared by curing ESO with anhydrides such as norbornene dicarboxylic acid anhydride, hexahydrophthalic anhydride, succinic anhydride, maleic anhydride, and phthalic anhydride in the presence of cure catalysts such as tertiary amines, imidazoles, or aluminum acetylacetonate [120]. Highly flexible and rubber-like crosslinked polymers with the T_g below room temperatures (between –5 and 10°C) were obtained with the use of norbornene dicarboxylic acid anhydride, hexahydrophthalic anhydride, and succinic anhydride. The use of maleic anhydride and phthalic anhydride as curing agents of ESO resulted in rigid and stiffer polymers with high flexural moduli in the range of 500–1000 MPa and T_g varying between 43°C and 75°C. The highest stiffness and T_g were observed for ESO cured with phthalic anhydride at stoichiometric ratios of epoxy and anhydride groups and 2 wt% content of aluminum acetylacetonate or benzyldimethylamine accelerators.

7.4.2 Resins of Acrylated-Epoxidized Plant Oils

The main aim from manufacturing the acrylated epoxidized plant oil is to make radiation-curable precursors of polymers.

The majority of the commercially available radiation-curable monomers and oligomers are derived from petrochemical-based materials [121] and used for applications such as in the coatings industry for the protection of wood, plastic, metal, and paper surfaces; in manufacturing printing plates, digital video disk printing, fast-drying printing ink; pressure-sensitive adhesive (PSA) manufacturing and electronic industries [122]. New environmentally friendly UV-curable acrylated-epoxidized polymer precursors from biobased sources are being actively developed and have been described [96,123,124]. Plant oil-based networks from the photooxidation, styrenization, thiol-ene coupling (TEC), acrylate coupling, and the epoxy ring-opening reactions are illustrated in the literature [125] along with the structures of some photocurable glycerol-based monomers.

Acrylated polyester prepolymers (PEPP) from RBD (refined, bleached, and distillated) and crude palm oils containing reactive diluents and photoinitiator were prepared for UV-curable wood coating applications [96]. The formulations of PEPP with reactive diluents of trimethylol propane triacrylate (TMPTA) and 1,6-hexanediol diacrylate (HDDA) were found to be most suitable for wood coating application with acceptable adhesion, scratch, solvent, and chemical-resistant properties.

Acrylated epoxidized soybean oils (AESO) have been used as a renewable reactive diluent (up to 40%) for partial replacement of commercial epoxy resins to decrease the overall cost of the thermally cured epoxy coatings [123,124]. The authors [124] have suggested that the substitution of a 10–40% of the aromatic epoxy by cycloaliphatic epoxy resin (particularly with AESO) could reduce the cost of coatings to a \$0.30–\$1.30 per pound without substantial loss in mechanical performance.

The free radical polymerization of the AESO was promoted with commercially available photoinitiators (Darocur and Irgacure series) in order to prepare photocrosslinked materials [122,126]. The kinetics of photopolymerization upon UV curing with up to 4% photoinitiators are studied in infrared spectroscopy. High gel content and conversion in the photopolymerized AESO (within 10 s of irradiation) is observed with 2% of photoinitiators [126]. The use of these UV-cured acrylated epoxidized systems in fast-drying protective coatings and the rapid manufacture of composite materials are suggested, although the mechanical performance of UV-cured materials was not addressed in these studies.

Acrylated epoxidized canola oil (AECO) and maleinized acrylated epoxidized canola oil (MAECO)-based resins were synthesized with various commercially available initiators such as Luperox LP and Luperox 26 (from Arkema), Trigonox C (from AkzoNobel) [127]. The effect of the type and amount of initiator, and the cure temperature on the cure and mechanical and rheological properties of resin were optimized. The T_g and the storage moduli of the resin cured with Luperox LP were higher (70°C and 800 MPa for MAECO and 50°C and 400 MPa for AECO, respectively) compared to the resins cured with other initiators. A similar trend was observed in the mechanical performance of the biocomposites made with hemp and flax mats, while the resin impregnation rate was better for AECO-based resin.

Maleinized acrylated epoxidized soybean oils (MAESO) with varied numbers of maleic acid groups per TAG (from 1 mol to 2.5 mol) were prepared from AESO at different molar ratios of maleic anhydride [128]. The resulting monomers were then copolymerized with 33 wt% styrene to form rigid polymers. Dynamic mechanical analysis (DMA) showed the high moduli of these polymers at room temperature (1.9–2.2 GPa), which also had a T_g in the range of 100–115°C. These properties were increased by increasing the molar ratio of MA in AESO, and were found to be comparable to commercially available polyesters.

Several companies, such as Rust-Oleum (www.rustoleum.com, Varathane series clear coatings and Ultimate Poly series interior wood coatings), ECO safety products, LLC (www.ecosafetyproducts.com, Acri-Soy series of nontoxic penetrating clear concreate and wood sealer), Sherwin-Williams (www.sherwin-williams.com, ProMar and ProClassic series of low VOC soy/acrylic/polyester paints), are deploying soybean oil acrylated epoxy products in their low VOC, environmentally friendly biobased product lines. Allnex (www.allnex.com) is proactively adding AESO to their product lines as a modifier to improve the flow and leveling of ultraviolet (UV) light or electron beam (EB) curable inks and coatings.

7.4.3 Direct Polymerization of Epoxidized Plant Oils

Epoxidized soybean oil (ESO) and epoxidized castor oil (ECasO) were synthesized and polymerized via thermally induced ring-opening reaction initiated by a cationic latent thermal catalyst, *N*-benzylpyrazinium hexafluoroantimonate (BPH, 1%) [129]. The reaction is carried out at 1% of BPH load and at a temperatures of 110–150°C for 4 h. It was expected that the thermal decomposition of BPH at high temperature should yield the protic acid ($HSbF_6$) and catalyze the cationic polymerization of the epoxides, according to the Scheme 7.18. BPH showed an excellent thermally latent initiator role for epoxy curing that functions in the absence of coinitiators. Characterization of the thermal properties of the resulting polymers was carried out by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermal mechanical analysis (TMA). The cured ECasO/BPH resin showed a higher T_g (43°C), while a low crosslinking density (0.57×10^{-3} mol/cm^3) and storage modulus (7.9 MPa, at 30°C) was noticed. This behavior was attributed to the greater number of intermolecular interactions in ECasO/BPH system, such as hydrogen bonding. The ESO/BPH resin had low T_g (25°C), but the crosslinking density (1.12×10^{-3} mol/cm^3) and storage modulus (14.7 MPa, at 30°C) were twice higher than those resins made from ECasO. This was related as a result of high epoxy numbers in ESO.

Polymerization of epoxidized soybean oil (ESO) has been carried out with maleinized soybean oil (MSO), and as well as in the presence of maleic anhydride grafted polypropylene (MA-g-PP) with 1 and 2.9% MA group (MW = 110,000 and 3900 g/mol, respectively) [130]. In all experiments the epoxy:maleate groups ratio were kept at 1:1 to provide the best reaction conditions. The resulting polymer yield was about 94%. Thermogravimetric analysis of the resulting polymers showed that that the thermal properties of the polymers were not dependent on MA-g-PA content or molecular weight, while a dramatic increase in storage modulus of polymer with the increase of high MW MA-g-PA content was noticed. The authors of this study concluded that higher MW and therefore higher entanglement is more important in accomplishing the high mechanical properties than the crosslinking density, which was high in polymers with low MW PP-g-MA. The use of MA-g-PP films copolymerized with ESO is described to enhance adhesion of low density polyethylene to polyesters and metal foils. These authors also reported the polymerization of ESO with maleinized polybutadiene having different maleate content [131] and with different pyridine derivatives such as 4-methylpyridine (4MP), 4-vinylpyridine (4VP), and poly(4-vinylpyridine) (P4VP) [132]. The dynamic mechanical and thermal properties of the resulting polymers were evaluated, and a possible application for the new pyridine-based thermoset resin was described as its use as a gel molding resin due to its decent set of mechanical and thermal properties.

The *in-situ* reactive blending of ESO with phthalic anhydride in polypropylene melts (at 200°C) in the presence of aluminum acetylacetonate cure accelerator was performed using an anhydride/epoxy molar ratio of 0.75 to prevent sublimation of unreacted phthalic anhydride [120]. Interfacial adhesion of the ESO resin to the polypropylene was enhanced by adding PP-g-MA (with 5% MA content). Incorporation of 60 vol% of biobased polymers into polypropylene to afford flexible thermoplastic multiphase polyolefins has been reported [120]. A dramatic decrease of the Young modulus (from 1150 MPa to 150 MPa) and elongation at break (from 800% to 8%) were noticed in the resulting polymer blend, which could match the performance of flexible PVC-type materials.

Direct epoxy ring-opening polymerization of ESO was initiated with a different amount of boron trifluoride diethyl etherate ($BF_3{\cdot}OEt2$) catalyst in methylene chloride at different temperatures (between 0°C and 50°C) to develop biodegradable polymers [133]. A thermally stable and white colored polymer was obtained in high yield (>99%). These biobased polymers of ESO were found to be highly crosslinked (gel fraction about 73–99%) with T_g ranging from –16 to –48°C. It was suggested that these products could be converted into hydrogels by saponification, which makes them suitable for use in personal care and health-care applications.

Various in-house made and commercially available epoxidized plant oils have been used in photoinitiated cationic polymerization to make thin films using diaryliodonium and triarylsulfonium salt photoinitiators bearing long-chain alkoxy substituents [134]. The photopolymerization rates were evaluated and found to be dependent epoxy content of the monomers. Characterization of the resulting polymers films by thermomechanical techniques revealed that they possess good adhesion and mechanical properties. Biodegradation studies (under 1 inch of soil for 6 months) of the films showed that polymer had eroded and lost their integrity due to bacterial and environmental attack. They explained these phenomena as a result of degradation of the glycerol triester units within the polymerized films.

7.5 Conclusions

Plant oils have been used as feedstocks for paints, soaps, cosmetics, lubricants, and coatings for a long time. We have seen throughout the discussion in this chapter that there are enormous possibilities for the use of epoxidized plant oils and oil derivatives in manufacturing intermediate chemicals, monomers, and polymers.

However, the direct polymerization of biobased epoxides has received less attention in making polymeric end-products due to their relatively poor mechanical performance compared to conventional petrochemical-based counterparts. This poor mechanical behavior of biobased epoxides has been associated with the low reactivity of epoxy groups together with a tendency for intramolecular bonding, leading to a low degree of cross-linking. However, it should be noted that the plant oil-based polymers are potentially biodegradable via hydrolytic cleavage of glycerol ester bonds present in the triglyceride oils [27].

Nevertheless, currently, plant oil-based epoxides are being used to replace a portion of petroleum based epoxides in manufacturing polymers and composites, thus preserving acceptable mechanical performance while increasing the renewable content of the final product. Although there are many problems that exist and manufacturing cost-effective drop-in replacements for petroleum-based epoxides remains challenging, progress is being made in this area and their further adoption is likely.

By designing and synthesizing new (co) curing agents in combination with the use of novel polymerization methods, it is likely that better as well as unique epoxidized plant oil-based polymers will be manufactured in the future to expand the application and use of this class of materials.

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Further Reading

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8 Enzyme-Assisted Synthesis of Plant Oil-Based Polymers

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8.1 Introduction

Plant oil is an attractive renewable resource for polymer synthesis based on its availability and relatively low price. From the perspective of green manufacturing, we should consider not only feedstocks but also the synthesis process. Traditional chemical catalysis for polymer synthesis usually requires high temperature and toxic catalysts. The harsh reaction conditions could result in lack of selectivity. Chemical polymerization becomes more challenging when synthesizing complex or well-defined polymers. Enzymes can be an alternative to the process. Enzymes work under milder reaction conditions and are generally highly chemo-, regio-, enantio-, stero-, and choroselective [1,2]. Therefore, enzymatic processes are cleaner (no metal used and less byproducts), consuming less energy, having better structural control, and easier for operation

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(protection–deprotection not required). Currently, lipases are the predominantly used enzyme in polymer syntheses [3]. Lipases do not require any cofactor and thus can be applied as cell-free biocatalysts. In this chapter, several examples are discussed on enzyme-catalyzed polymerization. Furthermore, biotransformations of plant oil are discussed in the second part of the chapter to demonstrate the diverse application of enzymes. The functionality of important enzymes discussed in this chapter is summarized in Table 8.1.

Table 8.1 Representative Reactions Catalyzed by Enzymes for Plant Oil Polymerization and Transformation

Enzymes	Reactions	Reactants	Products
Lipase CA	Polycondensation	DVS, glycerol, and unsaturated fatty acids (C18:2, C18:3)	As shown in Figure 8.1
Lipase CA	Polycondensation	DVS, glycerol, and epoxidized fatty acids (C18:1, C18:2, C18:3)	As shown in Figure 8.2
N435	Epoxidation	Oleic acid	As shown in Figure 8.3
N435	Polycondensation	Diols (C3, C4), unsaturated/ epoxidized α,ω-DMDA (C18, C20, C26)	As shown in Figure 8.4
N435	Polycondensation	Diols (C3, C6, C16), unsaturated/epoxidized α,ω-diacid (C18, C22)	As shown in Figure 8.5
Lipase RM	Polycondensation	Pentaerythritol, ricinoleaic acid	As shown in Figure 8.6
Lipase PC	Polycondensation	Ricinoleaic acid or methyl ricinoleaic acid	As shown in Figure 8.7
N435	ROP	Ambrettolide epoxide	As shown in Figure 8.8
N435	Polycondensation	Isopropyl aleuriteate	As shown in Figure 8.8
N435	Polycondensation	*cis*-9,10-epoxy-18-hydroxyoctadecanoic acid	As shown in Figure 8.9
Lipase CA	Esterification	Sucrose, palmitic acid	As shown in Figure 8.10
Lipase RD	Transesterification	Tripalmitin, ethanol, oleic acid	As shown in Figure 8.11
P450 (*CYP52*)	ω-Hydroxylation	Palmitic acid	16-hydroxy palmitic acid
P450 (*CYP102*)	ω-2 Hydroxylation	Arachidonic acid	As shown in Figure 8.14b
FAO	Oxidation	ω-Hydroxy fatty acid	Fatty acid semialdehyde
FALDH	Oxidation	Fatty acid semialdehyde	α,ω-Diacid
Hydratase	Hydroxylation	Linoleic acid	As shown in Figure 8.14c

Abbreviations: CA, Candida Antarctica. N435, Novozym 435. P450, Cytochromes P450 monooxygenase. DVS, divinyl sebacate. DMDA, α,ω-dicarboxylic acid methyl esters. RM, Rhizomucor miehei. *PC,* Pseudomonas cepacia. *ROP, ring opening polymerization. RD, Rhizopus delemar. FAO, fatty alcohol oxidase. FALDH, fatty aldehyde dehydrogenase.*

8.2 Enzyme-Assisted Synthesis of Plant Oil-Based Polyesters

8.2.1 Lipase-Catalyzed Synthesis of Functional Polyesters

8.2.1.1 Biodegradable and Cross-Linkable Polyesters

Cross-linkable polyesters with an unsaturated fatty acid moiety in the side chain have been produced from renewable plant oil by lipase-catalyzed synthesis. These polyesters were synthesized by the polymerization of divinyl sebacate and glycerol in the presence of higher unsaturated acids, which are plant-oil derivatives (Figure 8.1) [4,5]. To identify enzymes that are active for the polymerization, lipases from *Candida antarctica*, *Mucor miehei*, and *Pseudomonas cepacia* were used as catalysts for the polymerization of equimolar ratio of divinyl sebacate **1** and glycerol **2** in the presence of linoleic acid (**3a**) (Figure 8.1) in bulk at 60°C for 24 h. All the three candidates could catalyze the regioselective polymerization of **1** and **2** [6]. Among these enzymes, *Candida antarctica* lipase had the highest catalytic activity for the production of **4** in a 58% yield; however, the other two lipases showed no or very low activity toward the synthesis of this oily polymer. The estimated molecular weight of **4** (Figure 8.1) determined by size-exclusion chromatography (SEC) was 4700. Therefore, *Candida antarctica* lipase was used to optimize the process parameters on both linoleic acid (**3a**) and linolenic acid (**3b**) (Figure 8.1). Compared with the optimal concentration, when an excessive amount of enzyme was used, the yield decreased because of the more frequent hydrolysis of the vinyl ester. With a smaller amount of enzyme, higher molecular weight was observed but the unsaturated acid content and the yield were lower. The yield and molecular weight were improved if the polymerization was carried out in a small amount of toluene; nonetheless, the acid content was lower compared with that of the bulk polymerization. The effect of temperature on the polymerization reaction has been studied. Both the yield and molecular weight increased when temperature increased up to 75°C, while the acid content of the polymer remained almost the same. Reducing pressure usually improves the molecular weight in the enzymatic synthesis of polyesters since the removal of the leaving group (vinyl alcohol) drives the equilibrium to the production of polymer [7]. Compared with the polymer produced under atmospheric pressure, the yield and molecular weight increased when the polymerization was carried out under reduced pressure at 2700 Pa. The polyester produced under reduced pressure using linoleic acid or linolenic acid was subjected to hardening by cobalt naphthenate or thermal treatment to give transparent and gloss films. The pencil-scratch hardness [8] of the thermally treated films from linoleic acid and linolenic acid after 24 h was 5 and 2 B,

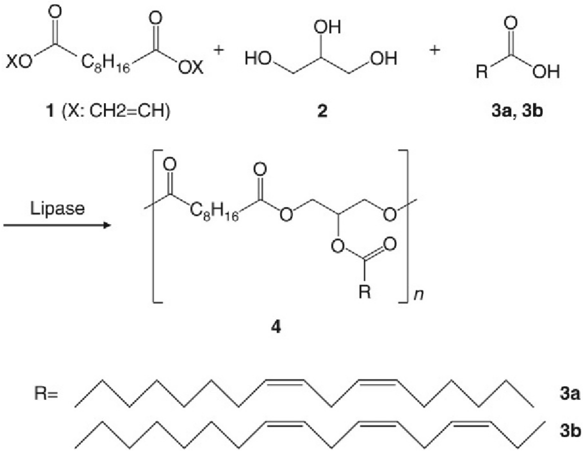

Figure 8.1 Lipase-catalyzed synthesis of cross-linkable polyesters.

respectively, which were superior to that produced by cobalt naphthenate oxidation. The biodegradability of the cross-linked film was evaluated by biochemical oxygen demand (BOD) in an activated sludge. Results showed that the film could be degraded gradually to 45% after 42 days, which demonstrated the good biodegradability of this cross-linked film.

8.2.1.2 Epoxide-Containing Polyesters

Plant oil-based unsaturated fatty acids such as oleic, linoleic, and linolenic acids were used as starting substrate for the enzymatic synthesis of epoxide-containing polyesters. Theses polyesters containing an epoxide moiety in the side chain were synthesized using lipase catalysis via two routes (Figure 8.2) [9]. In both routes, *Candida antarctica* lipase was used to catalyze the polymerization and the epoxidation of unsaturated groups in fatty acids. In route A, polyester **4** possessing an unsaturated group in the side chain was first synthesized by the lipase-catalyzed polymerization of divinyl sebacate **1** and glycerol **2** in the presence of unsaturated fatty acids **3** (Figure 8.2). The reaction was catalyzed by *Candida antarctica* lipase at 60°C and was carried out under reduced pressure (2700 Pa) to shift the equilibrium to polymer production. The unsaturated fatty

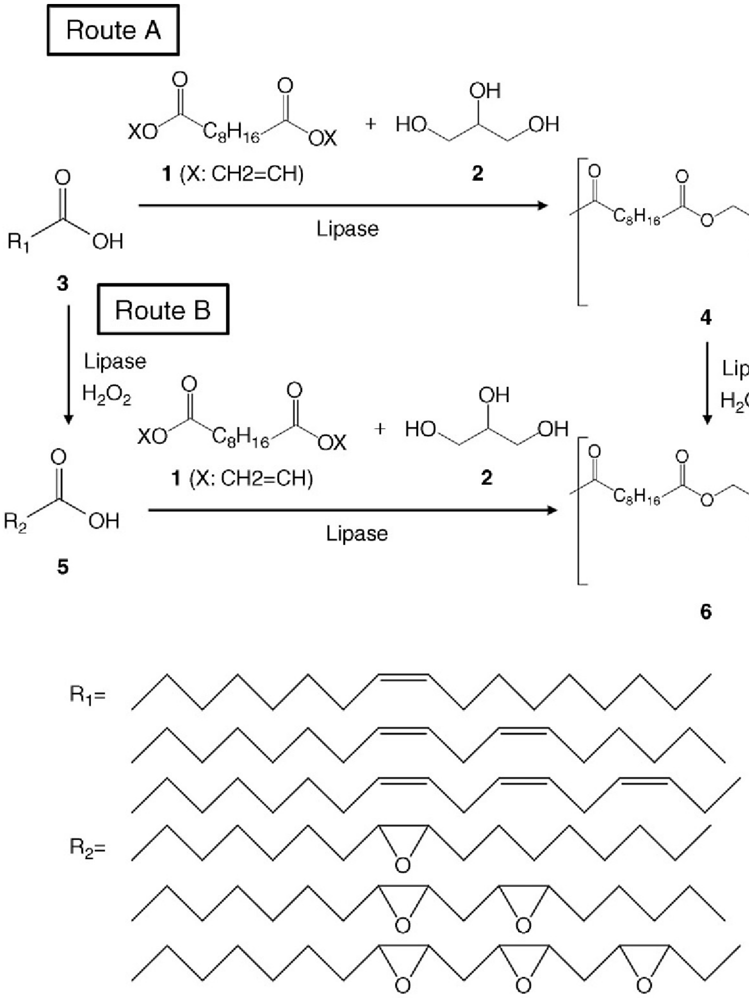

Figure 8.2 Two routes for lipase-catalyzed synthesis of epoxide-containing polyesters.

acid groups in polyester **4** were then enzymatically epoxidized using hydrogen peroxide as oxidizing agent at room temperature to generate the target epoxide-containing polyesters **6** (Figure 8.2). To synthesize the epoxide-containing polyesters **6** via the other route B, the epoxidation of unsaturated fatty acids **3** was first catalyzed by lipase using hydrogen peroxide as the oxidizing agent, followed by the lipase-catalyzed polymerization of divinyl sebacate **1** and glycerol **2** in the presence of the epoxidized fatty acids **5** under reduced pressure (Figure 8.2). The epoxidized ratio of **5** and **6** was similar, indicating that the epoxy groups remained intact during polymerization. NMR and IR spectra were used to confirm the polymer structure. High epoxidized ratios (>75%) were achieved by both routes. The epoxide-containing polyesters produced via route B were subjected to curing by thermal treatment at 150°C for 2 h to give transparent and glossy films. The pencil-scratch hardness of the cured films increased with the increasing epoxidation content. Compared with the films produced from the polyesters possessing unsaturated acid moieties in the side chain mentioned in Section 8.2.1.1, the hardness of the epoxide-containing films was improved. The hardest cured film reached pencil-scratch hardness 3H was achieved using linolenic acid as the starting substrate. The cured film prepared from linolenic acid showed good biodegradability which was tested by BOD in an activated sludge and the biodegradation reached more than 50% after 50 day.

8.2.1.3 Oleic Acid-Based Polyesters

Besides using plant oil-derived fatty acids to introduce functional side-chain moieties, fatty acids can also be polymerized to produce polymers with lipids in the backbone structure. Linear and cross-linked poly(oleic acid) was synthesized via a chemo-enzymatic route (Figure 8.3). The fatty acid derived monomer was produced via epoxidation of oleic acid. Instead of achieving the epoxidation chemically by reacting unsaturated fatty acids with peroxy acids, enzyme-catalyzed epoxidation [10] provides a better alternative with fewer side reactions and can be performed under milder conditions (enzymatic epoxidation will be further discussed in Section 8.3.3). Hydrogen peroxide was used as the oxidizing reagent to epoxidize unsaturated fatty acids catalyzed by lipase. *Candida antarctica* lipase B has been broadly used as catalysts in polymerization and epoxidation reactions

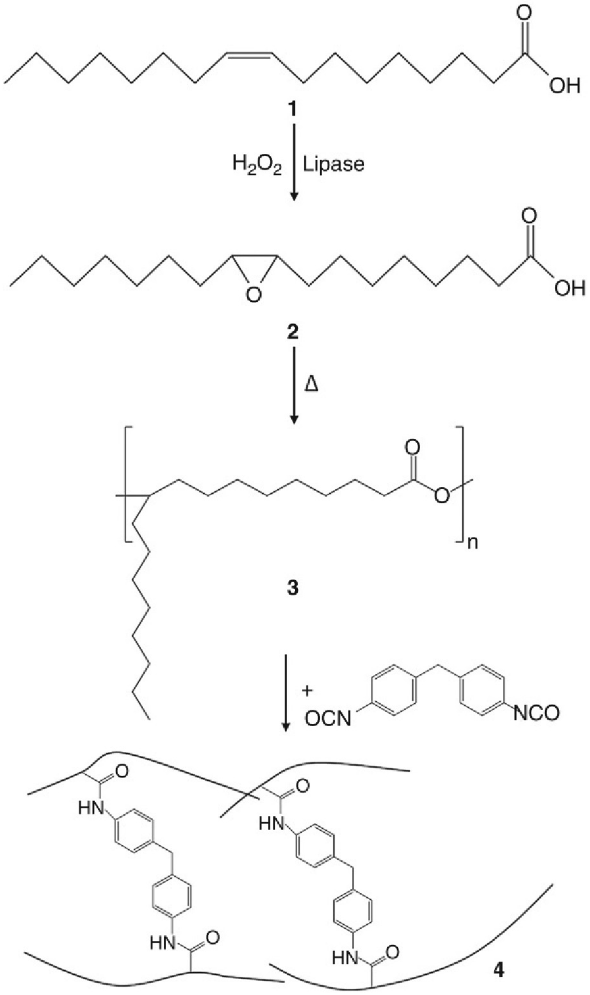

Figure 8.3 Chemo-enzymatic synthesis of cross-linkable oleic acid–base polyesters.

because of its high thermal stability, activity, as well as its high regio-, chemo-, and enantio-selectivity [1]. Therefore, Novozym 435 consisting of immobilized *Candida antarctica* lipase B on a macroporous poly(methyl methacrylate-*co*-butyl methacrylate) resin was used as the catalyst for epoxidation of oleic acid **1** into oleic acid epoxide **2** (Figure 8.3). Since the produced epoxide was not thermally stable, the reaction was performed at 40°C and oleic acid was completely converted within 5 h based on HPLC tests. Oleic acid epoxides produced were recovered by solvent evaporation and were polymerized by heating up to different temperatures at 90, 120, or 150°C for 6 h. IR spectra of the produced polymers suggested that better conversion yield and faster reaction rate could be achieved with higher reaction temperature. However, polymers produced at 150°C solidified within several minutes and could not be dissolved in common organic solvents like chloroform. On the other hand, polymers produced at 120°C had lower molecular weight but stayed as a viscous liquid, which made them feasible for downstream processing. NMR spectra showed the existence of ether bond from ring opening of the epoxy moiety, but polyesters were dominant which accounted for 90% in the polymer structure. Hydroxyl groups in the produced polyesters **3** provide the opportunity of synthesizing more cross-linked polymers **4** (Figure 8.3). Transparent films were produced by mixing poly(oleic acid) with diisocyanate compound such as 4,4′-methylenebis(phenyl isocyanate). The hardness of the cross-linked films could be adjusted by the amount of diisocyanate added. Thermal gravimetric analysis (TGA) was applied and three decomposition peak temperatures (260–350, 350–395, and 395–475°C) were identified which were corresponding to the decomposition of urethane bonds, the ester bonds, and the gasification of remaining, respectively.

8.2.2 Lipase-Catalyzed Polycondensation of Unsaturated or Epoxidized α,ω-Dicarboxylic Acids and Diols

Symmetrically unsaturated and expoxidized α,ω-dicarboxylic acid methyl esters (C_{18}, C_{20}, and C_{26}) were copolymerized with 1,3-propanediol or 1,4-butanediol catalyzed by Novozym 435 (Figure 8.4) [11]. Unsaturated fatty acid methyl esters serving as the starting materials were obtained by tranesterification of vegetable oil with methanol; for example, methyl oleate and methyl erucate were derived from high oleic sunflower oil and high erucic rapeseed oil, respectively. First, Grubbs catalysts [12] were applied to metathetically cleave these methyl esters to yield 1-decene and methyl 9-decenoate **1a** or 1-decne and methyl 13-tetradecenoate **1c** (Figure 8.4a). It is worth noting that methyl 10-undecenoate **1b** is available as a product from castor oil. Subsequently, Grubbs catalysts were used to perform the metathetical dimerization of **1a**, **1b**, and **1c,** resulting in long-chain, symmetrically unsaturated α,ω -dicarboxylic acid dimethyl esters (**2a–2c**) (Figure 8.4b). Catalyzed by Novozym 435, these diesters (**2a–2c**) were converted to epoxidized diesters (**3a–3c**) by hydrogen peroxide in methyl acetate with yields of more than 97% (Figure 8.4b). The diesters (**2a–2c**) and their epoxidized derivatives (**3a–3c**) were then polymerized with 1,3-propanediol or 1,4-butanediol in diphenyl ether using Novozym 435 as catalysts (Figure 8.4c). Temperature effect of the lipase-catalyzed

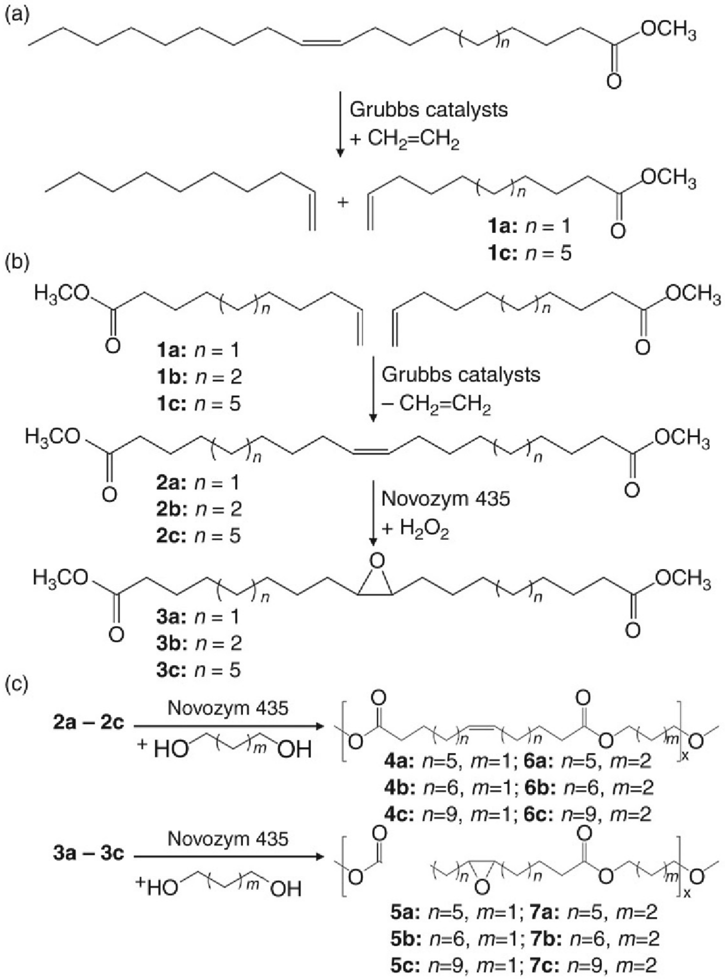

Figure 8.4 Novozym 435-catalyzed copolymerization of unsaturated and epoxidized α,ω-dicarboxylic acids and diols.

polycondensation was examined and the results showed higher yield (62–79%) and higher molecular weights (1900–7860 g/mol) could be achieved with higher reaction temperature (30–70°C). The molecular weights increased with increasing reaction time up to 4 h. Determined by SEC, molecular weights of the unsaturated polyesters from 1,3-propanediol (**4a**–**4c**) ranged between 1950 g/mol and 2250 g/mol and marginally higher molar masses with the corresponding epoxidized polyesters (**5a**–**5c**) were 2450–3300 g/mol (Figure 8.4c). The polyesters had melting temperatures between 47 and 75°C determined by differential scanning calorimetry (DSC). The polyesters prepared from 1,4-butanediol had higher molecular weights than those of the corresponding polymers from 1,3-propanediol. Molecular weights were within the range of 7900–9900 and 9000–11,600 g/mol for the unsaturated polyesters (**6a**–**6c**) and the expoxidized homologues (**7a**–**7c**), respectively (Figure 8.4c). These polyesters had melting temperatures between 55°C and 74°C. Compared with the unsaturated polyesters, epoxidized polyesters homologues produced via lipase-catalyzed polycondensation did not give higher melting temperature. All the double bonds or epoxy groups remained intact during the polymerizations. With these functional groups, the produced polyesters were capable of being further derivatized or cross-linked.

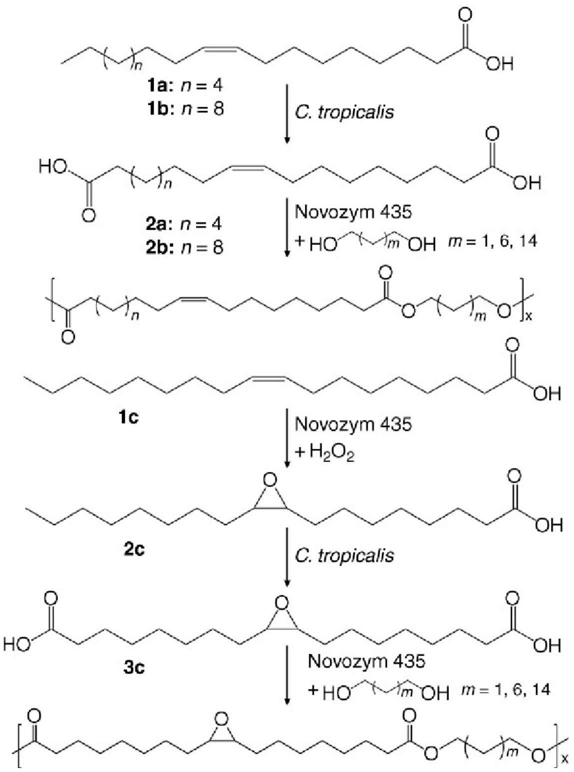

Figure 8.5 Whole-cell biocatalyst applied for α,ω-dicarboxylic acid generation followed copolymerization with diols catalyzed by immobilized lipase.

Alternatively, α,ω-dicarboxylic acid monomers could be prepared from fatty acids via whole-cell biocatalysis using *Candida tropicalis* ATCC20962 or related engineered strains. This biotransformation could be realized by endogenous enzymes when β-oxidation pathway was blocked. Cytochrome P450 monooxygenase (*CYP52*) first catalyzed ω-hydroxylation (more discussions about P450 monooxygenase can be found in Section 8.3.4). The ω-hydroxy fatty acid was further transformed to the corresponding fatty aldehyde catalyzed by fatty alcohol oxidase and to the target compound, α,ω-dicarboxylic acid, via fatty aldehyde dehydrogenase. For example, three α,ω-dicarboxylic fatty acids, 1,18-*cis*-9-octadecenedioic, 1,22-*cis*-9-docosenedioic, and 1,18-*cis*-9,10-epoxy-octadecanedioic acids (**2a**–**2b**, **3c**), were synthesized from renewable fatty acids, oleic, erucic, epoxy stearic acids (**1a**–**1c**), respectively (Figure 8.5) via whole-cell biocatalysis catalyzed by *C. tropicalis* ATCC20962 [13]. The biotransformations were conducted in 30 mL conversion media in shake flasks supplementing with 20 g/L fatty acids. The production dicarboxylic acids and the consumption of fed fatty acids were monitored by liquid chromatography (LC)–mass spectrometry (MS). The production titers of target dicarboxylic acids reached 17.3 (77.6 mol%), 14.2 (64.8 mol%), and 19.1 (86.2 mol%) g/L after 48 h for oleic acid and 72 hours for erucic and epoxy stearic acids, respectively. The low solubility of longer-chain fatty acids might cause their slower conversion rates. Biotransformation of oleic acid to 1,18-*cis*-9-octadecenedioic acid was further scaled up in a 3-L fermentor with better pH, glucose feeding, and dissolved oxygen controls, resulting in 31 g/L of the dicarboxylic acid after 60 h with higher productivities up to 0.5 g/L/h. These α,ω -dicarboxylic acids were then copolymerized with diols (1,3-propanediol, 1,8-octanediol, and 1,16-hexadecanediol) to produce functional polyesters using immobilized *Candida antarctica* lipase B (Novozym 435) as catalysts (Figure 8.5). For example, molecular weight of polyester produced by in-bulk polycondensations of 1,18-*cis*-9-octadecenedioic with 1,8-octanediol increased from 15,000 to 37,000, and then to 44,000 g/mol at 2, 24, and 48 h, respectively. Overall, polyesters with molecular weights from 25,000 g/mol to 57,000 g/mol were produced with different combinations of diols and α,ω-diacids. Although higher molecular-weight polyester was produced when the reaction was performed in diphenyl ether, in-bulk polymerization was preferred due to difficult separation of diphenyl ether and low efficiency of the overall process. Similar to the previous example, molecular weights of polyesters from the same diacids increased with increasing diol molecular weights. Unsaturated and epoxy moieties on these diacids remained intact during polymerization. These polyesters had lower melting points (23–40°C) than their corresponding saturated polyesters due to the disruption of crystallization by functional groups.

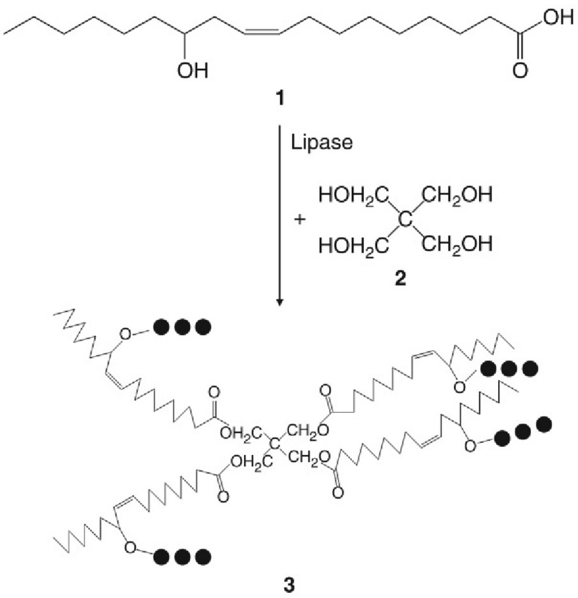

Figure 8.6 Branched star polyesters synthesis catalyzed by lipase.

8.2.3 Lipase-Catalyzed Polycondensation of Hydroxy Fatty Acids and Derivatives

8.2.3.1 Poly(Ricinoleaic Acid) and its Derivatives

Ricinoleaic acid (RA), a hydroxyl fatty acid formally named as 12-hydroxy-9-*cis*-octadecenoic acid, is a main component of the seed oil of castor (*Ricinus comminus*). RA is a bifunctional molecule containing a secondary hydroxyl group and a double bond. Poly(hydroxyl acids) such as poly(RA) and their derivatives are biodegradable and can be used as environmentally friendly lubricant materials because of their low melting point and high viscosity. Poly(RA) was prepared via lipase-catalyzed polycondensation under mild temperature to avoid problems of discoloration, odour, dehydration, and high energy costs associated with high-temperature chemical processes. Poly(RA) **1** acyl donors and polyols (trimethylolpropane (TMP), pentaerythritol **2** (PE), and dimer diol(DD)) acyl acceptors could then be used to synthesize branched star polyesters such as pentaerythrotol-poly(ricinoleic acid) polyester **3** in bulk by lipase-catalyzed polyconsensation [14] (Figure 8.6). Poly(RA) was first prepared using immobilized *Candida antarctica* lipase B as the catalyst. Lipase-catalyzed polymerization of RA proceeded slowly since RA has a high viscosity and only contains a secondary hydroxyl group for esterification. Poly(RA) with an average MW of 724 and 1040 was obtained from technical grade RA in bulk polymerization at 70°C for 7 and 10 days, respectively. The propagation step in the polymerization of RA was rate-limiting, following first-order kinectics in respect of monomer concentration. In the next step, the enzymatically synthesized Poly(RA) was mixed with polyols (TME, PE, DD) for the synthesis of polyol-poly(RA) polyesters catalyzed by immobilized lipases from *Candida antarctica* or *Rhizomucor miehei*. The synthesis was carried out at 70°C for 14 days and the reaction rates catalyzed by both lipases were similar. All three polyols were successfully used as acyl donors. The highest molecular weight product was synthesized from PE and poly(RA) with an average molecular weight of 4850 according to ^{1}H-NMR. Gel permeation chromatography indicated that the product mixture was composed of 82.7% of the polyol tetraester and 17.3% noncondensed linear poly(RA). 78% of the hydroxyl groups of PE were esterified and the average acyl groups per chain were 5.4. The produced polyesters had melting points below 7.5°C. Their high viscosity and viscosity index (155) enable their applications as environmentally friendly lubricant materials.

In another example, poly(RA) was prepared by polymerization of RA **1a** or methyl RA **1b** via the catalysis of lipases from various organisms [15] (Figure 8.7). First, five different lipases from *Candida antarctica*, *Porcine pancreas*, *Candida rugosa*, *Pseudomonas* sp., *Pseudomonas cepacia* were screened for their activities on the polymerization of RA. Among these enzymes, immobilized lipase from *Pseudomonas cepacia* showed the best activity, achieving the production poly(RA) with an average MW of 5600 at 60°C after 7 days. Thus, further optimization of the process was based on this enzyme. Temperature effect was studied on the range of 60–100°C and highest MW of poly(RA) was obtained at 80°C. For the polymerization of methyl RA catalyzed by 50% (w/w) immobilized *Pseudomonas cepacia* lipase, placing 4 Å molecular sieves MS4A in the vapor phase significantly improved the MW of produced poly(RA) from 2100 to 73,200 since the absorbed methanol by MS4A shifted the equilibrium toward polymer formation. This result is intriguing since polycondensation activities of lipases are generally low via esterification of secondary hydroxyl groups; however, this process can be optimized by shifting reaction equilibrium. Moreover, increasing the lipase concentration to 150% led to the highest molecular weight of 98,000 and the produced poly(RA) was a viscous liquid at room temperature with a low glass transition temperature of –74.8°C. BOD biodegradability of this poly(RA) by activated sludge reached over 60% after 28 days. It showed no crystallinity and was readily cured by dicumyl peroxide at 170°C for 30 min (Figure 8.7). The cross-linked poly(RA) was insoluble in chloroform with a hardness of 50 A based on measurement of a durometer A.

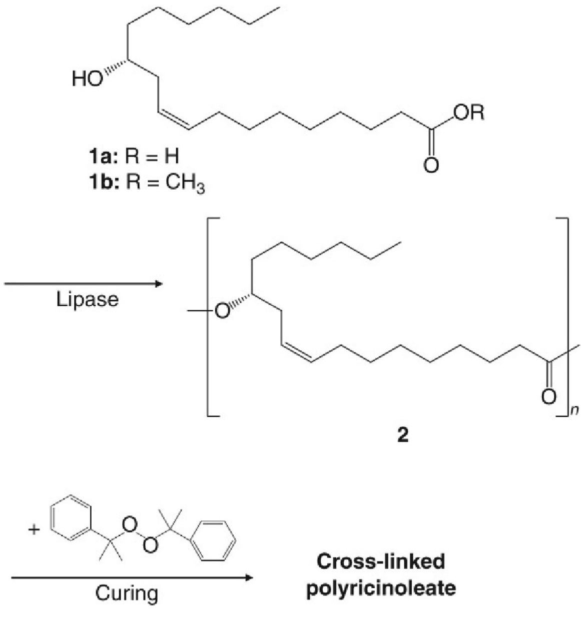

Figure 8.7 Polycondensation of ricinoleic acid and methyl recinoleate catalyzed by lipase.

8.2.3.2 Poly(Ambrettolide Epoxide) and Poly(Aleuritic Acid)

Ambrettolide, 17-oxacycloheptadec-6-en-1-one, used widely in perfume industry, is a compound found in the oil of musk mallow (*Abelmoschus moschatus*) seeds. Aleuritic acid ((9R,10S)-9,10,16-trihydroxyhexadecanoic acid) is a derivative of ambrettolide which contains three hydroxyl groups, two secondary and one primary (on ω-position). To prepare monomers, ambrettolide was epoxidized by *meta*-chloroperoxybenzoic acid to produce ambrettolide epoxide and isopropyl aleuriteate was synthesized by the esterification of aleuritic acid and isopropanol in the presence of sulfuric acid. These two transformations are both one-step with high conversion yields (>87%). These monomers were then used to synthesize poly(ambrettolide epoxide) and poly(aleuritic acid) by the catalysis of immobilized *Candida antarctica* lipase B (Novozym 435) [16] (Figure 8.8). Ring-opening polymerization of ambrettolide epoxide **1** was catalyzed by Novozym 435 (10 mg/mmol lactone) carried out in toluene at 90°C for 18 h; molecular weight of the resulting poly(ambrettolide epoxide) **2** was 9700 g/mol with a polydiversity index (PDI) of 1.9 determined by GPC analysis (Figure 8.8). According to the NMR spectra, the epoxide group was not affected during the polymerization. Polymerization of isopropyl aleuriteate **3** to poly(aleuritic acid) **4** was catalyzed by Novozym 435 in toluene/2,4-dimethyl-3-pentanol solvent mixture at 90°C and 55 kPa for 21 h (Figure 8.8). The released isopropanol from the reaction was removed because of reduced pressure to drive the equilibrium toward polymer. Upon precipitation in pentane, poly(aleuritic acid) was isolated in moderate yield (43%) with molecular weight of 5600 g/mol and PDI of 3.2. It is worth noting that this lipase-catalyed polymerization is highly selective for primary ω-hydroxyl group with no detectable esterification at the other two secondary hydroxyl moieties. However, when the polymerization of isopropyl aleuriteate was carried out chemically using Ti(IV)(*n*-BuO)$_4$ at high temperature (200°C), a yellow and hardly soluble product was obtained with ester bonds formed at both primary and secondary hydroxyl groups. Furthermore, copolymerization of isopropyl aleuriteate and ε-caprolactone (ε-CL) were applied to synthesize polyesters with tunable hydrophilicity and biocompatibility. Polymerizations were catalyzed by Novozym 435 in toluene at 90°C under different molar ratios of ε-CL resulting in poly(ε-CL-*co*-isopropyl aleuriteate) with molecular weights ranging in 10,400–27,200 g/mol with good yields (71–78%). Selective esterification on the primary hydroxyl groups was again observed and the composition of these copolymers agreed consistently with the feeding ratio. In a post-modification reaction of the copolymers, the secondary hydroxyl groups in the polymer backbone were easily reacted with hexyl isocyanate, suggesting the potential use of poly(ε-CL-*co*-isopropyl aleuriteate) as a next-generation biomaterial. Prepolymers based on ε-CL aleuritic acid may play an important role in thermoplastic elastomoers

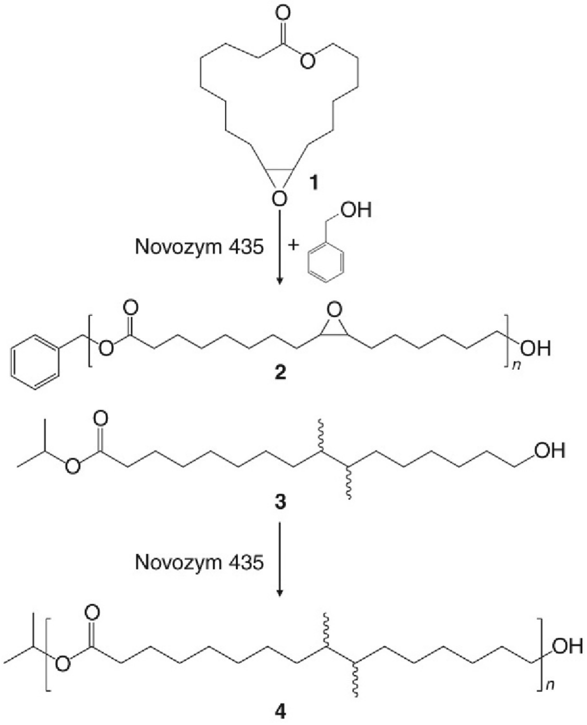

Figure 8.8 Lipase-catalyzed syntheses of poly (ambrettolide epoxide) and poly(aleuritic acid).

because not only their hydrophilicity and biodegradation are tunable, but also bioreactive molecules can be easily attached.

8.2.3.3 Polyesters from the Monomer *cis*-9,10-Epoxy-18-Hydroxyoctadecanoic Acid

Polymers with reactive functional groups such as epoxides can play an important role in the development of biomedical or commodity materials. A naturally occurring fatty acid, *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid, can serve as a "green" starting material for the synthesis of functionalized polymers. Polyesters found in higher plants are usually composed of complex monomers and differ between species, which makes them challenging for further applications. Fortunately, *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid is an exception, which is a main constituent of dry outer bark (100 g/kg) in *Betula verrucosa*. Alkali hydrolysis can be easily applied on the outer bark to produce this epoxy acid with a high yield. For polymerization of epoxy-containing monomers, lipase-catalyzed polycondensation was attractive due to its mild reaction condition. Therefore, Novozym 435-catalyzed polymerization of *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid **1** to its corresponding functional polyester **2** was investigated (Figure 8.9) [11]. Four solvents, acetonitrile, dioxane, toluene, and monomer melt (bulk), were tested. The highest molecular weight (20,000 g/mol) was obtained after 68 h using toluene; however, bulk polymerizations resulted in a close molecular weight (16,000 g/mol) in a much shorter time (5 h). The H-NMR spectra of the produced polyesters showed that the *cis*-epoxy group was intact during polymerization.

8.3 Enzyme-Assisted Plant Oil Transformations

8.3.1 Sugar Fatty Acid Esters

Sugar fatty acid esters such as polyoxyethylene sorbitan esters (Tween®) are extensively used as nonionic biosurfactants and emulsifiers. They have been used in food, cosmetic, and pharmaceutical industries since they are antimicrobial, nontoxic, and biodegradable. Moreover, the functional characteristics can be tuned by the constitutive sugar and fatty acid moieties. Although both carbohydrates and fatty acids are derived from renewable resource, almost all the current commercial sugar esters are produced via chemical syntheses. Due to the safety concerns with chemical synthesis,

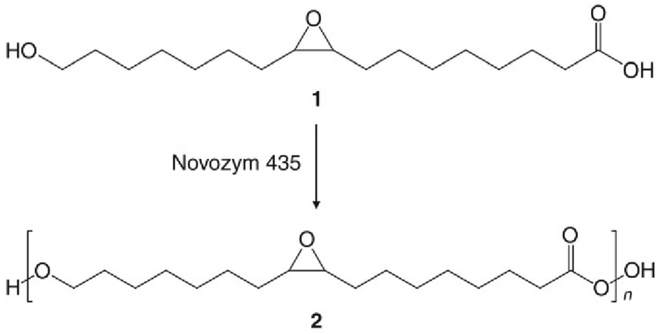

Figure 8.9 Lipase-catalyzed polymerization of *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid.

enzyme-catalyzed processes seem a better alternative for the production of food-grade sugar esters. Compared to the chemical processes, enzymatic processes have advantages such as low energy input, excellent regioselectivity, simple operational procedures, and simple product purification [17]. The lipase-catalyzed syntheses of sugar esters have been recently reviewed [17,18]. It is noteworthy that several monosaccharides such as D-glucose, D-galactose, and D-fructose can be converted regioselectively into 6-*O*-acyl esters using immobilized *Candida Antarctica* lipase B (Novozym 435) as the catalyst in aprotic solvents such as tetrafuran or dioxan. Several plant oil-derived fatty acids caprylic, capric, myristic, lauric, palmitic, stearic, and erucic acids have been successfully applied as acyl donors [19]. Chemical versus enzymatic catalysis for the synthesis sucrose fatty acids has been studied (Figure 8.10) [20]. Chemical process normally requires high temperature (>100°C) and reduced pressure in the presence of a basic or metallic catalyst. High-temperature reactions not only consume more energy but also result in different degrees and positions of esterification and various undesirable byproducts (route A in Figure 8.10). In the opposite, enzymatic synthesis provides a low-energy (usually <60°C), highly chemo-, regio-, and enantioselective, and environmentally friendly alternative. The product is typically a monoester and easy for downstream separation (route B, Figure 8.10).

8.3.2 Transesterification

Transesterification can be used to convert natural triglycerides found in plant oils into various fatty acid esters monomers with a

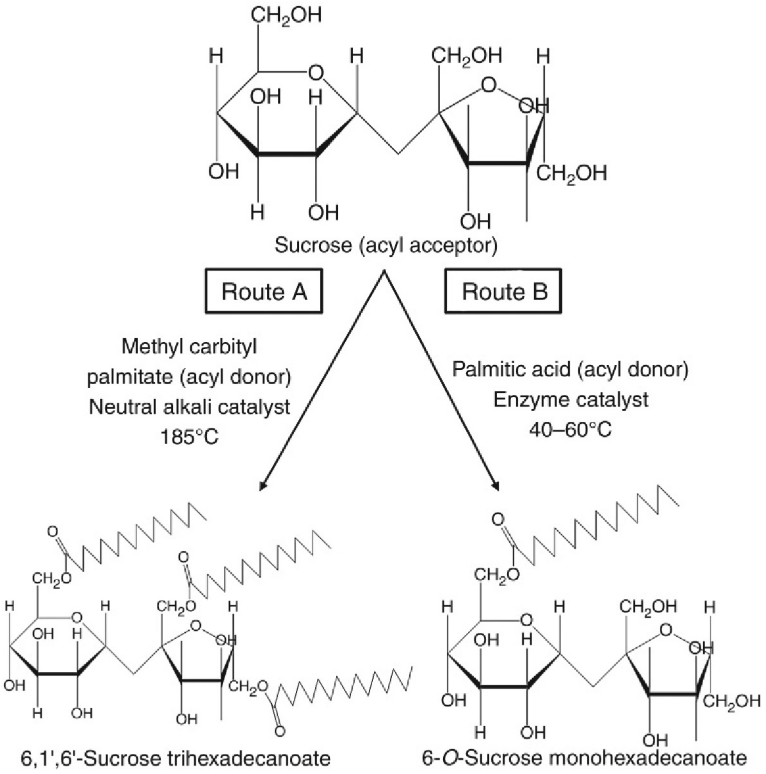

Figure 8.10 Comparison between chemical (a) and enzymatical (b) syntheses of sugar fatty acid esters.

wide range of functional characteristics. For example, as demonstrated in previous examples, many fatty acid methyl esters can be used as better monomers in polycondensation since methanol is a better leaving group than water. Transesterification reactions were catalyzed by alkaline in most commercial processes such as sodium hydroxide (NaOH) and potassium hydroxide (KOH). These chemicals are economically feasible and can achieve fast rate and high conversion yield. However, highly pure triglycerides are required since free fatty acids (FFA) in the feedstock are converted to soap and presence of water further increases soap formation. Multistep purification is necessary since the end products are a mixture of glycerol, tri-, di-, monoglycerides, alcohol, catalyst, and so on. For enzymatic transesterification, no soap formation due to FFA and FFA can be converted into according esters in one step. This suggests that low-cost feedstocks with high FFA and water content such as waste cooking oil or lard can be directly used for the enzymatic process. Reaction condition for biocatalyst transesterification is milder (reducing energy consumption) and downstream processing is not required. Overall, enzymatic transesterification is an attractive alternative to chemical transesterification in terms of the reduced energy cost, environmental impact, feedstock sustainability, and downstream processing [21]. The high enzyme cost is the main challenge for commercialization, which can be overcome by immobilization. Although the conversion yields of most enzymatic transesterifications (<90%) are lower than chemical processes (nearly 99%), some biocatalyst processes showed great yields and productivity. For example, it has been reported that rapeseed oil can be converted to its corresponding methyl esters by the catalysis of immobilized *Candida antartica* lipase with a conversion yield of 95% and productivity of 2.6 g methyl esters/g enzyme/h. Recently, synthesis of fatty acid methyl esters by enzymatic transesterification has been extensively reviewed [21,22]. Other than methanol, various alcohols have also been used as acyl acceptors in transesterification reactions. For example, trimethylolpropane esters were synthesized by lipase-catalyzed transesterification with rapeseed oil methyl esters [23]. Total conversion of trimethylolpropane esters could reach 98% using *Candida rugosa* lipase as the catalyst at a reduced pressure of 2.0 kPa, 42°C, and 15% added water. The maximal conversion to the tri-ester reached 64% in 24 h when the reaction temperature was slightly increased to 47°C. The produced trimethylopropane esters of rapeseed oil can be used as hydraulic fluids with superior properties such as good cold and oxidation stability, and excellent frication and wear resistance.

Moreover, due to the high regioselectivity of some lipases, they have been applied to tailor natural lipids by transesterification to improve nutritional values or material properties. The most well-known example is the conversion of palm mid fraction and shea stearin into cocoa butter equivalents (CBE). Cocoa butter is mainly composed of oleic, palmitic, stearic acids in the form of 1,3-disaturated-2-oleyl-glyceride. Unilever [24] and Fuji Oil [25] have developed the process using 1,3-specific lipase to convert palm oil and stearic acids into CBE. The 1,3-specific lipase catalyzes the transesterfication that replaces palmitic acid with stearic acid at the 1- and 3-position to produce CBE. The produced CBE is crystalline with a melting temperature around 32–35°C, which is completely compatible with natural cocoa butter. Similar strategies have been applied for the production of structured triglycerides

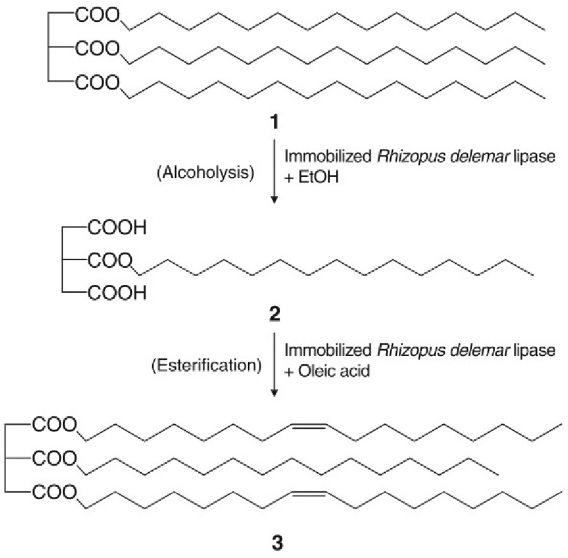

Figure 8.11 Convert tripalmitin to Betapol using 1,3-specific lipase.

(sTAG) such as Betapol. Betapol is a sTAG used for infany nutrition containing oleic acid at the 1- and 3-position and plamitic acid at the 2-position (1,3-oleoyl-2-palmitoylglycerol). A two-step lipase-catalyzed process was developed to convert tripalmitin **1** into Betapol **3** (Figure 8.11) [26]. First, *Rhizopus delemar* lipase immobilized on polypropylene (EP-100) was used for alcoholysis of tripalmitin to produce the corresponding 2-monopalmitin. The 2-monopalmitin **2** was then isolated with >95% purity and then further esterified with oleic acid with the same enzyme in *n*-hexane to produce Betapol **3** (Figure 8.11). The conversion yield reached 70% in 5 h and the produced Betapol contained 92% palmitic acid in the β position. More studies related to enzyme-catalyzed reactions have been discussed in [27].

8.3.3 Enzyme-Catalyzed Epoxidation

As shown in Sections 8.2.1.2 and 8.2.1.3, epoxide functional groups are versatile moieties that not only can be used for cross-linking but also can alter functional characteristics of polymers. Currently, epoxide groups were mainly generated chemically using peroxicarboxylic acids as the oxidant. The highly acidic condition associated with *in situ* production of peroxy acid results in hazardous handling and formation of undesired byproducts. On the other hand, enzyme-catalyzed epoxidation can be carried out in a much milder condition with high regioselectiviry. Lipase-catalyzed epoxidation of simple olefins was first reported in 1990 [28]. Five different lipases were screened for the epoxidation reaction and *Candida Antarctica* lipase showed the best activity. Lipase was first catalyzed by the production of peroxycarboxylic acid from the parent carboxylic acid using hydrogen peroxide as an oxidant. The produced peroxy acids were then used to expoxidiz the alkenes (Figure 8.12). This enzymatic transformation has then been applied to different substrates. Unsaturated fatty acids having a carboxyl group can be used for percarboxylic acid generation and carbon double bond(s) can be epoxidized. Therefore, if hydrogen peroxide is used to treat an unsaturated fatty acid in the presence of Novozym 435, the unsaturated acid

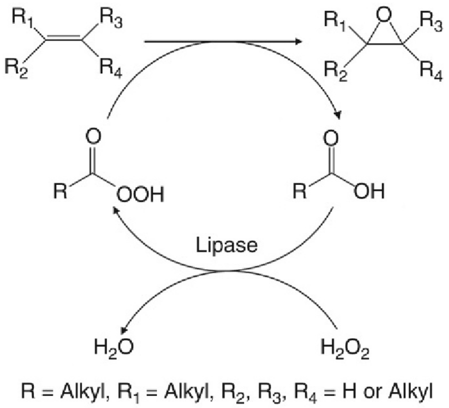

Figure 8.12 Lipase-catalyzed epoxidation of alkenes using hydrogen peroxide as oxidant.

is epoxidized (hence, this is called a chemoenzymatic process) [29]. Taking oleic acid as an example, the mechanism of the reaction is that some unstaturated fatty acids **1** are first converted to peroxy acids **2** by hydrogen peroxide catalyzed by the lipase, and then the peroxy acids epoxidize the unsaturated moieties chemically without other catalyst to produce the expoxidized fatty acids **3** (Figure 8.13). It has been demonstrated that unsaturated fatty acids with varying chain length can be epoxidized with high yields (72–95%) and superior selectivity (>98%). Either terminal or internal unsaturated groups can be enzymatically epoxidized. For fatty acid containing hydroxyl group such as ricinoleic acid, the hydroxyl group was involved in the epoxidation reaction. The enzymatic epoxidation process has also been applied to meadowfoam (*Limnanthes alba*) fatty acids to produce a mixture of 5,6-epoxyeicosanoic, 13,14-epoxydocosanoic, 5,6-epoxydocosanoic, and 5,6-13,14-diepoxydocosanoic acids with 98% yield [30]. These highly pure epoxy products provide great starting materials for the subsequent production of 6-hydroxy-δ-lactone. Besides free fatty acids, unsaturated triglycerides can be epoxidized enzymatically. If triglycerides were treated with hydrogen peroxide directly in the presence of lipase, the undesired byproducts such as epoxidized mono or diglycerides were found in the product mixture. Adding a small amount of free fatty acids (5 mol%) at the beginning of the reaction was found to completely inhibit the production of mono- and diglycerides [31]. The product mixture consists of only epoxidized triglycerides and epoxidized free acids since any free hydroxyl group produced was immediately re-esterified by the excess free fatty acid. Since transesterification occurred in the reaction, free fatty acids with the same composition as the triglycerides were used to maintain fatty acid distribution of the triglycerides. It has been demonstrated that rapeseed, sunflower, soybean, linseed, and castor oils could be epoxidized enzymatically with conversion yields of 88–96% and a selectivity of >92% [31]. Besides complete epoxidation, controlled partial epoxidation by optimizing H_2O_2/C = C-bonds ratio could be applied to accurately predict the oxirane oxygen contents and prepare synthetic substitutes that mimic natural epoxy oils such as vernonia oil [32]. Moreover, the immobilized lipase can be easily recovered and can maintain activity after multiple runs.

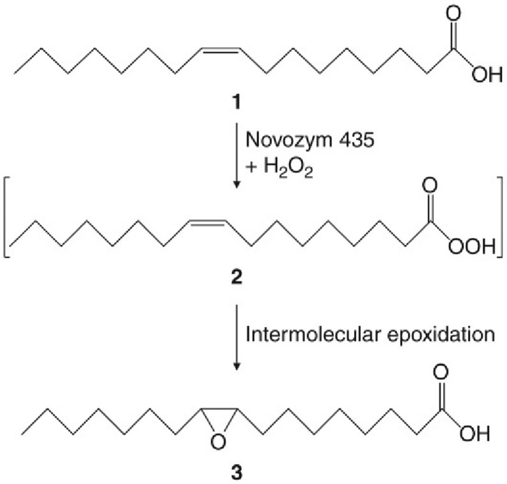

Figure 8.13 Mechanism of lipase-catalyzed epoxidation of oleic acid.

Recently, enzymatic epoxidation of *Sapindus mukoross*i seed oil (SMSO) was studied. SMSO composed of oleic, linoleic, linolenic, and eicosanoic acid was epoxidized using hydrogen peroxide as oxidant and stearic acid as active oxygen carrier catalyzed by Novozym 435. The effect caused by varying amount of stearic acid added was first studied. Response surface methodology (RSM) was then applied to investigate and optimize reaction parameters on the epoxy oxygen group content (EOC). Reaction temperature and enzyme load were found to be the most important parameters. Under the optimal conditions of 50°C, 7 hours, 2% enzyme load, and 4:1 molar ratio of H_2O_2/C = C-bonds, the EOC could reach 4.6%. Chemoenzymatic epoxidation of soybean oil has also been optimized [33]. Oleic acid was used for peroxy acid production. The optimization was performed step by step with one parameter at a time by the order of catalyst concentration, solvent concentration, H_2O_2/C = C-bonds ratio, initial oleic acid concentration, and reaction temperature. The conversion yield after optimization reached over 90% after 24 hours under the condition at 50°C, 4.0 wt% Novozym 435, 2:1 molar ratio of H_2O_2/C = C-bonds, in 110 wt% toluene and 8.0 wt% of oleic acid. More works about this chemoenzymatic epoxidation catalyzed by lipase can be found in these reviews [34–36]. Besides lipase, peroxygenase from oat (*Avena sativa*) seeds was found to be able to catalyze the conversion of double bonds to epoxide groups in the presence of an oxidant [37]. Among the oxidants tested, *tert*-butyl hydroperoxide showed the best activity. Oleic acid with a *cis* double bond was preferred compared to its *trans* analog, elaidic acid. This selectivity toward double bond *cis* configuration was not observed with lipase-catalyzed epoxidation.

8.3.4 Fatty Acids Hydroxylation

Hydroxy fatty acids are important chemical derivatives from plant oil due to the extra hydroxyl functional group(s). For example, the secondary hydroxyl group in ricinoleic acid (RA) has been transformed through various reactions such as esterification (as discussed in Section 8.2.3.1) dehydration, hydrogenation, sulfonation to produce versatile platform chemicals. Hence, RA can be used for the synthesis of a vast amount of polymers such as polyamides, polyurethanes, and polyesters that are widely used in lubricant, cosmetic, and candle industries [38]. Moreover, some hydroxyl fatty acids have antibiotic, antitumor, or anti-inflammation activities, suggesting their applications in pharmaceutical industry. For example, 9-hydroxy-10,12-octadecadienoic acid found in plants is a ligand for peroxisome proliferator-activated receptor-γ [39] and thus provides antitumor activity. Another polyhydroxyl fatty acid, 7,10-dihydroxy-8*E*-octadecenoic acid, produced by *Pseudomonas aeruginosa* can reduce surface tension and inhibit growth of the pathogenic microorganism *Candida albicans* [40]. Since chemical hydroxylation cannot provide the required regio- and steroselectivity for most applications, enzyme-catalyzed hydroxylation of fatty acid is preferred. Several enzyme families were found to catalyze fatty acid hydroxylation reactions by different mechanisms. Therefore, enzymes catalysts provide synthetic routes to regiospecific but diverse hydroxyl fatty acids. Recently, these fatty acid hydroxylation enzymes were extensively reviewed [41]; therefore, we will focus on two important enzyme families, P450s and hydratases, to demonstrate the versatilities of different enzyme families.

Cytochrome P450 monooxygenases (one example is mentioned in Section 8.2.2) are one of the largest and oldest enzyme superfamilies and are reported in all kinds of organisms [42]. They are divided into families starting with *CYP* followed by an Arabic number. P450s incorporate an oxygen atom from molecular oxygen into an organic substrate using cofactors NADH or NADPH as reducing equivalents. Fatty acid-hydroxylating P450s can be categorized into terminal (α-hydroxylases and ω-hydroxylases) and subterminal fatty acid hydroxlases. For example, some enzymes belonging to *CYP*52 family from *Candida* species [43] show specifically terminal hydroxylation activity toward C$_{12}$ to C$_{18}$ fatty acids. The ω-terminal hydroxylation followed by fatty alcohol oxidases and dehydrogenases can convert fatty acid into its corresponding α,ω-dicarboxylic acid. For example, palmitic acid **1** can be converted into 16-hydroxy palmitic acid **2** by *CYP52*, as shown in Figure 8.14a. Another P450 family *CYP*102 isolated from *Bacillus* species is self-sufficient and has higher turnover rates since they are fusion proteins with FAD- and FMN-containing reductase. *CYP*102 family also belongs to ω-hydroxylases and *CYP*102A1 is found to mainly (80%) catalyze the hydroxylation of arachidonic acid **3** at the ω-2 to produce enantiomerically pure (*R*)-18-hydroxyeicosatetraenoic acid **4** (Figure 8.14b) [44].

Hydratases add the hydroxyl group at the unsaturated functional group. These enzymes catalyze the regio-, steroselective irreversible reaction by adding water to the carbon–carbon *cis*-double bond of unsaturated fatty acids. Hydratase activity was first observed in 1962 [45]: an isolated *Pseudomonas* species hydrated oleic acid at the unsaturated 9,10-position to produce 10-hydroxystearic acid. The overall yield was only 14%. Hydration reactions of fatty acid on the unsaturated group have then been observed in many bacteria species such as *Nocardia*, *Rhodococcus*, *Enterococcus*, *Pediococcus, Corynebacterium* [46–49]. *Mycobacterium fortuitum* was reported to produce 10-hydroxystearic acid from oleic acid with an 80% yield [50]. *Stenotrophomonas nitritireducens* showed the highest activity using linoleic acid as the substrate, but the hydroxylation is regioselective at the 9-, 10-position. The strain could convert linoleic acid **5** into 10-hydroxy-12(*Z*)-octadecenoic acid **6** (Figure 8.14c) with a yield of 67.5% [51].

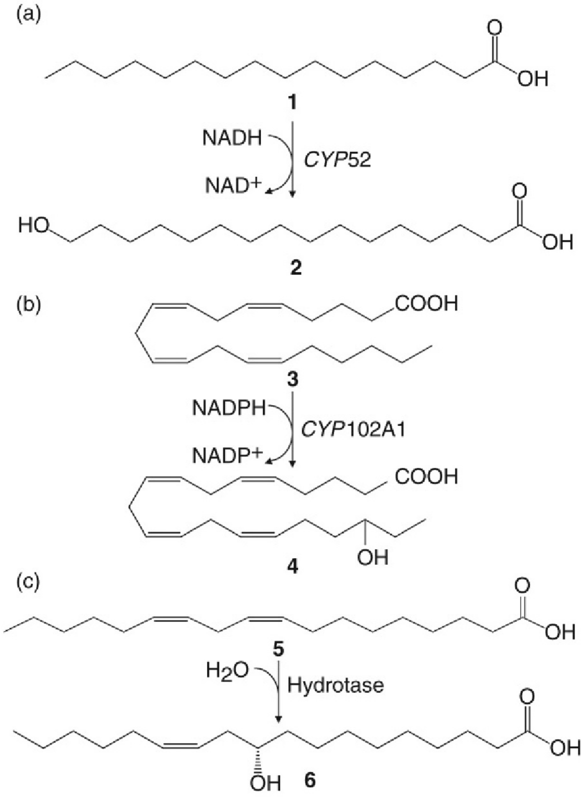

Figure 8.14 Comparison between different fatty acid-hydroxylation enzymes.

8.4 Conclusion

This chapter provides an overview of enzyme-assisted processes applied in plant oil-based polymer industry. Enzymes are versatile and promising alternatives to chemical catalysts due to some characteristics. For example, they are able to catalyze reactions at mild conditions with excellent regio-, chemo-, and steroselectivity [1], and thus reduce energy consumption and the use of protection–deprotection reagents. This is especially important for polymerizing multifunctional or temperature-sensitive monomers and for structural control. Besides polymer synthesis catalyzed by isolated enzymes, whole-cell biocatalysts can be a useful tool for transforming plant oil into a variety of functional monomers by epoxidation, oxidation, and transesterification. Furthermore, biotechnology techniques can be applied to optimize enzyme efficiency or to engineer production of nonnatural chemicals derived from plant oil.

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9 Plant Oil-Based Nanocomposites

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9.1 Introduction

Plant oil-based polymer nanocomposites can be defined as a mixture of a sustainable polymer matrix and nanosized particles, such as fibers, platelets, or tubes. The plant oil-based polymer matrix can be an amorphous thermoplastic material or a crosslinked three-dimensional polymer network. The plant oil-based polymer matrix holds or binds the fillers together and protects them from damage by distributing any stress through the whole specimen. Recently, plant oil-based polymer composites have received considerable attention due to their potential to significantly improve and enhance the properties of neat polymer matrix. Incorporation of small amounts of filler leads to an improvement in material properties, such as modulus, strength, heat resistance, flame retardancy, and lowered gas permeability [1–14]. Furthermore, addition of nanofillers to the plant oil-based polymer matrix could also yield novel functions, such as electrical [15–18], magnetic [19–25], and optical functions [26–29], as well as biofunctionality [30–33]. In principle, the improvement of material properties and creation of novel functions has been linked to the interfacial interaction between the polymer matrix and fillers as well as the formation of a network of interconnected filler particles. The interconnected particles can conduct heat and electrical current [15–25].

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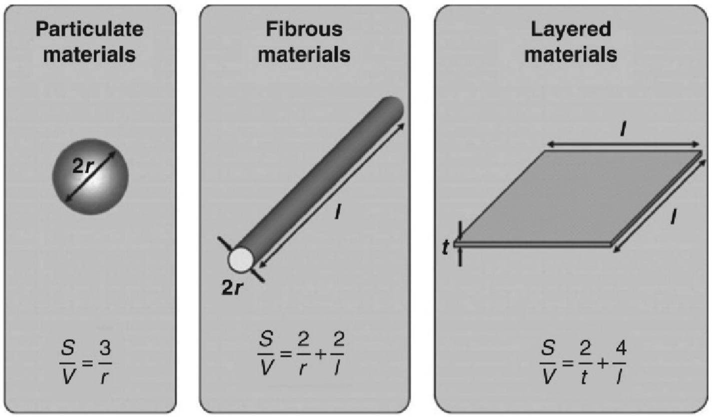

Figure 9.1 Surface/volume (*S*/*V*) ratios for varying filler geometries, *r* is the radius, *l* is the length, and *t* is the thickness of filler. Taken with permission from [37].

Development and tailoring of polymer composites offer the possibility to promote their use in automotive, aerospace, building, electrical, optoelectronic, and biomedical applications [34–36]. The novel functions and properties enhancement of polymer composites can also be controlled by micro or nanostructural parameters such as dimension, shape, distribution, volume fraction, alignment, and packing arrangement of fillers. Anisotropic properties could be obtained from fiber filled composites, except for the very short, randomly distributed fibers, whereas physical properties of polymers with randomly distributed particles are isotropic. Furthermore, composites with nanometer-sized fillers had different properties compared to those filled with macrosized fillers. Some of the properties of nanocomposites, such as increased tensile strength, may be achieved by using higher macrosized filler concentration at the expense of increased weight and decreased gloss. Other properties of nanocomposites such as optical clarity or improved barrier properties could not be achieved by high concentration of macrosized fillers. The filler concentration required for substantial improvement in the overall material properties is called critical filler volume fraction. The fillers could be classified either by their geometry or by their size. Three different categories of filler materials could be found, namely particles (e.g., silica, metal, POSS, and other organic and inorganic particles), layered materials (e.g., graphite and layered silicate), and fibrous materials (e.g., nanofibers and single- (SWCNTs) and multiwalled nanotubes (MWCNTs)).

The surface area/volume ratio of the fillers is a very important morphological factor normally used to understand and control the structure–property relationship of nanocomposites [37]. As shown in Figure 9.1, the change in particle diameter, layer thickness, or fibrous material diameter from micrometer to nanometer changes the surface area/volume ratio by three orders of magnitude. According to this scale, there is a distinct size dependence of the material properties. In addition, the properties of the composite are normally controlled by the properties of the interface or interphase when the interfacial area drastically increased. Major challenges in design and fundamental understanding of polymer composites are related to the complexity of the composite structure, dispersibility of fillers, and the relationship between dispersion and optimal properties.

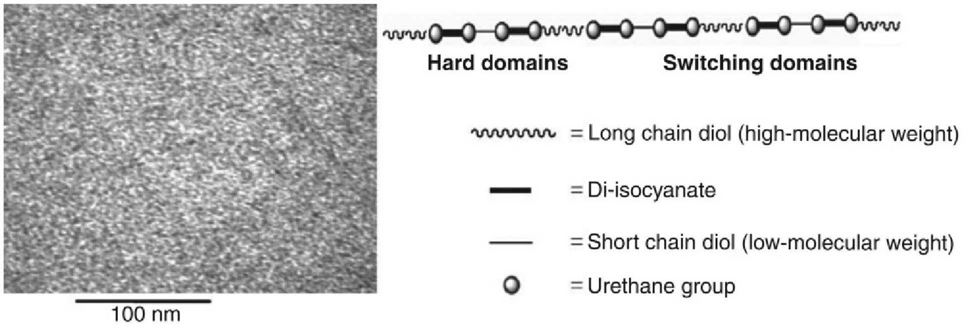

Figure 9.2 Schematic diagram of the hard and soft domains of PU structure. The TEM shows microphase separation morphology for the hard domains (*dark particles*) and soft domains (*bright matrix*). Adapted with permission from [41].

Uniform dispersion of nanoparticles and nanotubes against their agglomeration due to van der Waals bonding is the first step in the processing of nanocomposites [38–40]. Exfoliation of clays and graphitic layers are essential. Several strategies have been studied to achieve well-dispersed fillers in polymer matrix, including melt processing, solvent casting method (often with surface functionalization and/or sonication pretreatment), and *in situ* polymerization. Melt processing by itself often led to limited filler dispersion in the polymer matrix. Blending polymer and fillers in solvent or *in situ* polymerization resulted in a better dispersion. It is well established that the modification of the filler surface by grafting of macromolecules onto its surface is preferable. In this case, the filler is highly compatible to the polymer matrix. This is often desirable since it provides the best possible adhesion and allows for optimal transfer of stress from the matrix to the fiber.

Polyurethanes (PUs), typically synthesized through addition polymerization of polyisocyanates and polyols are among the most versatile polymeric materials and have been widely used as foams, coatings, and sealants. PU is normally comprised of alternating soft polyol and hard polyurethane–urea segments. These two segments are microphase separated into hard and soft domains [41]. The microphase separation is responsible for the excellent elastomeric properties of PU. Figure 9.2 depicts schematically the structure of PU elastomers (linear structure) as multiblock copolymers with hard (urethane) and soft (polyol) segments. The TEM shows how these two segments can segregate in different domains having a nanoscale morphology. The very small dark particles in the micrograph are the hard domains, and the bright matrix is the soft domain of the PU [41]. Currently, most of the polyisocyanates and polyols for PU production are derived from petroleum. Increasing concerns about the unsustainability of chemicals from petroleum resources and environmental problems caused by fossil fuels, have led to considerable efforts to develop materials based on renewable resources, such as natural oils, starch, cellulose, and lignin. For example, vegetable oil based PUs were successfully developed and their structure–property relationships have been extensively investigated.

In this chapter, the substantial enhancement in mechanical, thermal, and morphological properties of plant oil-based polymers (mainly PU) will be highlighted exemplarily for different types of surface modified and functionalized nanofillers including, natural fillers (e.g., cellulose and lignin), graphene, carbon nanotubes (CNTs), and silica.

9.2 Plant Oil-Based/Natural Filler Composites

Natural fillers, such as lignin and cellulosic fibers have good mechanical properties, low density, and they are available with huge amount with low cost from renewable resources. In addition, the surface of natural fillers has hydroxyl groups that allow chemical modification to enhance the interaction and improve the interface with the polymer matrix.

Lignin, one of the world's most abundant natural polymers, is found in all vascular plants, mostly between the cells and in the cell walls. Lignin is relatively hydrophobic and aromatic in nature, and is composed of up to three different phenyl propane monomers, namely; *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (see Figure 9.3a). These three lignols monomers are incorporated into a complex, ill-defined structure as shown in Figure 9.3b. Although pure lignin can be easily obtained with huge quantities as by-product of wood pulping or ethanol production from biomass, the industrial applications of lignin is very limited due to its complex chemical structure and complete insolubility in common organic solvents. Chemical incorporation of lignin to plant oil-based polymers is not an easy process because of the complex structure of lignin. Generally, the utilization of lignin during the polymerization process of plant oil monomers can be established through chemical modification and functionalization of lignin. The significant number of hydroxyl groups on the lignin backbone provides an excellent opportunity for chemical modification to tailor lignin properties to a certain application.

Soybean-based PU biofoam was investigated with different concentrations of lignin as a reinforcement filler by Luo et al. [43]. The PU/lignin biofoams were synthesized via self-rising method using water as a blowing agent. The mechanical properties of the PU biofoam composites increased significantly with increasing lignin concentration up to 10 wt%. In addition, the glass transition temperature, foam density, thermal stability, and storage modulus increased systematically with increasing lignin content. The authors provided a simple synthesis procedure to prepare a novel biofoams and explored the potential of using lignin as a biofiller in PU applications.

A series of natural fibers such as flax, cellulose, pulp, and hemp with different contents up to 50 wt% were used as reinforcement fillers for acrylated epoxidized soybean oil via resin vacuum infusion process or vacuum-assisted resin transfer molding [44]. Recycled paper, an example for a cheap cellulose fiber was found to have a significant improvement on the flow behavior and mechanical properties of the neat bio-based polymer matrix. The bio-based composites were cured at room temperature and flexural modulus of the obtained composites increased significantly to a range between 1.5 GPa and 6 GPa depending on the nature of the used fiber. In addition, the authors claimed that the low cost acrylated epoxidized soybean-based natural fiber composites have good mechanical properties suitable for applications in housing construction materials, furniture, and automotive parts.

Bio-based maleate castor oil and lignin composites have been synthesized through free radical polymerization. The composites chemical structure and morphology were

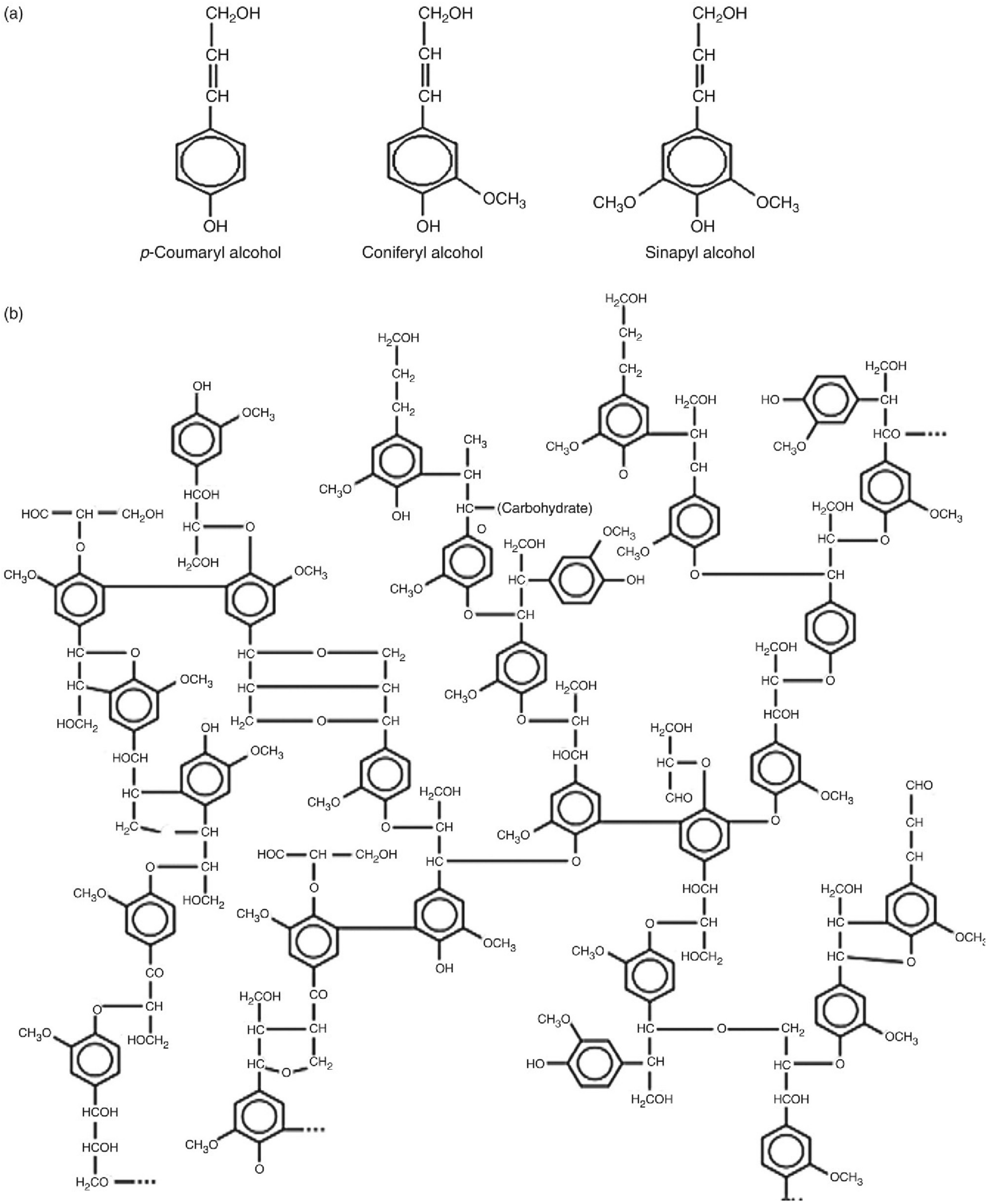

Figure 9.3 The three phenyl propane monomers in lignin (a) and the proposed chemical structure of lignin (b) [42].

characterized using Fourier transform infrared spectroscope (FTIR) and scanning electron microscope (SEM), respectively [45]. In addition, the mechanical properties of the composites showed a considerable improvement in the tensile properties by adding lignin.

Recently, polyol based on lignin and oleic acid have been synthesized with no organic solvent or catalyst [46]. The chemical structure of this new lignin–fatty acid-based polyol was characterized using ^{1}H NMR and FTIR analyses [46]. The lignin–fatty acid polyol was then used to synthesize bio-based PU via two steps procedure. The thermomechanical properties of this lignin–fatty acid-based PU were investigated using DSC, TGA, and DMA. This study depicted an important output for the valorization of lignin and they may be an optimal alternative to conventional PUs.

The effect of lignin and cellulose fibers obtained from sugarcane straw on the structure and thermal behavior of castor oil-based PU has been reported by Mileo et al. [47]. The milled cellulose and lignin were obtained from acid hydrolysis of sugarcane straw. The bio-based composites were prepared with different concentrations of lignin and cellulose fillers. A significant increase in the stiffness was observed by adding 40 and 30 wt% of lignin and cellulose fibers, respectively. At higher concentration of the bio-based fillers, the stiffness of the composites decreased greatly. In addition, the thermal stability of the composites improved by adding the bio-based fillers.

9.3 Plant Oil-Based/Carbon Nanotubes Composites

Polymer composites with CNTs as filler are highly conductive materials with significantly reduced in the electric resistance. The carbon compounds could conduct electricity in the plane of each covalently bonded sheet due to the delocalization of outer electrons to form π-cloud. This resulted in a lower bulk electrical conductivity for carbon than for most metals. Generally at atmospheric pressure, carbon took the form of graphite in which each atom can be bonded trigonally to three others in a plane composed of fused hexagonal rings, similar to aromatic hydrocarbons. The resulting network is two-dimensional, and the resulting flat sheets were stacked and loosely bonded through weak van der Waals forces (see Figure 9.4a). This gave graphite its softness and its cleaving properties (the sheets slip easily off one another). CNTs could be considered as the result of folding graphite layers into carbon cylinders and might be composed of a single shell-SWCNTs (Figure 9.4b) or of several shells-MWCNTs (Figure 9.4c) [48–50].

CNTs with their impressive mechanical properties are ideal material. Reinforcement bio-based nanocomposites from acrylated epoxidized soy oil (AESO) and CNTs with different concentrations has been reported by McAninch et al. [51]. Styrene and methyl methacrylate were used as dispersing agents for CNTs in AESO polymer matrix. It has been found that the MMA significantly improved the dispensability of CNTs in polymer matrix than styrene. The processing of composites was carried out using mechanical shear mixing method with considerable improvement in the mechanical properties. The homogenous distribution of CNTs was investigated by SEM and optical microscopy. The morphology of the composites revealed some aggregation of CNTs in the polymer matrix.

Liang et al. [52] developed bio-based PU foams from soybean oil and MWCNTs. The composites were prepared with different MWCNTs concentrations of 0.5–1.0 wt%. The

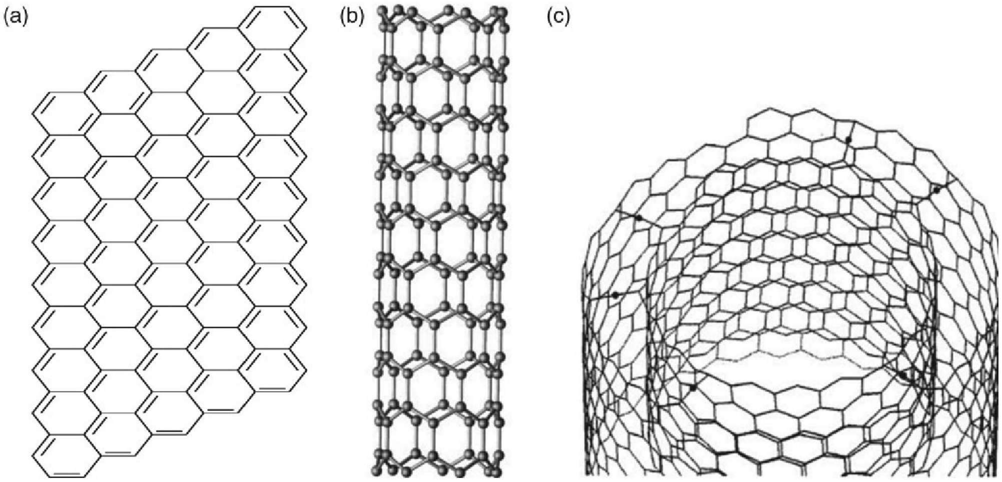

Figure 9.4 Schematic diagrams for graphene (a), single-wall carbon nanotube (b), and multiwall carbon nanotube (c). (a) Reprinted with permission from [59], (b) reprinted with permission from [66], and (c) reprinted with permission from [67].

mechanical properties of the soy-based PU nanocomposites increased significantly with adding MWCNTs. The compressive, flexural, and tensile properties of the composites foams improved to about 30% by adding MWCNTs. In addition the maximum improvement in the compressive and flexural properties of the composites were obtained at 0.5 wt% MWCNTs, while the tensile stress reached a maximum value at 1 wt% MWCNTs.

9.4 Plant Oil-Based PU/Graphene Oxide Composites

Graphene oxide (GO) can be made from chemical exfoliation by reactions that have been known for 150 years. Recently, interest in this old material has resurged, because GO is a promising solution-processable precursor for the bulk production of graphene. There are abundant oxygenated functional groups on GO's basal plane and edges, such as carboxyl, hydroxyl, and epoxy. Moreover, GO is a two-dimensional sheet with feature sizes at two abruptly different length scales. The apparent thickness of GO is approximately 1 nm, while the lateral dimensions can range from several nanometers to hundreds of micrometers. The di-isocynate can react easily with the oxygenated functional groups attached to GO to produce exfoliated PU nanocomposites with enhanced mechanical, physical, and thermal properties. Nguyen et al. prepared a cast nanocomposite film from a mixture of thermoplastic polyurethane (TPU) solution and functionalized graphene sheet (FGS) suspended in methyl ethyl ketone. The FGS efficiently reinforced the TPU matrix particularly in the temperature region above the soft segment melt [53]. Cai et al. reported the substantial improvement in the stiffness, toughness, and thermal stability of linear PU resulting from the incorporation of GO [54]. Kim et al. reported exfoliated GO reinforced TPU nanocomposites with improved gas barrier and electrical conductivity [55]. Lee et al. prepared waterborne polyurethane (WPU) nanocomposites with FGS by *in situ* method; the conductivity and modulus of nanocomposites improved, while the thermal stability and tensile strength of nanocomposites deteriorated [56]. Wang et al. prepared GO sheets reinforced linear PU composites by *in situ* polymerization. The authors found that, the nanocomposites displayed high electrical conductivity and good thermal stability [57]. Chen and Lu reported simultaneous improvement in strength and toughness while maintaining the good ductility of PU elastomers by adding FGS [58]. Little work has been reported for bio-based PU nanocomposites. In this section, the effects of surface modified GO on the mechanical, thermal, and morphological properties of bio-based PU will be considered. The thermosetting PU will be synthesized from epoxidized soybean oil and castor oil fatty acid.

9.4.1 Surface Modification of Graphene Oxide

Generally, graphene oxide can be synthesized via a modified pressurized oxidation method. Briefly, graphite, $KMnO_4$, H_2SO_4 (98%), Teflon reactor, and stainless steel autoclave were completely cooled, respectively, in a refrigerator at 0–4°C before use. The cooled graphite (2 g) and $KMnO_4$ (10 g) were put into the reactor, and then, H_2SO_4 (100 mL) was added to the reagent mixture. The reactor was then moved into an ice water bath and kept mechanical stir at 800 rpm for 1 h. After that, the reactor put into the stainless steel autoclave and tightly covered at 80°C for 2 h. The obtained mud was diluted with a large amount of deionized water. With mechanical stirring, H_2O_2 (30%) was dripped into the suspension until the slurry tuned golden yellow. The suspension was washed with hot HCl and deionized water until the pH reached 7.0 to obtain the GO.

Figure 9.5 shows the Raman spectrum, which reflects structural changes occurring in graphite and GO. Highly ordered graphite has a couple of Raman-active bands visible in the spectra, the in-phase vibration of the graphic lattice (G band at 1565 cm^{-1}), and the weak disorder band caused by the graphite edges (D band at 1343 cm^{-1}). Both the G and the D band undergo significant changes upon oxidation and exfoliation of graphite as GO contains a certain fraction of sp^3 carbons. In the case of GO, the D band shifts to 1355 cm^{-1}, and becomes broader with higher relative intensity compared with that of the G band, which indicates the

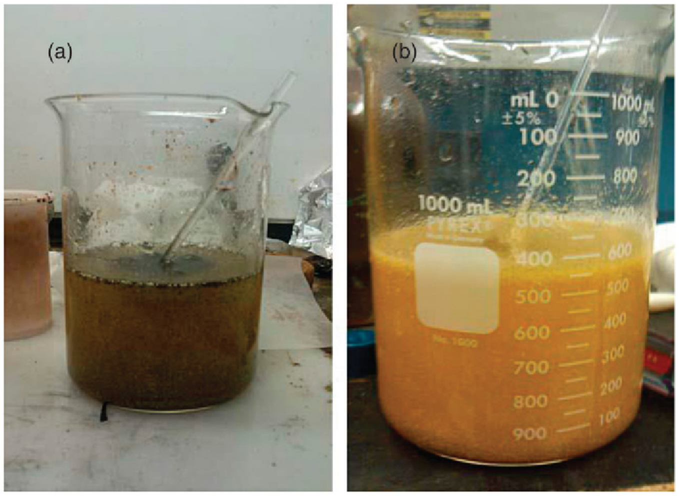

Figure 9.5 (a) Pressurized oxidation method and (b) modified pressurized oxidation method [59].

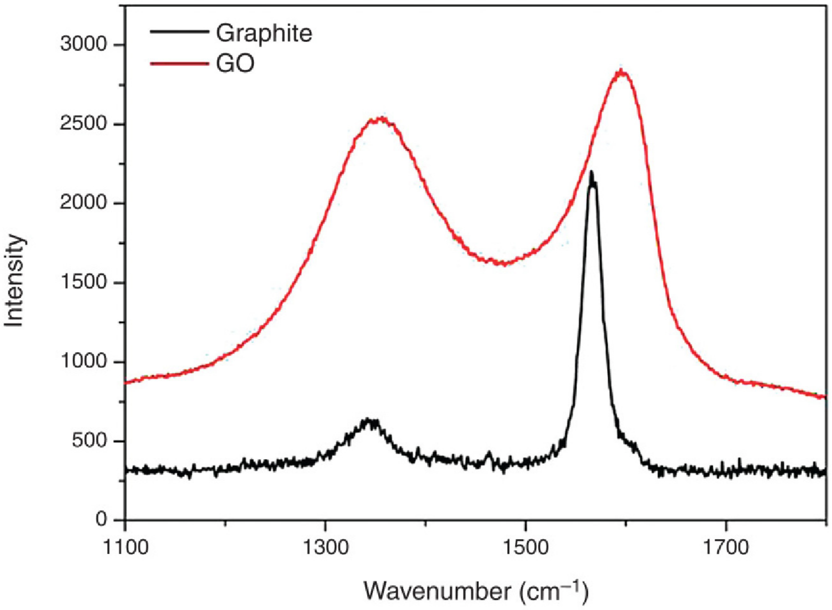

Figure 9.6 Raman spectra of graphite and GO obtained from the modified pressurized oxidation method [59].

higher disorder in GO. The broader G band also indicated the deconstruction of highly ordered graphite. Moreover, the blue shift of G band to 1595 cm^{-1} is mainly due to the isolated double bonds of GO resonates at higher frequencies than that in graphite [59,60] (Figure 9.6).

AFM was performed to observe the morphology of GO. It can be seen from the AFM profile that GO is fairly small (around 1 μm) and ultrathin. The thickness of GO is 0.8–1.2 nm (see Figure 9.7), which is typical for a one-atom-thick GO nanolayer. Such a small thickness indicates that the specific surface area of GO must be very large, which is important for polymer/layered compound nanocomposites [61]. The layers are a bit thicker than individual graphene due to the presence of oxygenated functional groups such as hydroxyl, carboxyl, and epoxy, which disrupt the original conjugation and introduce lattice defects to form folds and distortions

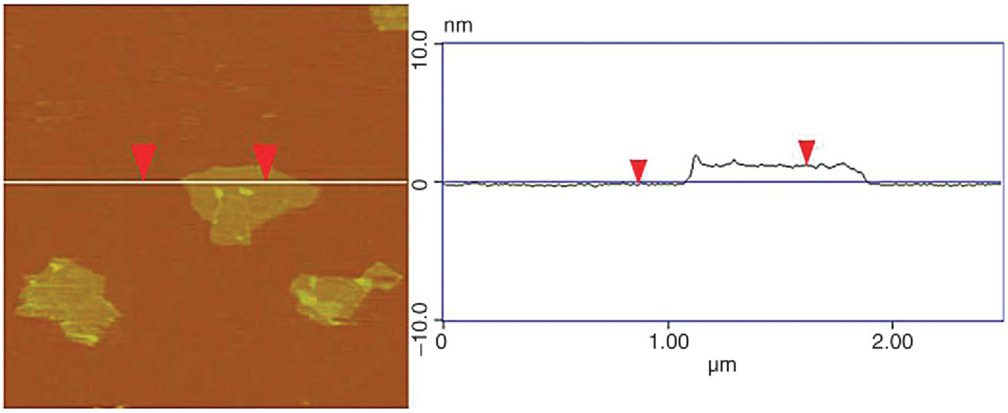

Figure 9.7 AFM profile for GO obtained from the modified pressurized oxidation method [59].

on the GO layers. Such disruption and lattice defects reduce the mechanical strength of the GO layers.

9.4.2 Synthesis and Characterization of Bio-Based PU/GO Nanocomposites

The obtained GO was dried at 60°C under vacuum overnight. The dried GO (0.1 g) was exfoliated in 10 g DMF using ultrasonication with a power of 70 W for 0.5 h at room temperature. Calculated amount of the obtained GO/DMF mixture was mixed with 1 g bio-based polyols at room temperature, and then 0.31 g IPDI and one to two drops DBTDL catalyst were added to the mixture and kept stirring at 70°C for 2 h. Afterward, the solution was poured into a Teflon mold to produce 100-mm length and 50-mm width film with approximately 0.5-mm thickness, which was cut into specific dimensions for characterization. The elementary steps of PU/GO synthesis are illustrated in Figure 9.8.

The thermal stability of the PU/GO nanocomposites was investigated using TGA. Figure 9.9 demonstrates a typical TGA measurement for PU/GO nanocomposites at 20°C/min heating rate under a nitrogen atmosphere. Clearly, all samples are thermally stable at temperatures up to 290°C. The onset of the thermal degradation process of all PU/GO nanocomposites is almost identical and slightly lower than that of pure PU. It is also clear from this figure that the soft segments of PU start to degrade first at 290–370°C and the hard segments degrades later on at a temperature higher than 370°C. The nanocomposites have more thermal stability at temperature higher than 400°C. In addition, the PU/GO nanocomposites with GO ≥ 0.4 wt% have about 5 wt% inert residues, while the pure PU and PU/GO with 0.2 wt% GO have no any inert residue remaining. In conclusion, incorporation of GO does not significantly enhance the thermal stability of PU under a nitrogen atmosphere [59].

The fracture surface of the PU/GO nanocomposites with different GO contents was investigated by SEM. As shown in Figure 9.10, the fracture surface of the neat PU film after tensile testing is relatively smooth, and exhibits stiffness. While the fracture surfaces of the PU/GO films after tensile testing become rough, and exhibit toughness until the

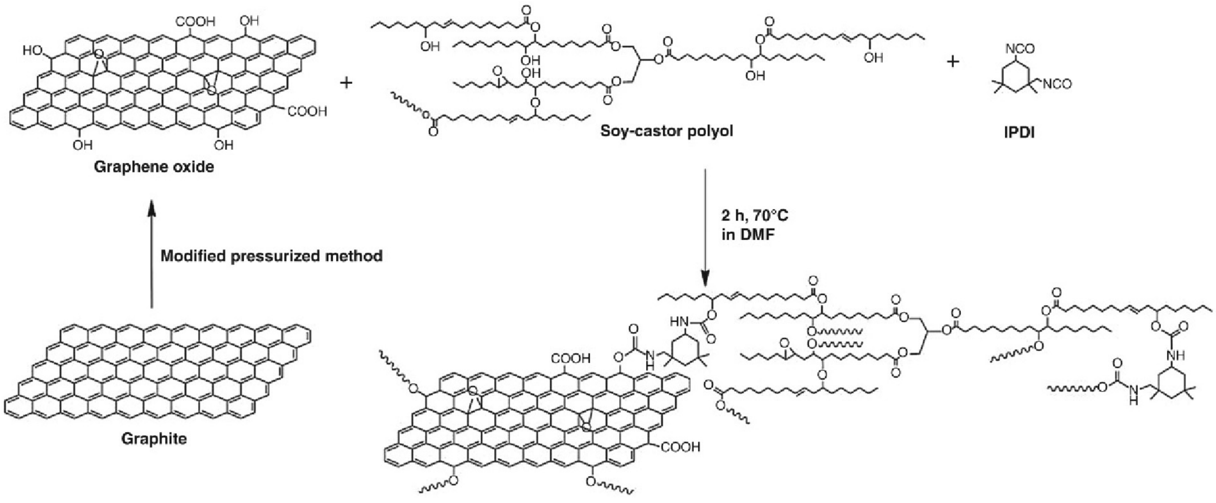

Figure 9.8 Elementary steps for the synthesis of PU/GO nanocomposite [59].

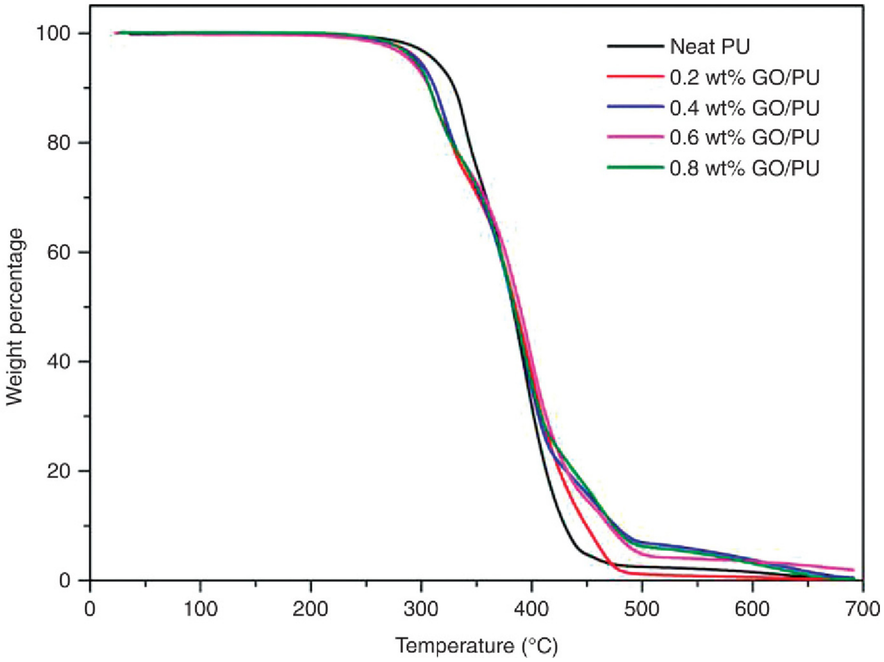

Figure 9.9 TGA measurement for PU/GO nanocomposites at 20°C/min heating rate under a nitrogen atmosphere [59].

concentration of GO reaches 0.4%. Moreover, most of the GO nanosheets were well dispersed and embedded into the PU matrix with the concentration of GO no more than 0.4%. With the addition of more GO, it began to aggregate, and the fracture-surface images of the films exhibit a stack of sheets (bright stripe), just like that of the GO membranes, which provided a barrier to cure by physically blocking functional group diffusion [59] (Figure 9.10).

9.5 Plant Oil-Based/Clay and Silica Nanocomposites

Epoxidized soybean oil (ESO) and nanoclay thermoset as reinforcement filler has been reported by Liu et al. [62]. The mechanical properties increased with adding nanoclay up to 8 wt% followed by a decrease in the mechanical properties with higher filler contents. The obtained results were related to the aggregation of the nanoclay at a high concentration.

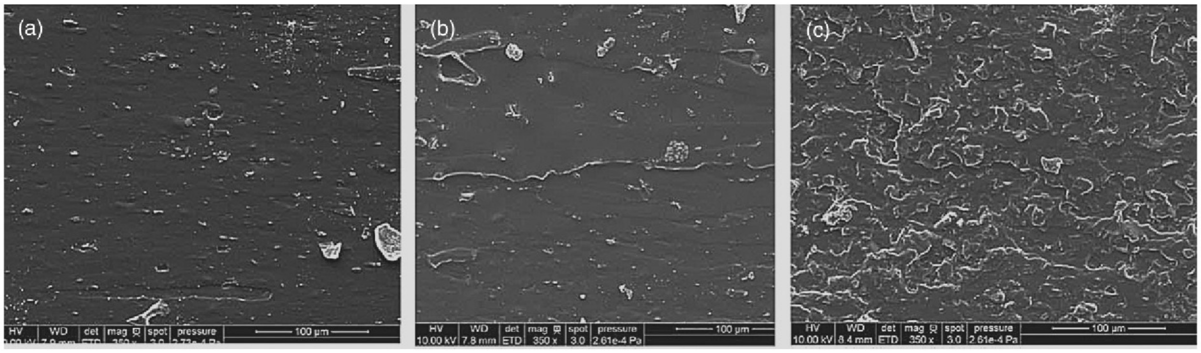

Figure 9.10 SEM images of (a) 0.2 wt% GO nanocomposite, (b) 0.4 wt% GO nanocomposite, and (c) 0.6 wt% GO nanocomposite [59].

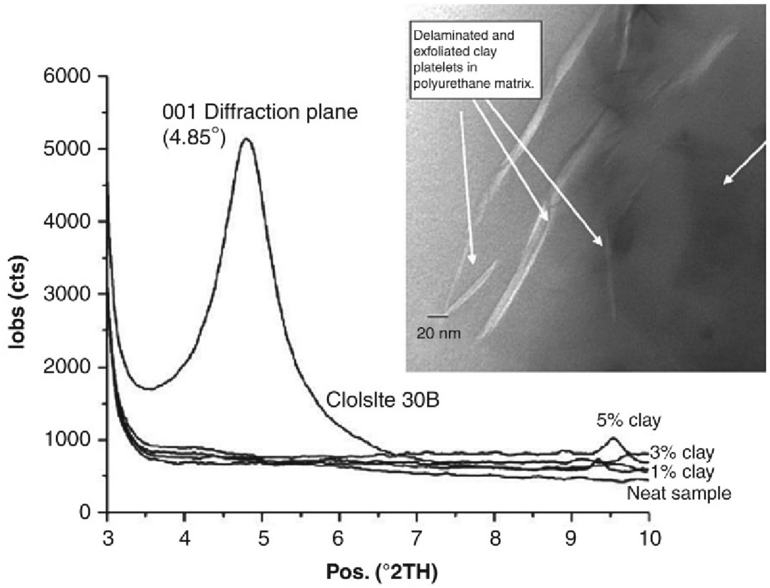

Figure 9.11 TEM and X-ray diffraction for castor oil-based PU/nanoclay composites with different concentrations of nanoclay. Reprinted with permission of Elsevier [64].

The glass relaxation process of these nanocomposites measured by DMA (peak maximum of tan δ) shifted to higher temperature from 11.8°C to 20.7°C with increasing the nanoclay concentration up to 5 wt% [62].

Organically modified montmorillonite with a wide range of concentration up to 15 wt% has been used as reinforcement filler for cationically polymerization of ESO [63]. The ESO/nanoclay composites have high storage modulus and glass transition temperature with high clay concentration. This improvement in thermomechanical properties of the nanocomposites was related to the copolymerization of the surface modified nanoclay with the ESO.

Nanocomposites from castor oil-based PU and a quaternary ammonium modified montmorillonite was reported by Kaushik et al. [64]. The nanocomposites were prepared with different modified clay contents from 0 wt% to 5 wt%. The X-ray diffraction technique was used to evaluate the exfoliation behavior of the nanoclay in the castor oil-based PU matrix. In addition, the TEM was also used to evaluate the morphology of the nanocomposites. Delaminated stacks of silicate and individual platelets as well as clay aggregation were observed in the TEM morphology. Figure 9.11 summarized both the TEM and X-ray data for the castor oil-based PU/nanoclay composites [64]. The mechanical properties (Young's modulus, tensile strength, and elongation at break) of the nanocomposites increased with increasing the content of modified clay. In addition, the thermal stability, barrier properties to the diffusion of vapor and liquid water of castor oil-based PU improved significantly by adding the modified nanoclay.

Aqueous castor oil-based PU and surface modified silica nanocomposites have been synthesized with different contents of silica through a sol–gel process [65]. Figure 9.12 shows the TEM morphologies of the diluted aqueous dispersions. The gray and black particles are the PU and silica nanoparticles, respectively. The black silica aggregated to large particles with increasing silica concentration. The authors also found that the silica particles are mainly embedded in

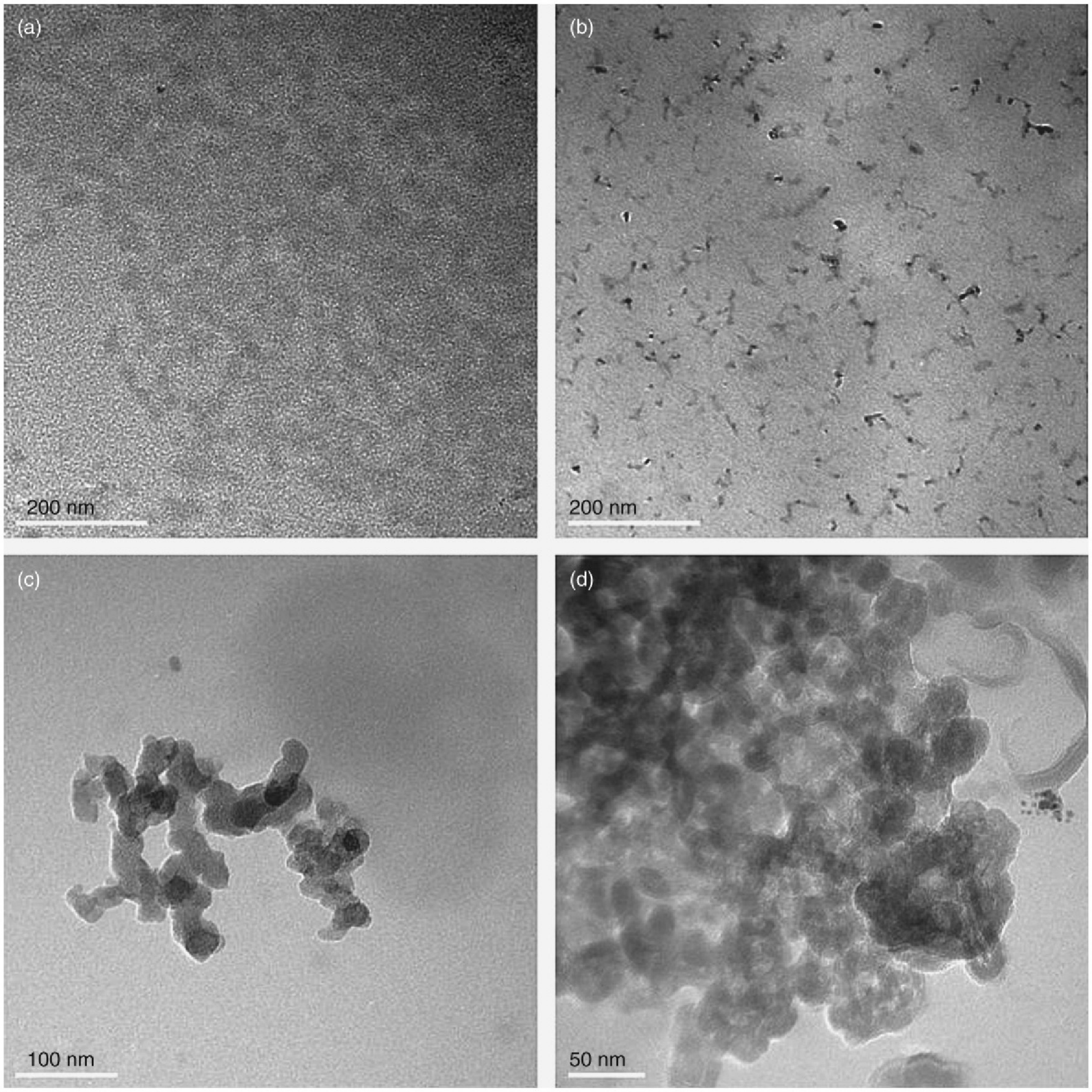

Figure 9.12 TEM images for PU/Si aqueous dispersion with (a) 0 wt% Si, (b) 0.5 wt% Si, (c) 1 wt% Si, and (c) 2 wt% Si. Reprinted with permission from Elsevier [65].

the PU particles (a core-shell structure). Both mechanical properties and thermal stability of solid films obtained from solvent cast of the aqueous dispersions increased significantly with increasing the nanosilica content. The crosslink density of the nanocomposites was also calculated from the storage modulus plateau of the DMA data at 40°C above the T_g based on rubber elasticity theory. The value of the crosslink density increased from 90 mol/m^3 for pure castor oil-based PU to 766 mol/m^3 for the PU/silica composite with 2 wt% silica. However, on the other hand the T_g of the nanocomposites slightly decreased with increasing silica contents.

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10 Fiber Reinforced Plant Oil-Based Composites

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10.1 Introduction

Due to the continuously increasing price of petroleum resources and an increase in environmental awareness, researchers are actively developing polymeric materials based on biorenewable resources to replace the traditional petroleum-based plastics. Thermoplastics such as polystyrene, polyethylene, polystyrene, poly(vinyl chloride) and thermosets such as epoxies and polyesters are used everywhere in our daily life. These plastics are used in applications including packaging, textiles, coatings, automobile components, biomedical devices, and household items. Even though plastics are versatile and essential materials in the modern society, one should not neglect the fact that petroleum resources are limited. It is proposed that all petroleum resources will be exhausted within the next 100 years [1]. As a result, it is important to continuously put effort in finding environmental-friendly starting materials and methods to synthesis plastics.

Plant oils have been widely used as the building blocks of polymers because they are relatively cheap, available in large quantity, and environmentally friendly. Plant oils are biorenewable and can be obtained from a variety of plants, soybean, castor, tung tree, and palm tree. Plant oils are excellent biorenewable materials because the triglyceride molecule consists of many reactive functional groups, such as double bonds and hydroxyl groups. Soybean oil and linseed oil contain relatively high amount of unsaturation content compared to other plant oils; thus, these two types

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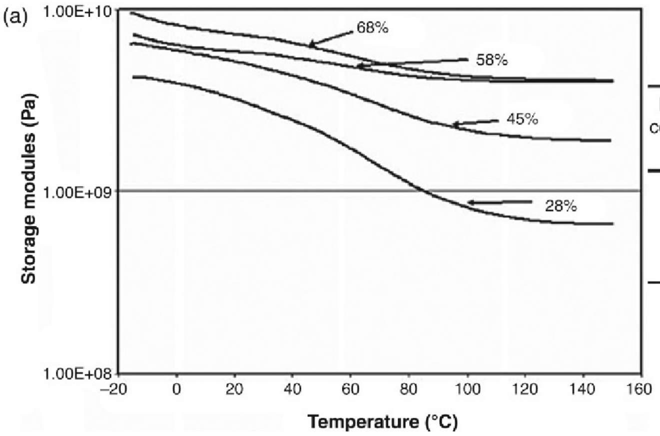
of plant oils are used most often to synthesize polymers. Higher unsaturation content in plant oils will lead to higher number of reactive crosslink sites, resulting in polymers with better mechanical properties. Castor oil is also a popular starting material for producing polymers such as polyurethane because the castor oil itself contains hydroxyl groups that can be used to react with isocyanates.

Fiber reinforcements have been widely used in plastic industry to produce composites that have higher modulus and high strength compared to the neat plastic alone. Fibers such as glass fiber and carbon fiber are strong materials because they have relatively small diameter; thus, there are less defects in fiber compared to bulk materials. Plastics such as epoxies act as the matrix that consolidates every single fiber into a solid entity. A variety of fibers have been incorporated into the plant oil-based thermosets, including the traditional synthetic fibers such as glass fibers and carbon fibers as well as biobased fibers. The use of biobased fibers can not only enhance the mechanical properties of the plant oil-based matrix, but also increase the biorenewable content in the final products. Due to the lower cost of some biorenewable fibers, the incorporation of the biorenewable fibers can also decrease the cost. Biorenewable fibers can be divided into two categories, namely, plant-based fibers and animal-based fibers. Plant-based fibers include flax, hemp, kenaf, jute, sisal, banana, cottons, etc. Animal fibers such as chicken feathers, wool, and silk have also been used as reinforcements. However, biorenewable fibers have several drawbacks compared to the synthetic fibers. Biorenewable fibers generally possess lower mechanical properties and lower thermal stabilities when compared to the synthetic fibers. In addition, their hydrophilicity makes them prone to water damage. Since polymer matrixes are hydrophobic, the hydrophilic biorenewable fibers may not interact well with the matrix, producing composites with low interfacial adhesion between the fiber and the matrix. In this chapter, the experiment details of composites prepared using different plant oil-based matrixes and fibers are discussed. Plant oil-based vinyl thermoset, epoxies, and polyurethane have been widely used as the matrix for composites.

10.2 Fiber-Reinforced Plant Oil-Based Vinyl Polymer Composites

Akesson et al. prepared a series of structural composites based on acrylated epoxidized soybean oil (AESO) and various natural fiber mats [2]. The AESO was cured using 1,1-di-(*tert*-butylperoxy)-cyclohexane free radical initiator, and the concentration of the initiator was kept at 1 wt%. The composite was made by first spraying resin on the fiber mats, followed by compression molding under elevated temperature and pressure. Three different types of natural fiber mats were used in this study, including air laid flax mat, coarse hemp mat, air laid flax mat-PET hybrid. In this study, the tensile properties of the composites with 40–70 wt% air laid flax fiber mat were recorded in order to investigate the effect of fiber mat percentage. As expected, the mechanical properties increased with increasing amount of fiber mat in the composite. The composites with 40% flax mat have a tensile strength and a Young's modulus around 50 MPa and 5.0 GPA, respectively. When the fiber mat content increased to 70 wt%, the tensile strength of the composite increased to 78 MPa to 9.7 GPa, respectively. Dynamical mechanical analysis (DMA) showed that the storage modulus



(b)

Fibre content (%)	Storage modulus (*E*′) at 20°C (GPa)	Loss modulus (*E*′) at 20°C (GPa)	T_g (°C)
68	7.4	0.34	84.6
58	5.9	0.26	81.7
45	5.2	0.34	75.0
28	3.2	0.24	73.2

Figure 10.1 (a) Storage modulus of air laid flax composites at different fiber contents. (b) Dynamical mechanical results for composites with varying fiber content [2].

also increased with fiber mat content (see Figure 10.1a), and this can be interpreted as a result of good interfacial adhesion between the fiber and the matrix. The glass transition temperatures obtained from the peak of tan δ curve also increased with increasing fiber mat content as shown in Figure 10.1b, and this increase was also attributed to the good adhesion between fiber and the polymer matrix. High interfacial adhesion will decrease the mobility of the polymer chains in the interface, resulting in an increase in glass transition temperature. The impact resistance was the composites made from AESO and air laid flax mat was measured using a Charpy impact strength tester, and the results showed that the composites with higher fiber content possess higher impact resistance. The author also compared the impact resistance of the natural fiber filled AESO composites with those of glass fiber reinforced polyester, and the test results indicated that the glass fiber reinforced polyester has much higher impact resistance than the biocomposites composed of AESO and flax mat reinforcement.

Besides AESO, other versions of modified soybean oil were also used to produce composite materials. Adekunle et al. produced composites with methacrylated soybean oil (MSO), methacrylic anhydride modified soybean oil (MMSO), and acetic anhydride modified soybean oil (AMSO) [3]. MSO was synthesized using a similar route to the synthesis route of AESO, except that methacrylic acid instead of acrylic acid was used to ring open the epoxy ring on epoxidized soybean oil (ESO). MMSO and AMSO were produced by reacting methacrylic anhydride and acetic anhydride with ESO, respectively. Two types of flax fibers were used in this study: airlaid flax mat and woven fabric. Six combinations of vegetable oils were utilized as matrix: MSO, MMSO, AMSO, and the addition of 30 wt% ST to each type of vegetable oil. Adding styrene to the soybean oil increased the flexural strength and moduli of the composites considerably because styrene can produce composites with longer crosslinks. Composites made from MMSO have higher strength and modulus when compared to those made from MSO because MMSO contains more reactive double bond in the structure. Composites with AMSO possess lower flexural properties than MSO. On the other hand, composites made from MMSO showed relatively low impact strength compared with composites made with AMSO and MSO, and this is attributed to the fact that the high crosslink density produce from MMSO makes the polymer chain less flexible.

The effects of fabric architectures on the properties of the MESO-based composites were also investigated by Adekunle et al. [4]. It was found that flax mats with plain-weave architecture can produce composites with higher flexural properties and impact strength compared to twill-weave architecture. Hybrid composites with Lyocell fiber mat as the inner ply were also prepared in this paper. The hybridization with Lyocell fiber can reduce the water absorption dramatically because the Lyocell fiber itself has lower water absorption than other natural fibers. In the other paper published by the same author, the effect of surface weight (distance between adjacent roving wefts and warps) of the woven jute fabric was also investigated [5]. It was found that increasing the surface weight results in a decrease in mechanical properties. Because the weight percentage of fiber reinforcement in this study was controlled at a fixed percentage, increasing the surface weight results in a reduce number of plies in composites.

Khot et al. also produced flax composites, hemp composites, and glass/flax composites using copolymer of AESO, ST, and divinylbenzene (DVB) as resin [6]. The resin injection molding process was utilized to produce glass fiber reinforced composites. The glass fiber reinforced AESO composites containing 35 wt% of glass fiber possessed a tensile modulus of 5.2 GPa and tensile strength of 463 MPa. When the fiber loading increased to 50%, composites with tensile modulus as high as 24.8 GPa can be observed.

Glass/flax hybrid composites were also produced to obtain composite materials with a wide range of properties [7]. It was found that the mechanical properties of the glass/flax hybrid composites are highly dependent on the glass/flax ratio and the arrangement of fibers (see Figure 10.2) in the composite. As expected, the flexural modulus, flexural strength, and impact resistance decreased with increasing amount of flax fiber in the hybrid composite. Symmetric arrangement can produce composites with higher mechanical properties when compared to unsymmetrical arrangement at the same glass/flax ratio. Impact test showed interesting results. For unsymmetrical composites, if the flax face was impacted, the composites can absorb higher energy when compared to the situation when the glass face was impacted. In flexural testing of unsymmetrical arrangement, when the load is on the glass face, the composites showed lower flexural modulus and higher flexural strength than if the load is on the flax face. This study showed that for hybrid composites, the ratio between different fibers as well as the construction of the laminates will have a significant impact on the properties of composites.

Figure 10.2 Different modes of arrangement of fibers in the composite: symmetic composites (a); unsymmetric composites, loading on the glass fiber face (b); unsymmetric composites, loading on the flax fiber face (c) [7].

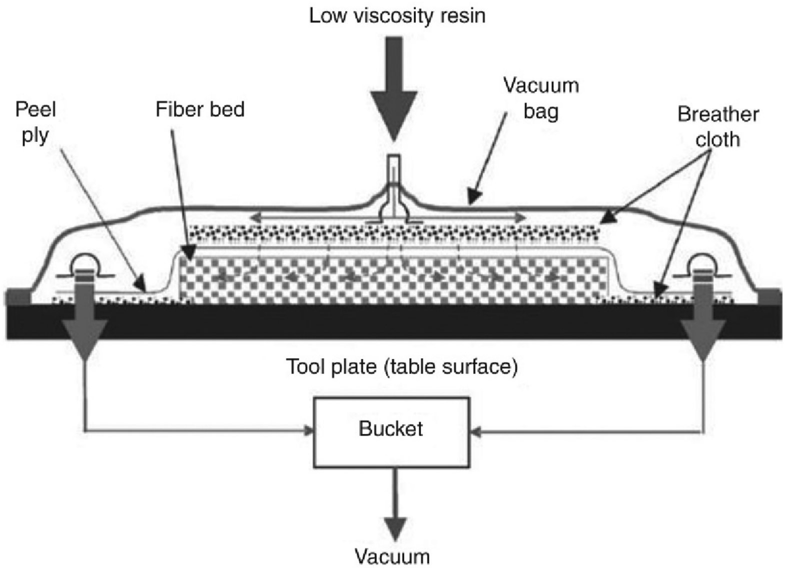


Figure 10.3 Schematic of vacuum-assisted resin transfer molding technique [8].

The vacuum-assisted resin transfer molding technique (see Figure 10.3) was also utilized to produce composite panel out of AESO-based resin [8]. Several kinds of natural fiber mats, including flax, cellulose, pulp, hemp, and recycled corrugated cardboard, were used as reinforcements. Among these reinforcements, recycled cardboard paper was found out to be the best reinforcement. With 55.2 wt% of the recycled cardboard paper, the storage modulus of the AESO resin was improved more than five times.

Hong et al. used keratin fiber to reinforce AESO-based and soybean oil pentaerythritol glyceride maleates (SOPERMA) resin [9]. Keratin fiber was obtained from chicken feather, and keratin fiber (KF) was made into mat. Composites containing 5–30 wt% of KF mat were put into the resin using vacuum-assisted resin transfer molding. The storage modulus was significantly increased with increasing amount of KF. For example, when 30% of KF was introduced into the AESO composites, the storage modulus increased by 58.8% when compared to neat resin. The glass transition temperature remains unaffected. However, when KF fiber was added to SOPERMA resin, the increase in modulus is not very pronounced. The maximum improvement in storage modulus is only 9.6% as shown in Table 10.1. On the other hand, the fracture toughness can also be increased by adding KF, and the increase in fracture toughness is more pronounced in AESO resin. In addition, the dielectric constants can be increased by adding more KF reinforcement.

Pyrolyzed chicken feather fibers (PFF) were also incorporated into vegetable oil-based resin to produce environmental friendly composite. A mixture of AESO and methacrylated lauric acid (MLAU) was used as the matrix. MLAU acts as a reactive diluent for AESO, and the ratio of AESO and MLAU was kept at 1:1 in this study. The storage modulus, tensile modulus, tensile strength, and fracture energy were found to be increased with increasing amount of PCFF; however, there is not a big difference in the reinforcement effect between untreated chicken feather and pyrolyzed chicken feather.

Bacterial cellulose (BC) was used as a binder for AESO-based resin and sisal fibers [10].

Table 10.1 Fracture Properties of AESO Composites Prepared by Vacuum-Assisted Resin Transfer Molding [9]

KF Content (wt%)	Max. Load *N*	Fracture Toughness K_{ic} (MPa $m^{1/2}$)	Fracture Energy G_{ic} (KJ/m^2)
0	97.6	1.458	1.420
5	97.1	1.455 (−0.2%)	1.610 (+13.4%)
10	103.0	1.524 (+4.5%)	1.759 (+23.9%)
20	113.0	1.672 (+14.7%)	1.820 (+28.2%)
30 (KF mat)	120.1	1.768 (+21.3%)	1.927 (+35.7%)
30 (hybrid mat)	130.7	1.931 (+32.4%)	1.945 (+37.0%)

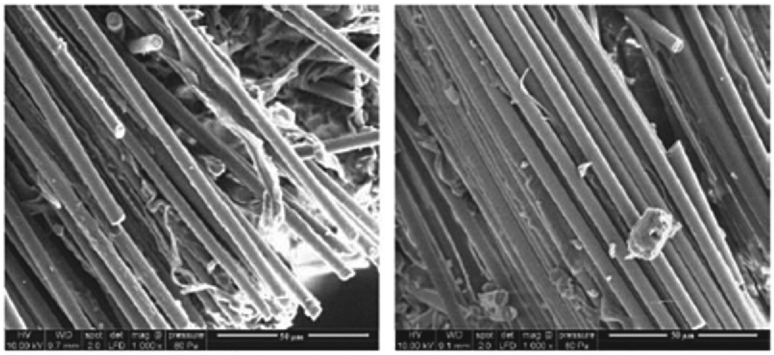
BC is a special type of cellulose produced by reacting *Gluconacetobacter xylinus* with cellulose, yielding a cellulose product with degree of polymerization around 6500. It was found that the BC can increase the mechanical properties of the sisal fiber. The BC-modified composites increased the tensile modulus and strength of neat AESO thermoset by 1300% and 600%, respectively. The reinforcement effect of BC-modified sisal fiber is much greater than the neat sisal fiber. The decrease in amplitude of tan δ was also observed after incorporating BC modified sisal, indicating that the fiber–matrix adhesion has been increased.

The effect of surface treatment on ramie fiber on the interfacial adhesion between the modified fiber and AESO was investigated [11]. Three different surface treatments were studied: (i) acetylation using acetic anhydride; (ii) silane treatment using triethoxyvinylsilane; and (iii) peroxide treatment using dicumyl peroxide. It was found that using surface treatment to modify or cover the OH groups on ramie fiber can lower the hydrophilicity of ramie fiber, and this can increase the interaction between the reinforcement and the matrix. In addition, the interfacial shear strength (IFSS) of AESO/ramie composites was increased significantly. Silane treatment yielded composites with highest interfacial adhesion between the fibers and the AEOS matrix. After the silane treatment, the IFSS increased around 75%. The author also investigated the effect of acetylation time on the IFSS of the final composites, and the result indicated that the IFSS of the composites increased with acetylation time. TGA data indicated that acetylation decreased the thermal stability of the ramie fiber, and this is ascribed to the etching and the disruption of the fiber structure. On the other hand, silane and peroxide treatments increased the thermal stability of the ramie fiber, which is due to the removal of hemicellulose and impurity by silane and peroxide treatments.

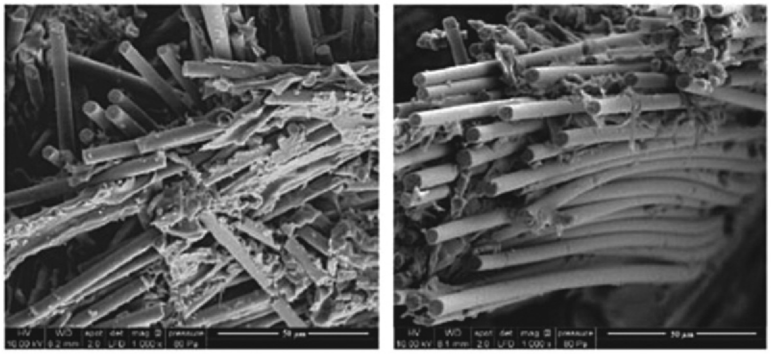
Green composites from maleated castor oil (MACO) and jute fibers were also studied [12]. The maleated castor oil was produced by adding maleic anhydride to castor oil in 3:1 molar ratio, followed by heating the mixture up at 125°C for 4 h. Due to the high viscosity of MACO, 20 wt% of tung oil was added to a reactive diluent. This resin system was polymerized using a free radical initiator. Nonwoven jute felts were used as reinforcement. In this study, the mechanical properties MACO/jute composites were compared to those of unsaturated polyester (UPE)/jute composites. The flexural moduli were very similar for these two composites; however, the flexural strength of MACO/jute composites was much lower than the flexural strength of UPE/jute composites. The UPE jute composites possess a flexural strength of around 35 MPa, while the MACO/jute biocomposites only have a flexural strength of 15 MPa, which can be ascribed to the higher hydrophobicity of the MACO resin compared to that of UPE. Because natural fibers are hydrophilic, the interfacial adhesion between the reinforcement and the matrix can be decreased if resin with higher hydrophobicity is used. The breaking strain of UPE/jute was about 60% lower. On the other hand, the impact strength of MACO/jute composites was 42% higher than that of UPE jute composites. The high impact strength of MACO/jute composite may be due to the presence of flexible fatty acid structure.

Vegetable oil thermoset synthesized by the ring-opening metathesis polymerization (ROMP) method was also utilized to produce composite materials. Henna et al. prepared glass fiber reinforced composites using a copolymer of Dilulin (a type of linseed oil modified with cyclopentadiene) and dicyclopentadiene (DCPD) as the matrix and the short glass fiber mat as the reinforcement. Second-generation Grubb's catalyst was utilized to initiate the polymerization process. An increase in DCPD content resulted in a dramatic increase in glass transition temperature, tensile strength, and Young's modulus because DCPD is a rigid crosslinker in the crosslink network. Thermoset containing 30 wt% of DCPD exhibits a tensile strength and Young's modulus of 0.5 and 0.91 MPa, respectively, while thermoset with 70% of DCPD possesses a tensile strength closed to 30 MPa and a Young's modulus around 525 MPa. Higher glass fiber content increased the tensile properties of the composites. Composites fabricated using 70% DCPD as resin and 56 wt% glass fiber can reach a tensile strength of around 170 MPa and a Young's modulus of around 1.5 GPa. The amount of glass fiber incorporated into the composites did not affect the glass transition temperature. In addition, SEM images indicated that there is a weak interfacial adhesion between this type of vegetable oil-based matrix and glass. The author also found that the modulus values of the obtained composites are far below those predicted by the Halpin–Tsai and Cox model, indicating that a weak adhesion exists between the fiber and the matrix.

The copolymer of Dilulin and DCPD showed weak adhesion with the fiber reinforcement; hence, Cui et al. investigated the possibility of using silane coupling agent to increase the fiber–matrix adhesion [13]. Norbornenylethyldimethylchlorosilane (MCS) and Norbornenylethyltrichlorosilane (TCS) were used because they contain norbornene groups that can participate in the ROMP reaction. MSC contains only one hydrolyzable group, while TCS contains three hydrolyzable groups. The silane is first hydrolyzed in the presence of water and then undergoes condensation reaction with hydroxyl groups on the surface of glass fiber to form strong siloxane bonds. The results indicated that grafting of silane onto the glass fiber can improve the interfacial adhesion between the matrix and the fiber, the storage modulus, interfacial shear strength, and interlaminar shear strength of the final composites have been improved. MCS can provide a better improvement of the mechanical properties compared to TCS because MCS has a higher covalent bond density as shown in Figure 10.4. Cui et al. also used the pultrusion process to fabricate glass fiber reinforced composites using Dilulin/DCPD as the matrix along with MCS as the silane coupling agent [14]. Flexural testing showed



(a) Untreated (b) Heat-cleaned



(c) MCS-treated (d) TCS-treated

Figure 10.4 SEM images of fracture surfaces for composites made with different types of fibers [13]. (a) Untreated, (b) heat-cleaned, (c) MCS-treated, (d) TCS-treated.

that the flexural strength and modulus can be increased by increasing silane concentration; however, if the concentration of silane coupling agent was above 3%, the increase in interfacial bonding became less pronounced.

A series of composites using conjugated vegetable oil as the matrix have been studied [15–22]. Most vegetable oils do not contain conjugated double bonds; as a result, the reactivity of the unmodified vegetable oils is very low, resulting in materials with low mechanical properties. The conjugation of vegetable oil can be achieved by using a rhodium-based catalyst [23]. Lu et al. produced glass fiber mat reinforced composites based on regular and conjugated corn oil. ST and divinylbenzene (DVB) were used as co-monomers in order to increase the mechanical properties of the corn oil-based thermoset [15]. The polymerization was initiated by a cationic polymerization initiator called boron trifluoride diethyl etherate (BFE). The tensile modulus of the conjugated corn oil-based composites increased from 4.7 MPa to 933 MPa, and the tensile strength increased from 2.0 MPa to 12 MPa when 45 wt% of glass fiber was incorporated. Composites using conjugated corn oil as the matrix showed higher mechanical properties than composites made from regular corn oil, which is ascribed to the increase in reactivity of corn oil after conjugation. An increase in DVB content can increase the crosslink density of the thermoset, resulting in a significant improvement in mechanical properties and thermal stability of the composites. Even though the mechanical properties have been improved significantly by adding glass fiber and DVB, the composites only showed a maximum tensile strength of around 12 MPa, which is relatively low compared to the commercially available polymer composites. Conjugated soybean oil and conjugated low saturation soybean oil were used by Lu et al. to produce composites reinforced by glass fiber mat [16]. ST and DVB were also used as comonomers. The conclusions are generally the same as those in Ref. [15]. However, the composites produced using soybean oil have higher mechanical properties than those produced from soybean oil because soybean oil contains more carbon–carbon doubles than corn oil.

Pfister et al. developed biocomposites using free radically polymerized conjugated linseed oil resin as the matrix and wheat straw (WS) as reinforcement. DVB and *n*-butyl methacrylate (BMA) were used as copolymer, and 5% *t*-butyl peroxide (TBPO) was used as a free radical initiator. Wheat straw acts as an effective reinforcement for the vegetable oil-based matrix. The modulus and tensile strength increased systematically with increasing amount of WS when the content of WS was in the range of 50–80 wt%. The mechanical properties of the composites with 90 wt% of WS do not follow the above trend due to improper wetting. Since agriculture fibers are generally not thermally stable, adding more WS resulted in a decrease in faster thermal degradation. When the length of the WS was reduced, the Young's modulus of the composite was decreased, while the tensile strength did not exhibit a clear tread. In addition, increasing the size of the WS fibers also resulted in significant increase in water absorption. The effect of compression molding pressure on the final mechanical properties was also investigated. When the molding pressure increased from 400 to 600 psi, the Young's modulus, tensile modulus, and thermal stability increased slightly, while the water absorption was reduced considerably. It was also found that incorporating maleic anhydride can increase the fiber–matrix interaction, thus increasing the thermal and mechanical properties. In addition, similar results were found when using switchgrass and corn stover (see Figure 10.5) as the reinforcement [19,22]. The same natural fibers were also incorporated into cationically cured

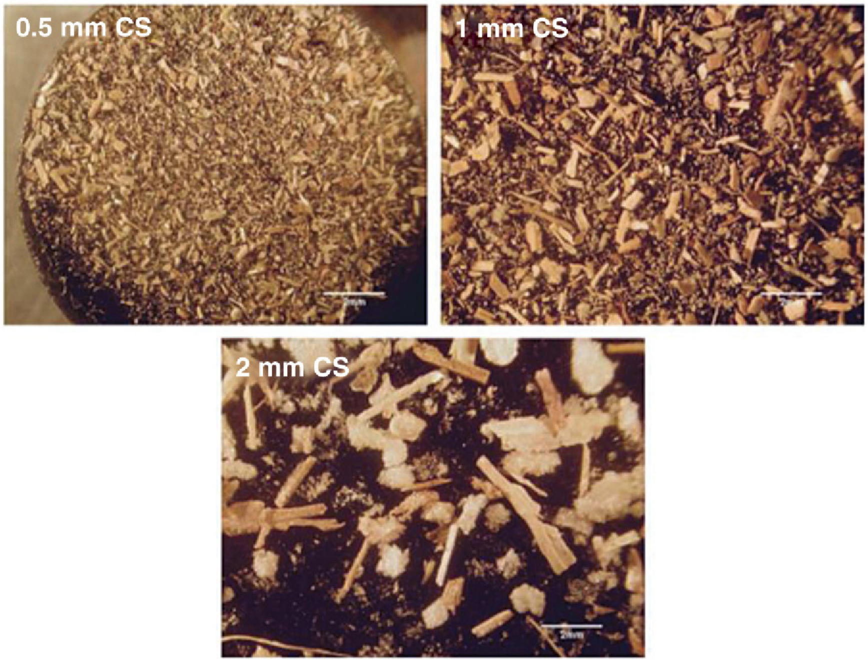


Figure 10.5 Microscope images of 0.5, 1, and 2 mm CS at 8× magnification [19].

vegetable oil thermoset, and the results were slightly different than the composites made with free radically cured resin. When the fiber content was controlled at 75 wt%, the Young's modulus increased significantly; however, unlike the composites made with free radically cured resin, the tensile strength of these cationically cured composites was inferior to the tensile strength of the pure resins. The decrease in tensile strength is probably due to the poor interfacial interaction between the fiber and the matrix. Among corn stover, wheat straw, and switchgrass, the wheat straw can provide the highest improvement in Young's modulus.

10.3 Fiber-Reinforced Plant Oil-Based Epoxy Composites

Chandrashekhara et al. reported composites produced by reinforcing partially biobased epoxy by glass fiber; the pultrusion process was used to fabricate composites [24]. Epoxidized allyl soyate (EAS) was blended with Epon 9500, a petroleum-based epoxy resin designed for the pultrusion process. The EAS was synthesized by first performing transesterification on soybean oil suing methyl alcohol and allyl alcohol to produce fatty acid methyl ester and fatty acid ally ester. Then, the fatty acid esters were epoxidized to produce soyate epoxy resin. 10% to 30% of EAS was blended with EPON 9500. Composites with 63% volume fraction of glass fiber were produced using a pultrusion machine. It was found that incorporation of 10–20 wt% of epoxidized allyl soyate into epoxy yielded a material with a toughness that is much higher than pure Epon 9500 resin. The epoxy with 10% EAS was found to have higher tensile strength and tensile strain than that of pure Epon 9500. The flexural strength of the composites decreased systematically with increasing amount of EAS in the resin. The composites containing 10% EAS in the resin have a flexural modulus about 100 MPa lower than that of composites made using 100% Epon 9500 as the resin. In addition, the incorporation of EAS can improve the impact damage resistance of the composites. It was also found that the average pulling force needed in pultrusion decreased with increasing amount of EAS in the resin, indicating that adding EAS can make the petroleum-based resin more suitable for the pultrusion process.

Boquillon et al. used epoxidized oil-based thermoset reinforced with hemp fibers to produce biorenewable composites [25]. The vegetable oil-based thermosetting resin contains epoxidized linseed oil with methyl terahydrophthalic anhydride as a hardener. The flexural modulus and flexural strength of the composites increased systematically when the hemp fiber volume fraction was in the range of 0–30%. Composites with more than 30% volume fraction of fibers possessed flexural properties lower than that of composites with less than 30% volume fraction of hemp fibers. A good level of interfacial adhesion was also observed under SEM. Composites with different lengths of hemp fibers were also produced. The flexural modulus increased with increasing fiber length. The flexural strength also increased with increasing fiber length, except when the fiber length is below 2 mm. Composites reinforced by hemp fibers with a length of 1 mm possessed lower flexural strength than the neat resin, indicating that the critical length for this composite system is between 1 mm and 2 mm. The DMA test showed that the introduction of hemp fibers significantly increased the storage modulus in rubbery region. On the other hand, the glass transition temperature of the composites decreased with increasing volume fraction of hemp fiber reinforcement. The decrease in glass transition temperature is probably due to the reaction between the anhydride hardener and the hydroxyl groups on the hemp fiber; as a result, less amount of anhydride was reacted with the epoxide group, producing materials with lower glass transition temperature.

Liu et al. fabricated composites using a blend of ESO and petroleum-based epoxy as resin using solid freeform fabrication (SFF) methods. SFF is a rapid prototyping technique that produces products without molds. This concept is very similar to 3D printing. In this study, ESO was blended with Epon 828 resin using a weight ratio of 1:0.3. Four different fibers were used as reinforcement, namely, E-glass fiber, carbon fiber, Franklin fiber, and wollastonite. It was found that the glass fiber and carbon fiber produced composites with better mechanical properties compared to those reinforced with mineral fibers. Combinations of fibers were also used to produce hybrid composite, and the result indicated that the hybrid composites have higher strength and modulus than composites made with a single type of fiber. Three different amine-curing agents were used, including diethylenetriamine (DETA), triehylenetetraamine (TETA), and polyethylenimine. It was found that polyethylenimine yielded composites with lowest properties, while TETA performed the best.

Composites from epoxidized soybean oil and flax fiber were studied [26]. ESO was blended with 1,1,1-tris(*p*-hydroxyphenyl) ethane triglycidyl ether (THPE-GE) in different ratios. The flexural modulus and flexural strength increased when the THPE-GE amount increased in the resin. The flax fibers were chopped into short fibers. In general, the mechanical properties of a composite will be improved by adding more volume fraction of fiber; however, in this study, the mechanical properties of the composites reached its maximum at 10 wt% of fiber. At fiber content above 10 wt%, the mechanical properties of the composites decreased. The decrease in flexural properties at high fiber loading is ascribed to the increase in fiber-to-fiber interaction and problems in fiber dispersion. In addition, it was found that the longer the fiber, the higher the mechanical properties. The other study performed by the same author focused on modification of flax fibers to produce biocomposites with enhanced properties [27]. Two methods of chemical modifications were investigated. The first method is to coat the flax fiber with a milk protein gel to increase the water resistance of the fiber. The second method involved acrylation in the presence of excess canola oil with Rhizopus oryzae lipase as the catalyst. Both these two modification methods can increase the water resistance of the composites, and lipid acrylation produced composites with lowest water uptake. When the flax fibers are coated with protein, methanol groups on the protein can react with hydroxyl groups on the flax fibers to form covalent bonds, which are more water resistant. On the other hand, the increase in water resistance of flax fibers after lipid acrylation may be due to the hydrophobicity of the fatty acid chain and high efficiency of acrylation catalyzed by enzyme. Lipid acrylation can also increase the tensile properties of the composites, which can be ascribed to the increase in interfacial adhesion between the fiber and the matrix. The increase in interfacial adhesion can also be due to the compatibility between the fatty acid chain on the lipid acrylated flax fibers and the ESO.

Besides using epoxidized vegetable oil and natural fibers to produce green materials, attempts have been made to use biobased anhydride to cure the epoxidized vegetable oil [28]. Takahashi et al. used a terpene-based acid anhydride (TPAn) to cure ESO. In addition, maleinated linseed oil (LOAn), hyxahydrophthalic anhydride (HPAn), and thermal latent cationic polymerization catalyst (CPI) were also used for comparison. Among these four curing agents, ESO-TPAn resin can produce materials with highest glass transition temperature and highest tensile properties. Lyocell fibers were used to reinforce the ESO-TPAn resin (with epoxy/anhydride ratio of 1:1). The tensile strength of the composites increased with increasing Lyocell fiber content. After 75 wt% of Lyocell fiber was added, composites with a tensile strength of 65 MPa and a tensile modulus of 2.3 GPa could be produced, and the mechanical properties of the composites were three times higher than those of neat ESO-TPAn resin.

Crivello et al. prepared glass fiber reinforcement composites using UV-cured epoxidized vegetable oils as the matrix [29]. ESO or epoxidized linseed oil (ELO) was blended with a petroleum-based epoxide. Onium salt cationic photoinitiator was added to the resin to allow for UV polymerization. With the photoinitiator, the gelation time of the resin can be as short as 7 s. It was also found that the sizing on the glass fiber increased the gelation time of the resin, indicating that the sizing agents retarded the photopolymerization process, but the retardation effect was not strong enough to completely inhibit polymerization. On the other hand, if the size agents were removed, the modulus of the composites decreased significantly, indicating that removing sizing agent decreased the fiber–matrix adhesion. This UV-cured epoxidized vegetable oil-based has almost infinite shelf life when it is not exposed to light, and this resin system does not require refrigeration.

Manthey et al. prepared composites based on epoxidized hemp oil (EHO) [30]. Unlike soybean oil, which is the most commonly used vegetable oil in polymer science research, hemp oil is not used in food production. Using hemp oil to produce polymeric materials can eliminate ethical issues. In this study, EHO or ESO is mixed with a petroleum-based epoxy resin, and the properties of EHO-based thermoset and ESO-based thermoset were compared. The impact resistance of the petroleum epoxy can be increased by adding EHO or ESO. The incorporation of fatty acid chain increased the flexibility of the crosslink network, resulting in an increase in impact resistance. Adding ESO to petroleum-based epoxy resulted in a more pronounced increase in impact resistance compared to adding EHO. This is due to the lower number of crosslinking sites of ESO when compared to EHO and the petroleum-based epoxy. On the other hand, adding EHO or ESO to the petroleum-based epoxy resulted in a decrease in ILSS due to the increase in interfacial strength. The flexural testing data indicated that EHO-based thermoset possessed higher flexural strength than the ESO-based thermoset. The same trend was observed for jute fiber mat-reinforced composite samples. Interestingly, the flexural strength of the biocomposites was lower than the flexural strength of the neat resin, and this may be a result of low fiber–matrix adhesion. Water absorption data showed that EHO-based resin and the composite have marginally lower water absorption than ESO-based resin and composites. The author concluded that the EHO can compete with the commercially produced ESO in terms of mechanical properties and water-absorption characteristics when using as the matrix material for jute fibers.

10.4 Fiber-Reinforced Plant Oil-Based Polyurethane Composites

Polyurethane (PU) composites were produced using soybean oil-derived polyol reinforced by glass fiber [31]. Soybean phosphate ester polyol (SEPEP) was combined with polymeric 4,4′-disphenylmethane dissocynate (pMDI) to produce PU. Increasing the glass fiber content increases the storage modulus and the glass transition temperature of the composite. Flexural testing and tensile testing both indicate that the strength and modulus of the PU can be increased when more glass fibers were added. Moreover, the impact strength was enhanced when more glass fiber was added, indicating that the incorporation of glass fiber introduces a new energy dissipation mechanism. SEM image showed that a good distribution of glass fiber, good wetting, and good interfacial adhesion can be observed in the composites with soybean oil-based PU as the matrix material.

Husic et al. compared the properties of the resins and the glass-reinforced composites prepared using soybean oil-based PU or petroleum-based PU as the matrix [32]. The soybean oil-based polyol used in this study has a hydroxyl number of 204 mg KOH/g, while the hydroxyl number of the petroleum-based polyol (polypropylene oxide-based triol) is 650 mg KOH/g. The soybean oil-based PU composites possessed similar flexural strength, tensile strength, and ILSS when compared to the composites prepared by the petroleum-based PU, even though the petroleum-based showed marginally better strength as shown in Figure 10.6. The flexural modulus and Young's modulus were lower for the soybean oil-based PU composite due to lower crosslinking density and the presence of dangling fatty acid chains. For the same reason, the glass transition temperatures of the soybean oil-based PU and composite were lower than those of petroleum-based PU and composite.

The fracture toughness of castor oil-derived PU/natural fibers composites was extensively studied by Silva et al. [33]. Sisal short fibers, coconut short fibers, and woven sisal fabric were used in their original states or after chemical treatment with sodium hydroxide. The alkaline treatment using sodium hydroxide decreased the fracture toughness of the sisal fiber composites due to the increase in interfacial adhesion between the fiber and the matrix. The increase in interfacial adhesion reduced the chance of debonding and fiber pull-out, which is

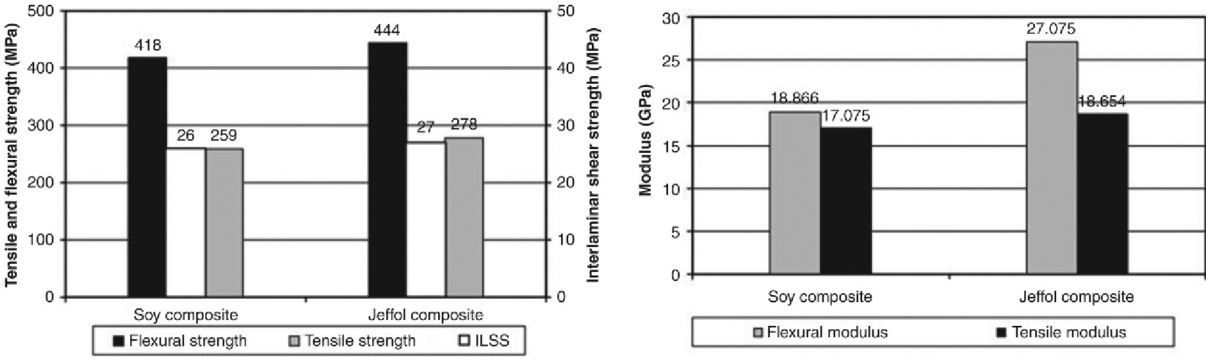


Figure 10.6 Flexural, tensile and interlaminar shear strength (ILSS), modulus of the soy and Jeffol composites [32].

the main energy absorption mechanism. In contrast, treating coconut fiber using sodium hydroxide was beneficial to the coconut fiber composites. The increase in fracture toughness could be ascribed to the fibrillation process after alkaline treatment. The fibrillation process promoted an easy pathway for crack propagation and increased the friction between split fibers under loading. The fracture toughness of the sisal fabric composites was higher than those composites containing sisal short fiber and coconut short fibers. The high fracture toughness is due to the contraction of yarns in the interlacement points of fabric and the friction and shear among the fibers. Even though alkaline treatment can enhance the fiber–matrix interfacial adhesion, resulting in the improvement of mechanical strength; however, at the same time a strong interfacial adhesion can decrease the fracture toughness, damping, and fatigue resistance [34].

Milanese et al. compared the flexural properties of the sisal/castor oil-based PU composites to sisal/phenolic composites [35]. Sisal fibers were used in its woven form. The effects of thermal treatment at 60°C for 72 h on the final mechanical properties of the composites were also studied. The thermal treatment can increase the adhesion between fiber and matrix and reduce the water absorption of the sisal fibers [36]. 44 wt% of sisal fibers was added to the sisal/PU resin and 33 wt% of sisal fibers was added to the sisal/phenolic resin. The addition of sisal fibers can increase the flexural strength of both the resin system, but the phenolic resin possessed much higher mechanical properties compared to the biobased PU. After thermal treatment of the sisal fibers, the flexural strength of the sisal/PU composites increased from 1.6 MPa to 3.7 MPa, while the flexural strength of the sisal/phenolic composites increased from 10.7 MPa to 11.2 MPa. The flexural modulus also increased if sisal fibers were thermally treated.

Polyester nonwoven fabric was used to reinforce castor oil-derived PU [37]. A significant increase in mechanical properties was observed after adding the polyester nonwoven fabric to the castor oil-derived PU. Two different isocyantes were used to react with castor oil-based polyol to produce PU, namely, toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI). The tensile strength increased about four times and seven times for PU using TDI and HMDI as isocyanate, respectively. Moreover, the tensile strength increased about nine times and seven times for PU made using TDI and HDMI, respectively. The increase in tensile properties indicates the good interfacial adhesion between the matrix and the fiber. The HMDI-based PU showed better chemical resistance compared to the TDI-based PU. The water resistance is very similar for both types of PU.

Composites produced from castor oil-derived PU and alfa stems fiber were studied [38]. The PU was prepared from directly using castor oil and HDI. The fibers were produced from using potassium hydroxide to extract the cellulose in the alfa plant. The composites were prepared by adding the alfa stem fibers to the PU prepolymer in acetone. The glass transition temperature of the composites increased as the percentage of fiber increased. The increase in glass transition temperature is due to the interaction between the fiber and the matrix due to hydrogen bonding and/or covalent bonding. The low thermal stability of the natural fibers made the thermal stability of the overall composites decrease with increasing fiber loading. The Young’s modulus increased with increasing fiber loading up to 20 wt%

fiber. The modulus of the composites started to increase with fiber loading above 20 wt% due to low fiber–matrix adhesion. The composites presented in this chapter possessed low mechanical properties even with the alfa stem fiber reinforcement. The maximum Young's modulus and tensile strength of this composite system were 110 and 3.17 MPa, respectively. Since the author reacted the castor oil directly with HDI without any co-monomers or other chemical modifications, the mechanical properties of the PU should be low due to the low number of hydroxyl groups in castor oil.

Manjula et al. used silk fibers as the reinforcement for a chain-extended castor oil-derived PU to produce biocomposites [39]. The chain-extended PU was synthesized by reacting castor oil with diisocyante, followed by adding glutaric acid as a chain extender as shown in Figure 10.7. Five to ten percent of silk fiber was added to produce composites. The purpose of adding chain extender is to increase the hydrogen bonding in the polymer. The addition of 10% fibers can increase the tensile strength and the tensile modulus of the composites around 100%. The surface hardness can also be increased with the incorporation of silk fibers. DMA test confirmed that the glass transition temperature of the composites increased with higher fiber loading. The increase in mechanical properties and glass transition temperature is due to the good interfacial adhesion between the matrix and the reinforcement.

PU composites prepared using palm oil-derived polyol and oil palm trunk (OPT) fiber were studied [40]. The PU was synthesized by reacting palm oil–oleic acid and glycerol to produce a polyol, and then the polyol is reacted with 4,4-diphenylmethane diisocyante (MDI) to produce PU matrix. Ten to forty percent of polycaprolactone (PCL) was also added as a compactabilizer of the fiber

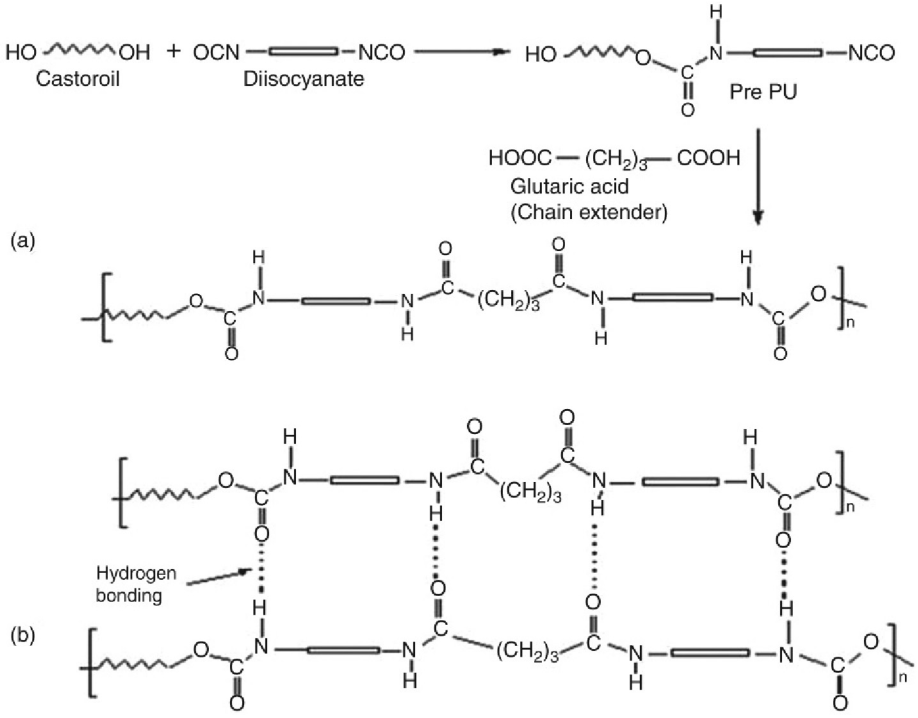


Figure 10.7 (a) Chain extended PU and (b) hydrogen bonding in chain extended PU [39].

and the PU matrix. The tensile strength and tensile modulus of the composites increased with increasing amount of PCL. SEM micrographs indicated that an improvement of interfacial adhesion was observed when more PCL was added. The addition of PCL can also increase the thermal stability of the composites. Moreover, PCL can also increase the glass transition temperature of the composites.

Rubber seed oil (RSO) was also used to produce biobased PU and composites [41]. Rubber seed oil contains about 77% of unsaturated fatty acids. RSO was saponified into monoglyceride by reacting RSO with glycerol at higher temperature in the presence of calcium oxide catalyst. Afterward, TDI was added to produce PU. Biocomposites were prepared by adding 10–30% of unidirectional long sisal fibers to the matrix. As expected, the tensile and flexural strength and moduli were enhanced with the addition of sisal fibers. The tensile strength of the neat PU polymer was 4.8 MPa. After 15% of reinforced was added, the tensile strength increased remarkably to 57.4 MPa. However, when the fiber content was at 30 wt%, the flexural modulus and flexural strength of the composites at this fiber loading were lower than the composites with 25 wt% fiber. The decrease of flexural properties at high fiber loading is due to fiber agglomeration and the formation of microvoids. The thermal stability of the composites was lower than that of the neat RSO-derived PU but higher than that of neat sisal fibers. In addition, the effects of water absorption on the mechanical properties of the composites were also investigated. Since natural fibers are hydrophilic, when more sisal fibers were added, the water absorption of the composites increased. A light loss in tensile strength and flexural strength was observed. On the other hand, enhancement in flexural modulus was observed after water immersion. The maximum tensile elongation was increased after water immersion. The increase in elongation is due to the fact that water molecules act as a plasticizer agent in the composites. Water molecule can fill the cavities and the cracks within the composites, leading to an increase in the flexural modulus [42].

The influences of alkaline treatment on short random banana fibers and the length of fibers on the properties of banana fibers/castor oil-derived PU were investigated [43]. After surface treatment, the tensile strength of the fiber was higher than those of the untreated banana fibers. The untreated banana fibers possess a tensile strength and tensile modulus of 162 MPa and 8.5 GPa, respectively. After alkaline treatment, the tensile strength and modulus increased to 269 MPa; however, the Young's modulus decreased to 7.1 GPa. The maximum elongation of the fiber doubled after alkaline treatment. The increase in tensile strength of the fibers after treatment is due to the removal of lignin and hemicelluloses, which allows the rearrangement of fibrils along the direction of tensile load. The IFSS increased dramatically after alkaline treatment. When the length of the embedded fiber increased, the IFSS was also improved. The tensile strength and Young's modulus also increased when treated fiber and longer fiber were used. The DMA test also showed the glass transition temperature shifted to higher temperature with the addition of banana fibers. The enhancements in mechanical properties and glass transition temperature are due to higher interfacial adhesion between the fibers and the matrix.

Merlini et al. developed electric conductive composites for pressure-sensitive applications by using polyaniline-coated coconut fibers as the reinforcement and castor oil-derived PU as the matrix [44]. The polyaniline coated coconut fibers (CF-PANI) were prepared by *in situ* oxidative polymerization. The reaction was carried out using hydrochloric acid as a solution and iron (III) chloride hexahydrate ($FeCl_3$) or ammonium persulfate (APS) as the oxidant. The composites were prepared by using compression molding. The electrical conductivity of the coconut fibers increased from 3.13×10^{-10} to 1.5×10^{-1} and 1.9×10^{-2} when using $FeCl_3$ and APS as the oxidant, respectively. The polyaniline-coated fibers have lower conductivity compared to polyaniline itself. The PU composites containing 20–25 wt% of CF-PANI with $FeCl_3$ as an oxidant showed a variation in electrical conductivity when a compress load was applied as shown in Figure 10.8. This property can be used to develop conducting polymer composites for pressure sensor applications.

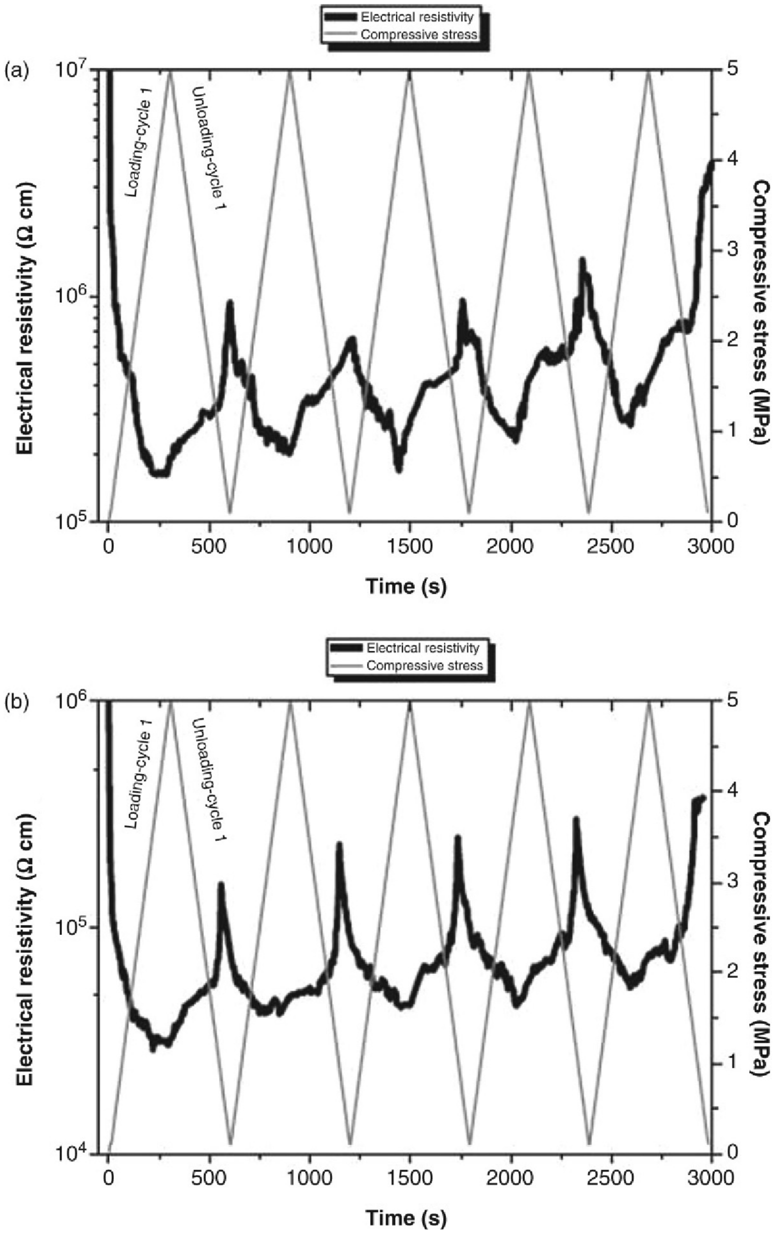


Figure 10.8 Electrical resistivity as a function of compressive loading–unloading stress cycles applied to PU/CF-PANI.$FeCl_3$ composites with CF-PANI.$FeCl_3$ contents of (a) 20 wt% and (b) 25 wt% [44].

10.5 Fiber-Reinforced Plant Oil-Based Foam Composites

Wu et al. prepared biobased foam composite using AESO as matrix and short sisal fibers as reinforcement [45]. This biobased foam composite can find their applications in car interior and acoustic insulation applications. The sisal fibers were chemically treated using alkali or silane coupling agent. AESO with 20 wt% of ST was used as the foam matrix. The foam was prepared by using a water-blown method with $NaHCO_3$ as the blowing agent. The addition of sisal fibers can increase the compressive modulus and the compressive strength of the composites. The compressive properties of these composites were also compared with a commercially available petroleum-based unsaturated polyester foam, and the SEM image showed the sisal fibers were embedded in the cell walls of the foam matrix, which resulted in good mechanical properties. Both alkali treatment and silane treatment led to increase in interfacial adhesion. The author also conducted a biodegradation test by burying the composites under soil. After 3 months, 12–20% of weight loss was observed depending on the fiber loading. Higher sisal fiber loading led to acceleration of the biodegradation rate. This study indicated that AESO-based foam reinforced with sisal fibers can replace the petroleum-based unsaturated polyester foam in terms of mechanical properties. Moreover, the biobased foam possesses biodegradability while the unsaturated polyester does not.

Zhu et al. fabricated soybean oil-derived rigid polyurethane foams composites reinforced by cellulose microfibers and nanoclays [46]. The foam was prepared using a water-blown method. SEM and X-ray study revealed that the addition of microfibers and nanoclays can modify the cellular structure of the foams. The average cell size was decreased and the cell size distribution was narrowed by the addition of microfibers and nanoclays as shown in Figure 10.9. The incorporation of cellulose nanofibers made the composite more thermally stable. The addition of cellulose nanofibers and nanoclays also increased the mechanical properties of the foam.

Aranguren et al. prepared microfoams based on castor oil-derived PU and vegetable fibers (see Figure 10.10) such as pine wood fibers and hemp fibers [47]. PU foams reinforced with hemp fibers showed better mechanical properties due to its larger aspect ratio. For pine wood fibers, the flexural properties decreased as the length of the fiber increased. The glass transition temperature was also increased by the addition of fibers. In addition, this PU foam contains no catalyst; as a result, these materials will suffer aging due to the secondary reaction of the unsaturation presented in the castor oil-based polyol. Since aging is the crosslinking reaction, the modulus and strength can be improved after aging.

Gu et al. investigated the effects of wood fiber and microclay on the properties of soybean oil-derived PU foams [48]. It was found that the NCO index greatly influenced the mechanical and thermal properties of the PU foams. Different NCO indexes will produce polyurethane with different rigidity. The author of this chapter produced three different types of PU foams by altering the NCO index: flexible foams, semirigid foams, and rigid foams. Both the wood fiber and microclay can increase the compressive strength of the semirigid to rigid foams. For semirigid and rigid foams, wood fibers can produce PU foams with higher compressive properties when compared to the microclay reinforced

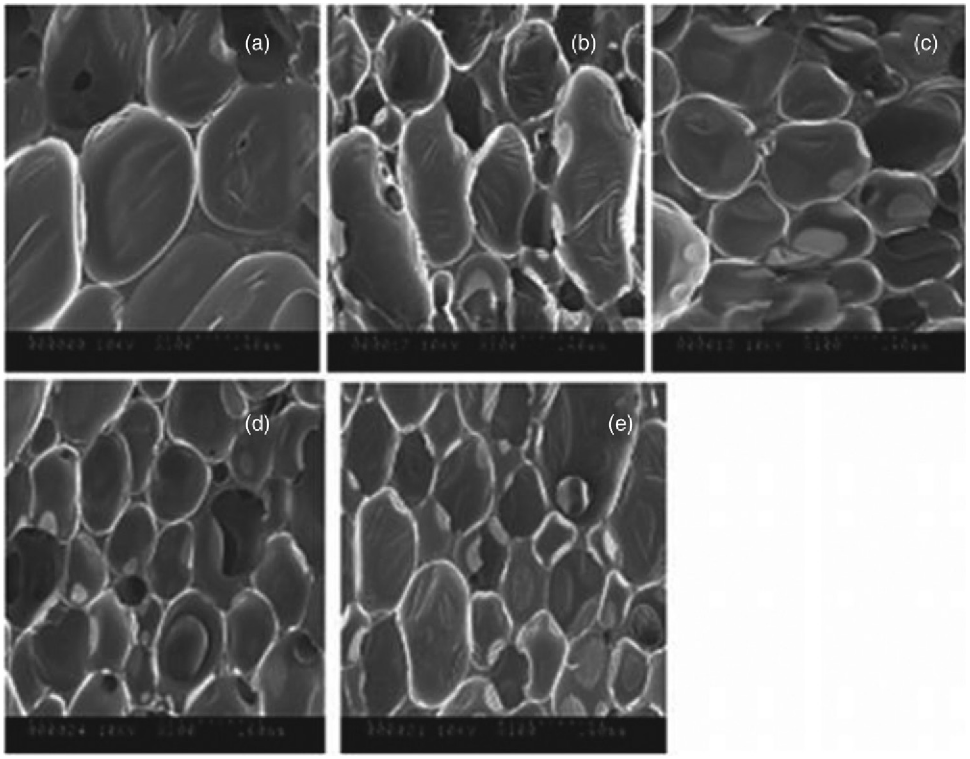


Figure 10.9 SEM micrographs (parallel to the blowing direction of foam): (a) neat foam; (b) foam with microfibers; (c) foam with Cloisite Na+; (d) foam with Cloisite 93A; (e) foam with Cloisite 30B [46].

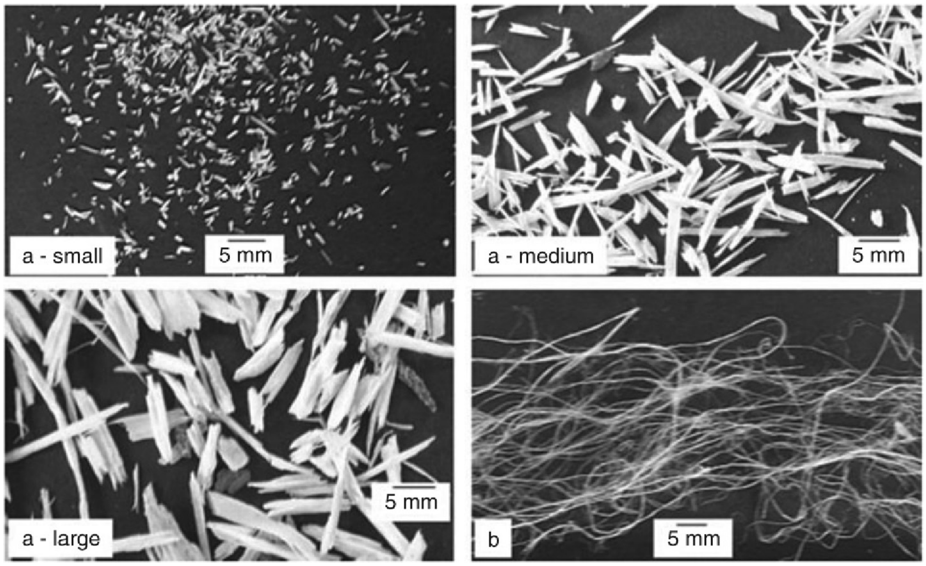


Figure 10.10 Images of reinforcing fibers (a) pine wood fibers, (b) hemp fibers [47].

foams. The tensile strength was degraded for the rigid foams with the addition of the wood fiber or microclay due to the formation of rigid polyurea, which deteriorates the tensile strength. For the flexible foam, the addition of wood fiber or microclay decreased both the tensile and compressive properties. The author also proposed that wood fibers and microclay exhibited different reinforcement mechanisms. Wood fiber tends to form chemical bonds during foaming, while microclay tends to form physical insertion.

10.6 Conclusion

In recent years, many plant oil-based polymers with a wide range of properties have been developed. Vegetable oils are attractive starting materials for preparing polymers because they are relatively inexpensive, commercially available, and most of them are not toxic to humans. Vegetable oils also contain many active functional groups, such as double bonds and hydroxyl groups, which can be chemically modified to produce polymers with desired properties. By using different chemical modification methods and different polymerization methods, plant oil-based vinyl polymers, plant oil-based epoxies, and plant oil-based polyurethane and polyurethane foams, both synthetic fibers and natural fibers have been incorporated into different kinds of plant oil-based polymer to produce composites. Glass fibers are the most commonly used reinforcement in the area of polymer science. Synthetic fibers such as glass fibers have high mechanical properties compared to natural fibers; however, synthetic fibers are relatively expensive and not biorenewable. On the other hand, natural fibers such as hemp fibers, jute fibers, sisal fibers, and cellulose fibers are relatively cheap and biorenewable, but they have drawbacks such as low mechanical properties and being hydrophilic. The addition of fiber reinforcement can generally increase the strength and modulus of the neat matrix. Depending on the level of interfacial adhesion, an increase in glass transition can also be observed in some cases.

When plant oil-based vinyl polymers were used as matrix, acrylate version of soybean oil, such as acrylated epoxidized soybean oil, is most commonly used as the plant oil component of the matrix due to its high availability, high mechanical properties, and high reaction rate during free radical polymerization. Due to the high viscosity of AESO, reactive diluent such as styrene is often added to AESO to make it more processable. Conjugated vegetable oils can be obtained by using Rhodium-based catalyst, and the conjugated version of vegetable oil has been reinforced by glass fibers and many other natural fibers to produce composites using free radical polymerization or cationic polymerization method. Ring-opening metathesis polymerization (ROMP) has been used to produce matrix with good mechanical properties. When using plant oil-based epoxy resin as the matrix, the epoxidized vegetable oil is always blended with petroleum-based epoxy resin to produce materials with acceptable mechanical properties. Normally, the percentage of the plant oil-based component is below 40%.

Surface modifications on the fibers can also influence the properties of the composites significantly. Alkaline treatment and silane treatment are the most important ones. Novel modification methods such as protein coating and peroxide treatment have also been developed. Surface modifications on fibers can increase the interfacial adhesion between the fibers and the matrix, resulting in composites with higher mechanical and thermal properties. Besides the surface modifications, the length, architecture, and the order of the fiber reinforcements also have great influence on the properties of the composites.

Almost all of the studies in vegetable oil-based composites involve the use of petroleum-based comonomers, so the composites matrix is not completely biobased. In the future, composites with increasing biorenewable contents and higher mechanical properties should be produced.

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11 Application of Plant Oil-Based Products in Structural Health Monitoring

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11.1 Introduction

Structural health monitoring (SHM) is the automated process of damage diagnosis, localization, and prognosis, which leads to structural condition assessment. Such automation is typically provided by a combination of sensors, data acquisition systems, and signal processing algorithms, and is meant to replace visual inspections, which are ineffective and judgement-dependent, and nondestructive evaluation techniques [1,2], which

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are expensive and require highly trained inspectors [3]. There is a particular challenge in SHM associated with condition assessment of large-scale structures, including energy systems (e.g., wind turbine blades), aerospace structures (e.g., aircrafts), and civil infrastructures (e.g., bridges), due to the lack of scalability of existing sensing solutions. Off-the-shelf sensors, for instance accelerometers and strain gauges, are expensive to deploy over large geometries and/or do not provide a clear link between the signal and the condition of a structure.

With the recent technological developments in conducting polymers [4], it is now possible to fabricate and deploy skin-type sensors. Such a sensing strategy has the potential to cover very large surfaces and detect local damages over a large surface by mimicking the biological function of skin. The field of SHM terms this technology as large area electronic (LAE).

Popular applications in SHM include the utilization of carbon nanotube (CNT) nanocomposites to create resistive strain sensors [5,6]. CNTs are typically used due to their strength and super-elastic attribute [7], but their utilization results in high fabrication costs and difficult scalability. Capacitance-based strain sensors have been proposed for various applications including strain [8,9], pressure [10], triaxial force [11], and humidity [12,13] sensing.

The authors have also developed an LAE-based sensor, termed soft elastomeric capacitor (SEC). The SEC is a strain gauge, and its measurement principle based on a measurable change in capacitance provoked by a change in its geometry. The SEC was originally constituted from a styrene–ethylene/butylene–styrene (SEBS) matrix filled with titania (TiO_2) particles to form the dielectric, sandwiched between compliant electrodes fabricated from the same SEBS, but filled with CB to provide conductivity. The fabrication method of this sensor is described in [14]. Figure 11.1 is a picture of a typical SEC measuring 75 × 75 mm^2 (3 × 3 in^2). The sensors' quasistatic behavior [15], dynamic behavior [16], and nanocomposite optimization [17] have been studied.

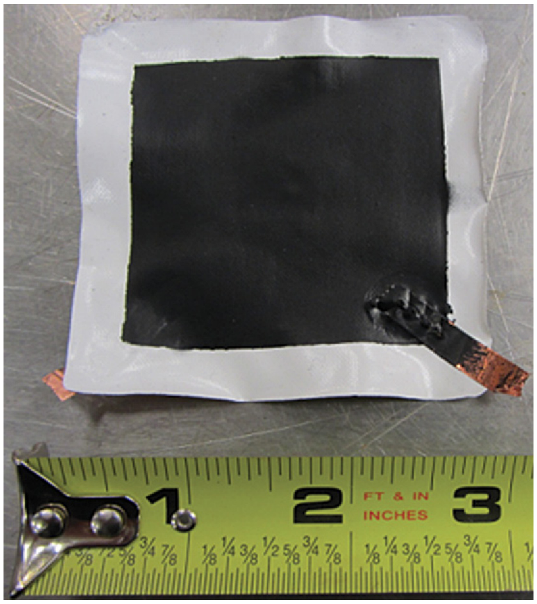


Figure 11.1 A single SEC.

The SEC discussed previously showed promising electrical and mechanical behavior, and its fabrication process and inexpensive nanocomposite enable scalability for large-scale deployment. However, like the vast majority of LAE, the SEC is also fabricated using a petroleum-based polymer [18]. The volatility of the natural oil markets and the increasing cost of petroleum have led to a push to reduce the dependence on petroleum products. Together with an increase in environmental awareness, this has promoted the use of alternative, biorenewable, environmentally friendly products, such as biomass. The growing interest in replacing petroleum-based products by inexpensive, renewable, natural materials is important for sustainable development into the future and will have a significant impact on the polymer industry and the environment, in particular, for any large-scale deployments.

The authors have studied the opportunity to fabricate a biobased LAE instead of petroleum-based. Plant oils represent one of the most promising renewable resources that can be used to create and develop a new class of bioplastics with tailored multifunctional properties due to their unique chemical structure. These natural oils exhibit a triglyceride structure linked with different fatty acids that can be functionalized/modified with more readily polymerizable groups to synthesize biobased copolymer thermosets with outstanding mechanical properties. These copolymer thermosets also offer sustainability, low cost, and are environmentally friendly, biocompatible, and potentially biodegradable. The plant oil can be also chemically converted to polyols to synthesis plant oil-based polyurethane (PU). With the exception of castor oil, nearly all vegetable oils do not naturally have the hydroxyl groups necessary to produce PU, but the carbon–carbon double bonds and the ester functionality present in triglycerides allow for the introduction of such groups. A majority of the vegetable oil-based polyols produced take advantage of the carbon–carbon double bonds to incorporate hydroxyl groups. The plant oil-based PU materials can be flexible and rigid, soft elastomers, or ductile and hard plastics, depending on the different types and concentrations of plant oil-based polyols. Plant oil-based polyurethanes have been studied to a much lesser extent in the literature than petroleum-based PUDs.

Vegetable oil-based waterborne polyurethane has recently emerged as a new branch of PU chemistry in an effort to reduce negative impacts on the environment and minimize fabrication costs. This branch has been rapidly growing, driven by the versatility and environmental friendliness of these polyurethanes. Integrating biobased composites with the concept of the SEC is a pioneer application of plant oil-based products in structural health monitoring. It is motivated by the improvement of the sensor's sustainability at both the material and fabrication process levels.

In this chapter, we discuss a biobased LAE for SHM applications presented in [19], developed by the authors as a possible replacement to the petroleum-based SEC aforementioned. The sensor is a biobased version of the SEC. Its dielectric is constituted from a castor oil-based polyurethane (PU) mixed with TiO_2 particles. The choice of castor oil is motivated by the presence of hydroxyl groups necessary to produce polyurethane dispersions (PUDs). In addition, waterborne castor oil-based PUD is used in order to partly eliminate organic solvents in the SEC's fabrication process [20–22]. This significantly reduces the amount toxic volatile organic compounds present in conventional PUs as well as hazardous air pollutants [21]. Unlike solvent-based PUDs, the aqueous PUDs can be applied with high solids content because their viscosity does not depend on the molecular weight of polyurethane. It is important to make the distinction that at this current state of research, only the dielectric is a biobased product. The compliant electrodes are still constituted from an SEBS-carbon black mix because the dispersion of carbon black within a castor-oil substrate requires further investigation.

The rest of this chapter is organized as follows. In the next section, the background of the sensor is described, which includes a description of the materials used, sensor fabrication process, and sensing principle. It is followed by a study of the sensor on a materials perspective, with a discussion on the dispersion of the filler and decay of the dielectric. Subsequently, the sensor's linearity and theoretical gauge factor are experimentally verified. The last section concludes this chapter.

11.2 Background

This section provides the background on the SEC. First, materials used in the fabrication process are discussed. Second, the fabrication process of the sensor is described. Last, the electromechanical model is derived.

11.2.1 Materials

For the dielectric, castor oil, isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA), and dibutyltin dilaurate (DBTDL) were obtained from Aldrich Chemical Company (Milwaukee, WI). Methyl ethyl ketone (MEK) and triethylamine (TEA) were purchased from Fisher Scientific Company (Fair Lawn, NJ). Titania-type rutile R320 was acquired from Sachtleben Chemie GmbH (Germany). The nanofiller was selected to increase the dielectric permittivity and durability of the nanocomposite [23].

For the electrodes, SEBS was acquired from VTC Elastoteknik AB, Sweden. SEBS is a block copolymer widely used for medical applications because of its purity, softness, elasticity, and strength [24]. CB-type Printex XE-2B (2% ash content and 500 ppm sieve residue 45 μm) was obtained from Orion Engineered Carbons (Kingswood, TX). It is characterized by a high structure (minimum oil absorption 380 cc/100 g), which facilitates higher conductivity [25]. All materials were used as received without further purification or analysis.

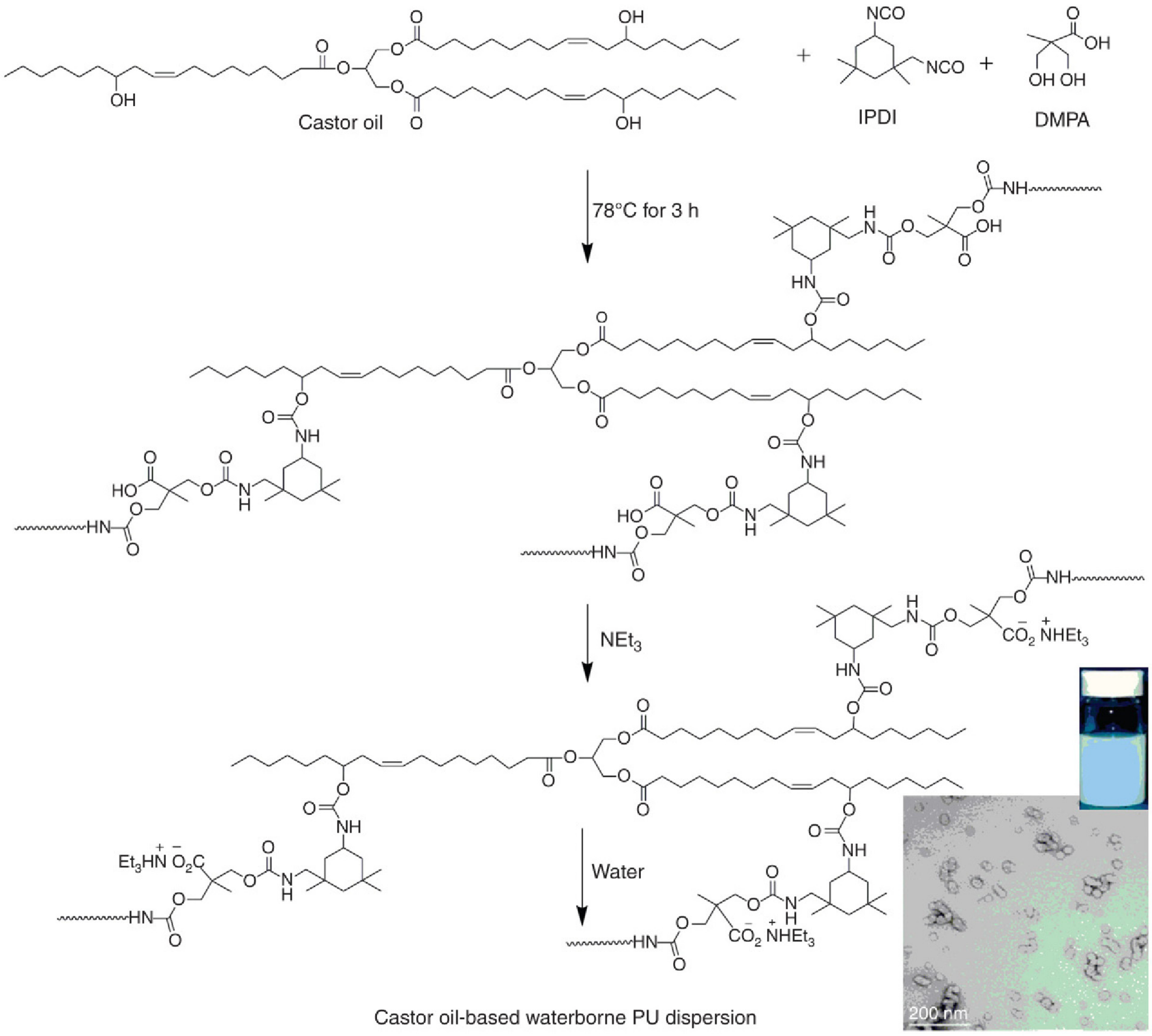
11.2.2 Sensor Fabrication

Details about the synthesis of castor oil-based PUD can be found in our recent publication [22]. Briefly, the castor oil-based PUD are synthesized by a reaction of IPDI, castor oil, and DMPA as internal surfactant. The DMPA incorporates carboxylic functionality in the prepolymer backbone. Tertiary amine (e.g., TEA) is then used to neutralize the carboxylic groups and produce ionic centers to stabilize the polymer particles in water. Scheme 11.1 shows the elementary steps for the synthesis of castor oil-based PUD and its TEM morphology. The PUD exhibited dispersed nano-PU particles with a diameter of approximately 30 nm.

Castor oil-based PU is then mixed with TiO_2, which both serve as a dielectric of the capacitor. TiO_2, an environmentally friendly and readily available filler [26], is added and dispersed in the castor oil to increase the permittivity of the PU [27]. The preparation of SEC is finalized by sandwiching the dielectric with two conductive electrodes fabricated from a carbon black and SEBS mix. Figure 11.2 illustrates the composition of a biobased SEC.

The sensor's fabrication process, as shown in Figure 11.3, follows a solution casting method:

1. TiO_2 nanoparticles are dissolved using methanol solvent before they are added to the castor oil PU at various volume percentages (5%, 10%, and 15%) and dispersed via sonication using an ultrasonic tip.
2. The resulting homogenous solution is drop casted onto a glass plate and dried at room temperature for about 3 days to allow evaporation of water.



Scheme 11.1 Elementary steps for the synthesis of anionic castor oil-based PUD and its TEM nanostructure morphology.

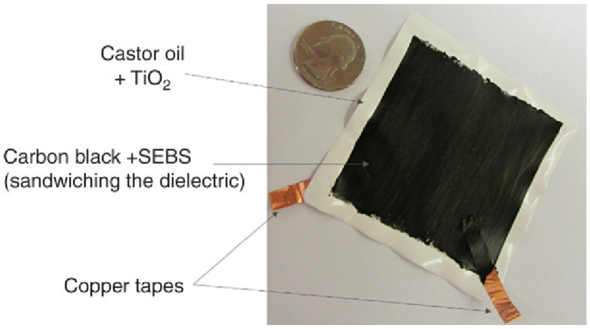


Figure 11.2 A single biobased SEC [19].

3. A 15 ml of SEBS/toluene solution is added to 0.79 g of carbon black to create the compliant electrodes. A sonication bath (Branson CPXH 2800) is used to disperse the carbon black particles.
4. The carbon black-SEBS solution is sprayed on both surfaces of the dried polymer to form the sensor.

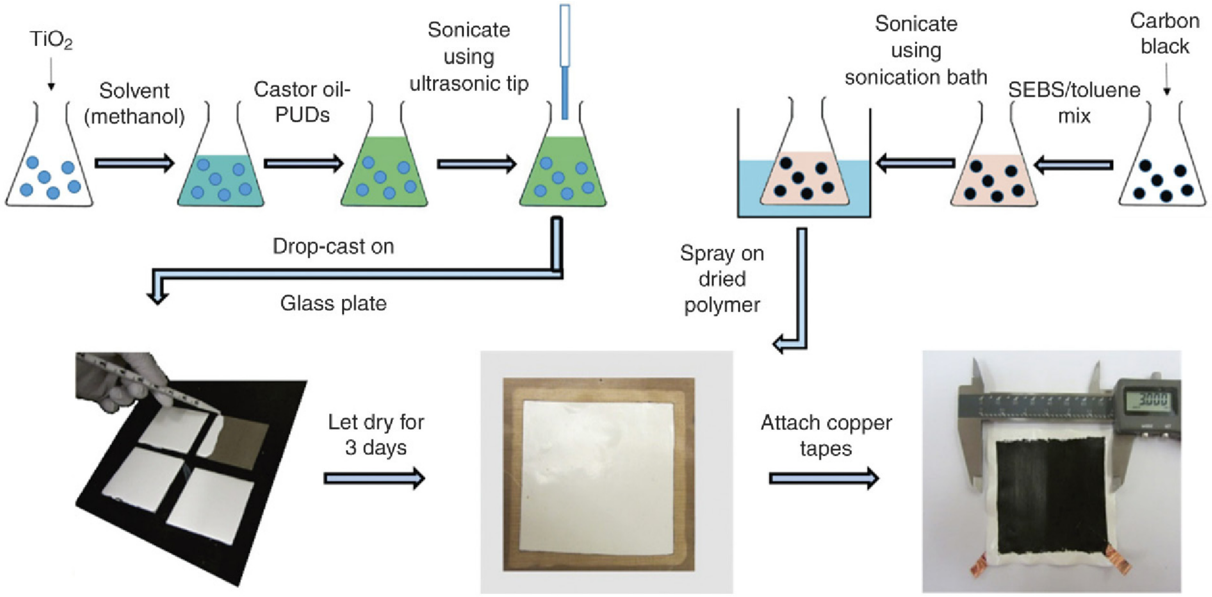


Figure 11.3 Sensor fabrication [19].

5. Two conductive copper tapes are attached to the electrodes during the drying process to create mechanical connections for connecting to the data acquisition system (DAQ).

11.2.3 Sensing Principle

The sensor is assumed to behave as a non-lossy capacitor when sampled at relatively low frequencies (≤1 kHz). The capacitance of the sensor is written as

$$C = \frac{e_0 e_r A}{h} \tag{11.1}$$

where $A = w.l.$ is the surface area of the electrodes of width w and length l, h is the thickness of the dielectric, $e_0 = 8.854$ pF/m is the vacuum permittivity, and e_r is the dimensionless relative permittivity of the composite. Assuming small deformation, the derivative of Equation (11.1) leads to the following expression:

$$\Delta C = \left(\frac{\Delta l}{l} + \frac{\Delta w}{w} + \frac{\Delta h}{h} \right) C \tag{11.2}$$

or

$$\frac{\Delta C}{C} = \varepsilon_X + \varepsilon_Y - \varepsilon_Z \tag{11.3}$$

where ε is the strain in the principal axes illustrated in Figure 11.4. The SEC is designed to be adhered to the surface of the monitored structure in the x–y plane using an epoxy. A surface deployment methodology is described in [28]. Using Hooke's law specialized for in-plane stress, one obtains an expression for ε_Z:

$$\varepsilon_Z = -\frac{v}{1-v} (\varepsilon_X + \varepsilon_Y) \tag{11.4}$$

where v is the Poisson's ratio of the sensor. Substituting Equation (11.4) into Equation (11.3) gives and expression for the gauge factor λ:

$$\frac{\Delta C}{C} = \lambda (\varepsilon_X + \varepsilon_Y) = \frac{1}{1-v} (\varepsilon_X + \varepsilon_Y) \tag{11.5}$$

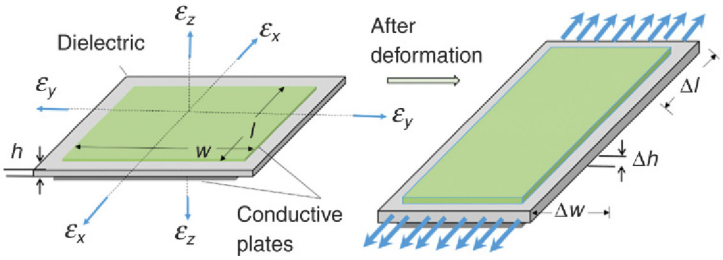


Figure 11.4 Sensing principle [19].

Equation (11.5) can be rearranged using Equation (11.1) to obtain an expression for the sensitivity of the sensor S:

$$S = \frac{\Delta C}{(\varepsilon_X + \varepsilon_Y)} = \frac{\lambda e_0 e_r A}{h} \qquad (11.6)$$

It is, therefore, possible to increase the sensor's sensitivity Equation (11.6) by altering the geometry or the dielectric permittivity. A formulation for uniaxial strain applications can be obtained by specializing Equation (11.5). Assuming that the monitored material (e.g., fiberglass, steel, concrete, aluminum) has a significantly higher stiffness than the nanocomposite itself, the strain along the y-axis is written as $\varepsilon_Y = -v_m \varepsilon_X$, where v_m is the Poisson's ratio of the monitored material. Here, Equation (11.5) becomes

$$\frac{\Delta C}{C} = \lambda \varepsilon_x = \frac{1 - v_m}{1 - v} \varepsilon_x \qquad (11.7)$$

11.3 Materials Properties

In this section, key mechanical properties of the nanocomposite are investigated. First, the dispersion of the nanofiller is examined. A homogenous dispersion is critical to ensure linearity of the sensor as a function of strain. Second, the dielectric properties are discussed. Such properties define the sensitivity of the sensor S. Last, a thermogravimetric analysis (TGA) is conducted to determine the thermal stability of the composite.

11.3.1 Dispersion of Nanofiller

The quality of dispersion was investigated by conducting a morphological inspection of the castor oil-based PU/TiO_2 nanocomposites using scanning electron microscopy (SEM). Three samples with different TiO_2 contents were studied. The test methodology consisted of fracturing the samples in liquid nitrogen, fixing them on the SEM holders, and sputtering with gold. The SEM equipment was a field-emission scanning electron microscope (FE-SEM, FEI Quanta 250) operating at 10 kV under high vacuum. Micrographs were taken 3 days after fabrication. Figure 11.5 shows typical SEM micrographs for PU/TiO_2 nanocomposites with 5, 10, and 15 vol% TiO_2 to polymer contents. Results show that the TiO_2 is dispersed well along the horizontal axis, but appears to have settled in the vertical axis. Figure 11.6 shows a blow-up on the region where TiO_2 has settled. TiO_2 dispersed well in the PU matrix with an average particle size as small as 200 nm in this region. Given the utilization of the sensor in an in-plane mode, uniform dispersion is only required along the horizontal axis, yet preferable among the entire volume. The section on laboratory experiments will confirm the

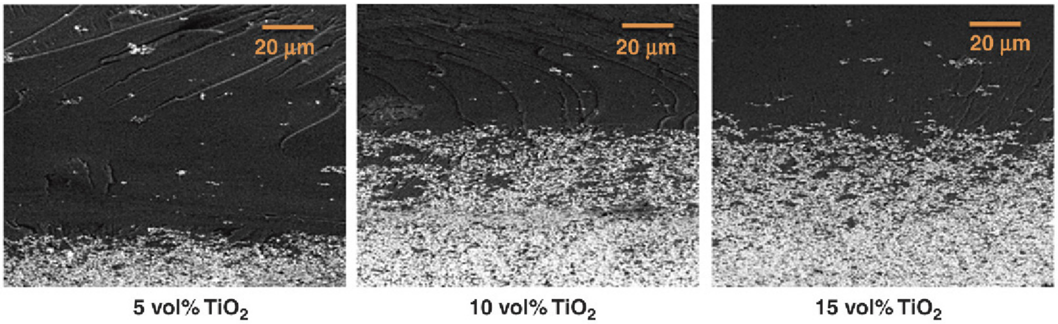


Figure 11.5 SEM micrographs for PU/TiO_2 nanocomposites for different compositions [19].

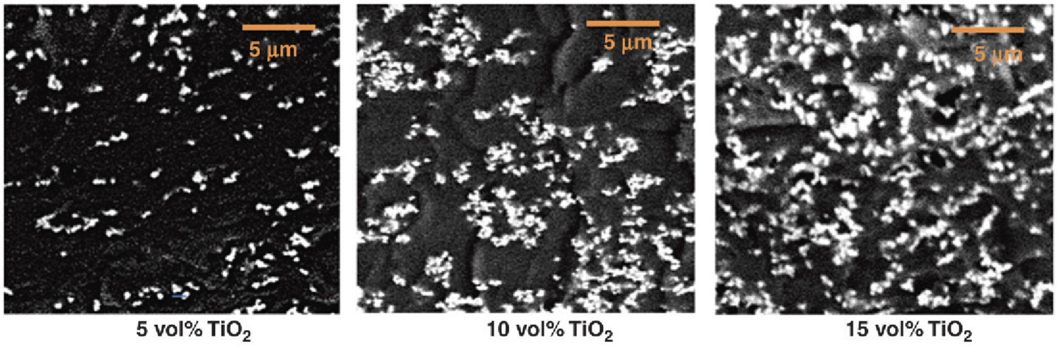


Figure 11.6 SEM micrographs for PU/TiO_2 nanocomposites for different compositions, blow up on dispersed TiO_2 particles [19].

homogeneous in-plane dispersion of the particles by demonstrating the linearity of the sensor and verifying the theoretical gauge factor experimentally. However, the nonuniform settlement along the sensor's thickness needs further investigation. In particular, other dispersion techniques need to be investigated, including the utilization of surfactants and coated TiO_2.

11.3.2 Dielectric Properties

Experience with the fabrication of castor oil-based SECs led to believe in a possible decay in the materials' dielectric over time. Such decay has never been observed with SEBS-based SECs. The authors have studied the change in the relative permittivity over time by recording the value of e_r over 3 weeks for three different TiO_2 concentration levels (5, 10, and 15 vol%). The methodology consisted of measuring the capacitance of each sample using an Agilent 4263B LCR Meter and back-calculating e_r from Equation (11.1). Three samples we used per TiO_2 concentration level. The average value of the relative permittivity for each set of specimens is plotted in Figure 11.7 (no recording was taken for the 9th and 10th days). The decay of the dielectric value is evident, and stabilizes after approximately 16 days. Possible causes include a slow evaporation of the soluble materials and a reorganization of the nanofiller. All experiments presented later in this chapter were performed on specimens older than 21 days to ensure a stable relative permittivity.

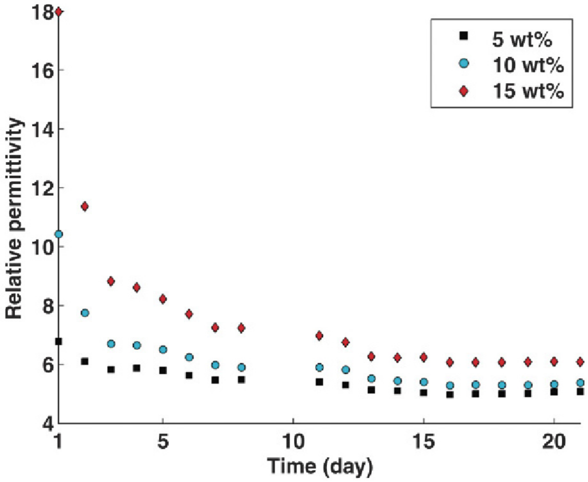


Figure 11.7 Average value of relative permittivity for each set over time [19].

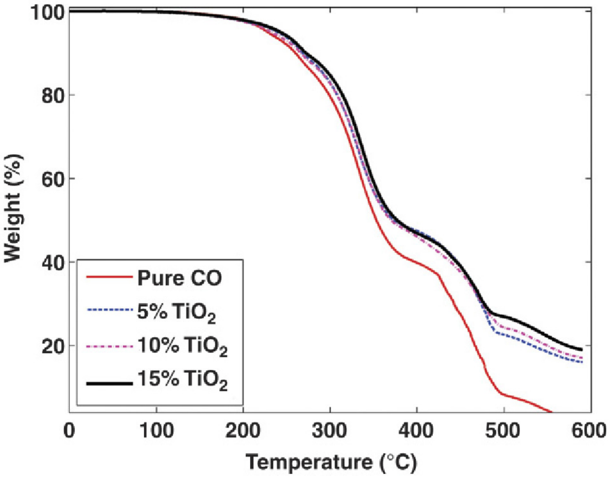


Figure 11.8 TGA measurements for PU/TiO_2 composites at 20°C/min heating rate under nitrogen atmosphere [19].

11.3.3 Thermogravimetric Analysis (TGA)

The thermal stability of the PU/TiO_2 nanocomposite at different TiO_2 concentration levels was investigated using TGA. The equipment consisted of a TA Instruments TGA model 50. Tests were conducted over a temperature range of 30–600°C at 20°C/min under nitrogen atmosphere. Figure 11.8 shows a typical TGA measurement for PU/TiO_2 nanocomposites for different TiO_2 concentration levels. Results show that the pure PU sample (0 vol% TiO_2) was thermally stable at a temperature range up to 250°C. Approximately 10 wt% of the sample was degraded at approximately 250–300°C due to the evaporation of soluble materials and unreacted oil fragments. With increasing the temperature up to 600°C, two fast degradation processes were observed. The first process occurred over the temperature range of 300–380°C. Approximately 60 wt% of the sample was lost due to the degradation of the polymer backbone. The second process occurred over the temperature range 400–600°C. It was possibly caused by further decomposition of the PU fragments. The multiple thermal degradation processes of biobased polymers from vegetable oils are very common in the literature. The addition of TiO_2 significantly increased the thermal stability of the nanocomposite, evidenced by a shift to higher temperature ranges. Results from this section showed that the TiO_2 dispersed well along the horizontal axis of the castor oil-based PU, and that it increased both its dielectric permittivity and thermal stability.

11.4 Laboratory Experiments

Laboratory experiments were conducted to verify the sensor linearity and compare its performance with the previous pretroleum-based version of the SEC. First, the experiment setup is described. Second, the results are presented and discussed.

11.4.1 Experimental Setup

The sensor linearity was verified on two different configurations: in a free-standing mode, and on a bending beam. Tests were conducted over the range 0–6% strain. The gauge factor was experimentally computed from the bending beam test and compared against the solution from Equation (11.7).

For the free-standing configuration, three SEC with 5, 10, and 15 vol% TiO_2 concentration levels were clamped separately into an Instron table-top mechanical testing machine (model 5569). Each specimen was subjected to six tensile strain cycles (from 1% to 6% strain with 1% strain increment), with each strain plateau attained at a loading rate of 5 mm/min. This range of strain was governed by the allowable elongation of the testing equipment for the sample sizes, and is well beyond the failure point of typical structural materials. Data from the SECs were acquired using an off-the-shelf capacitance data acquisition system (ACAM PCap01), and sampled at 95 Hz. Figure 11.9 shows the laboratory setup for the free-standing sensor test. Remark that Equation (11.7) cannot be directly verified in a free-standing configuration because of the nonuniform distribution of strain within the dielectric.

For the bending beam test, the SEC specimens were installed onto the bottom surface of a simply supported aluminum beam of dimensions 910 × 200 × 6.5 mm^3 (36 × 8 × 0.25 in^3) subjected to a four-point load setup as shown in Figure 11.10. Each sensor was

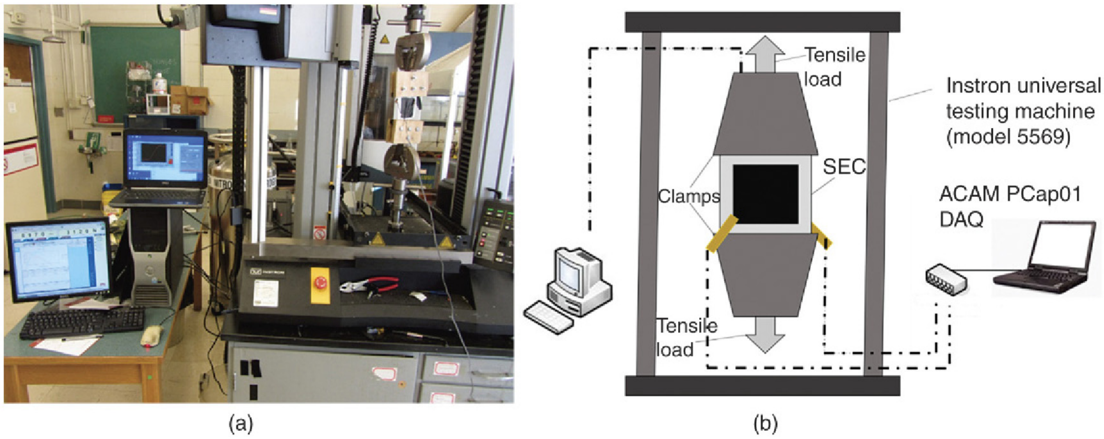


Figure 11.9 (a) Tensile test laboratory setup; (b) schematic of the clamped SEC on the Instron machine [19].

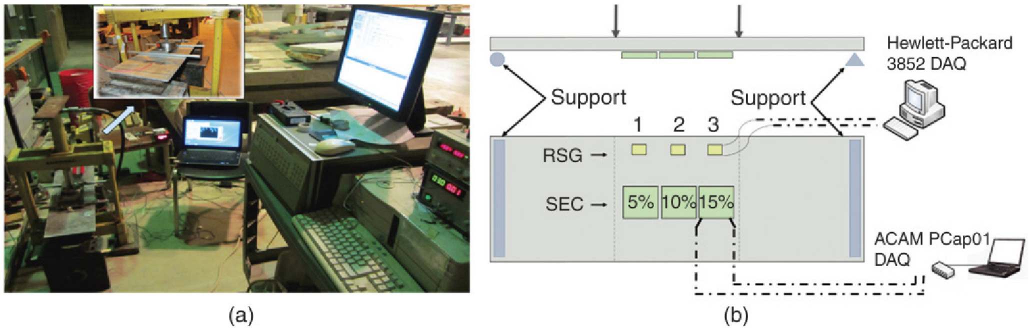


Figure 11.10 (a) Bending plate test laboratory setup; (b) schematic from side and under the plate (connection sensors-DAQ only shown for two sensors for clarity) [19].

deployed within the constant moment region using a thin layer of an off-the-shelf epoxy (JB Kwik) after sanding the plate surface and applying a primer. Step loads (approximately 20, 40, 60, and 80 lb.) were applied at $1/3$ and $2/3$ of the beam length using a hand operated hydraulic test system (Enerpac). Data from the SECs were acquired using an ACAM PCap01. Data from the RSGs were acquired using n Hewlett-Packard 3852 DAQ.

11.4.2 Results and Discussion

Figures 11.11 and 11.12 show the results from the free-standing tests. Figure 11.11 compares time series of strain input and capacitance measurements. Time axes of strain and capacitance were manually aligned given the inaccurate synchronization of both DAQs. The comparison of time series measurements shows an agreement between the experimental values of strain and measured capacitance. There is an upward slope in the capacitance measurements that becomes significant at high levels of strain. This slope is attributed to the viscoelastic behavior of the nanocomposite.

Figure 11.12 is a plot of the normalized change in capacitance versus strain. Normalized measurements provide a better comparison given that Equation (11.7) does not hold in a free-standing configuration. Data are

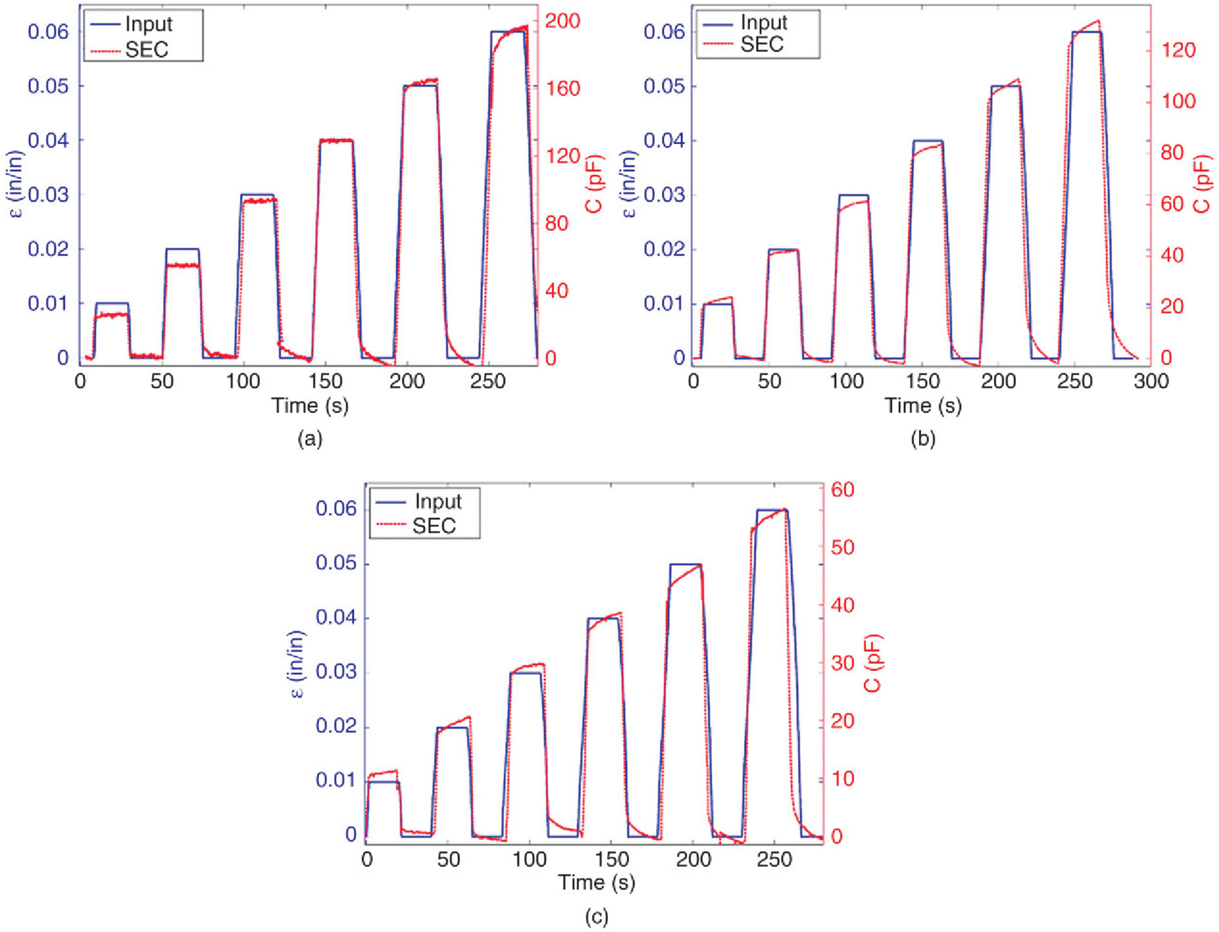


Figure 11.11 Strain history of SEC versus Instron RSG (free-standing test). (a) 5% TiO_2 content; (b) 10% TiO_2 content; (c) 15% TiO_2 content [19].

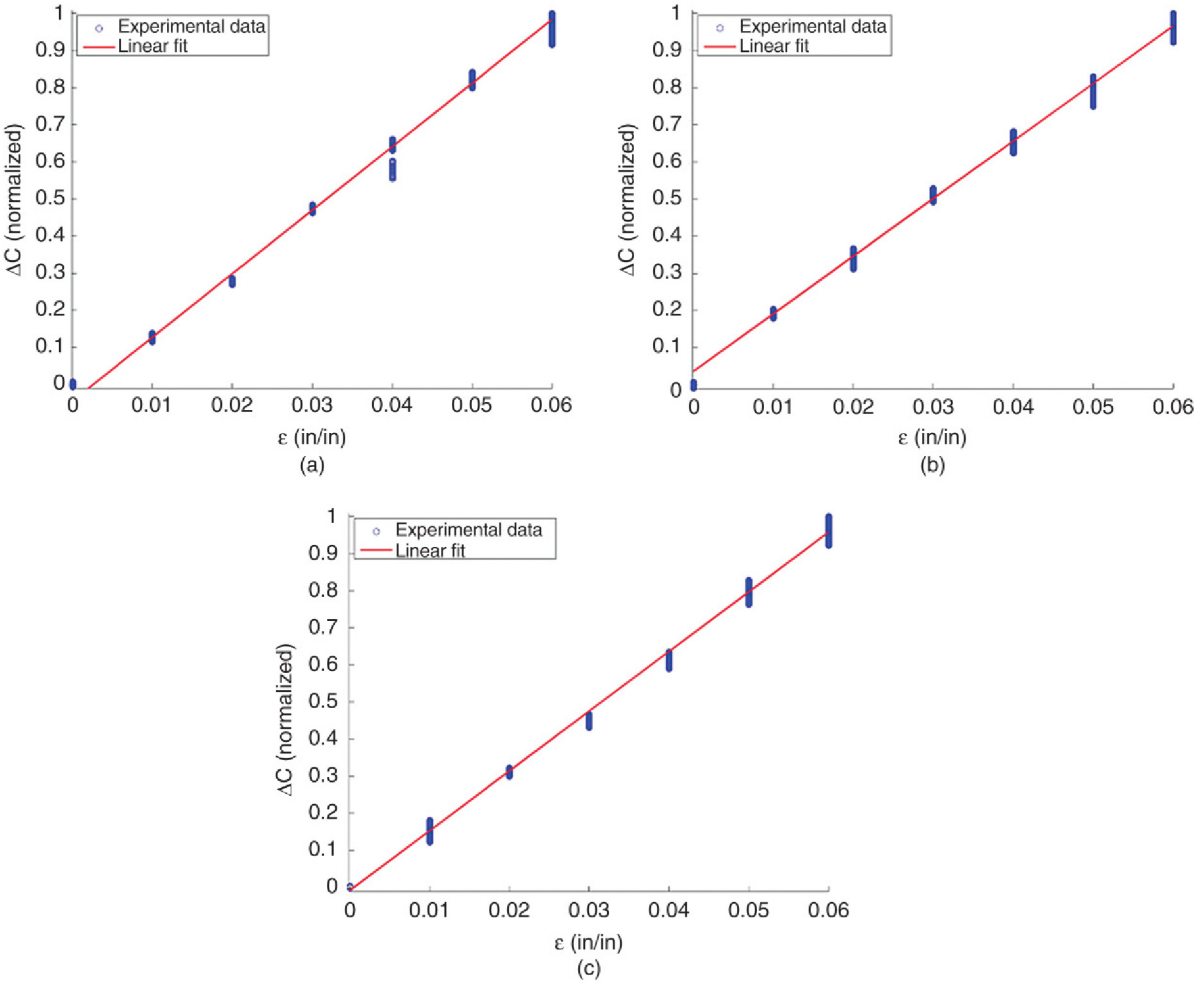


Figure 11.12 Verification of linearity for free-standing biobased SECs. (a) 5% TiO_2 content; (b) 10% TiO_2 content; (c) 15% TiO_2 content [19].

fitted linearly using a least-squares estimator. Results show that the sensor remains linear over the range 0–6% strain.

Figures 11.13 and 11.14 show the results from the bending beam test. Comparison of time series data (Figure 11.13) also shows agreement between strain load and measured capacitance. A noticeable feature in the signals is a drift of the signal after each step load. It is hypothesized that this drift is caused by the epoxy interface, which results in a slow relaxation process of the dielectric following a step load. The experimental gauge factor is obtained by plotting $\Delta C/C$ versus strain and taking the slope of the linear fit (Figure 11.14). Assuming a value of $\nu_m = 0.33$ for aluminum and $\nu = 0.45$–0.5 for thermosets, the theoretical gauge factor of the castor oil-based SEC is $1.34 < \lambda < 1.49$ (Equation (11.7)). Table 11.1 summarizes

Table 11.1 Strain Gauge Factors of SEC Installed on an Aluminum Plate

	5%	10%	15%
Gauge factor λ	1.415	1.376	1.463

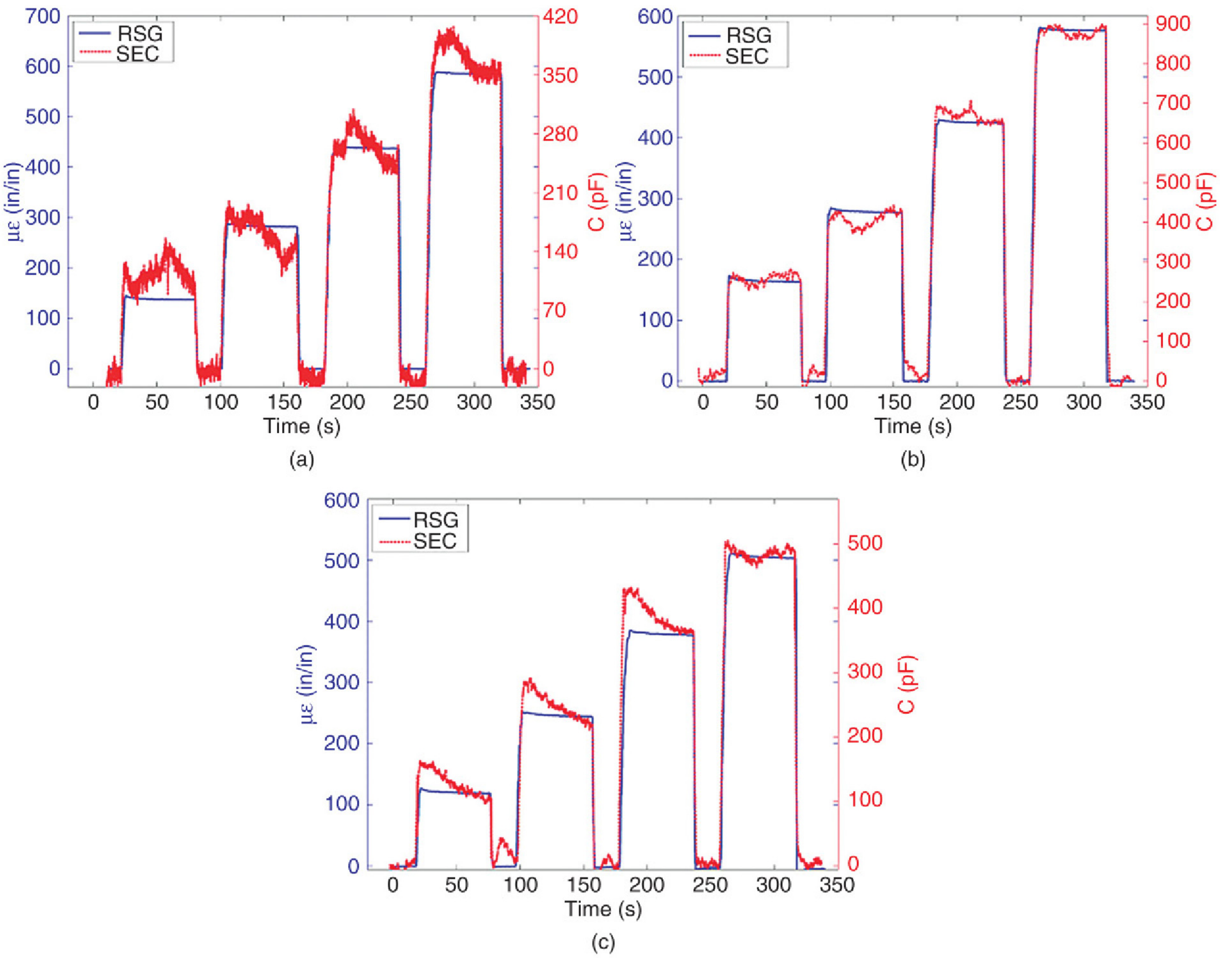


Figure 11.13 Strain history of SEC versus RSG (bending plate test). (a) 5% TiO_2 content; (b) 10% TiO_2 content; (c) 15% TiO_2 content [19].

the values obtained in Figure 11.14. The experimental gauge factors are all comprised within 1.34 and 1.49. Cross-specimens fluctuation can be explained by slight imperfections in the dispersion of the TiO_2, and changes in environmental conditions (temperature and humidity).

11.5 Conclusion

In this chapter, a pioneer application of plant oil-based polymer for structural health monitoring was presented. The proposed application is an SEC, constituted from a dielectric made of castor oil-based PU filled with titanium dioxide, and conductive plates made of SEBS filled with carbon black. The application was motivated by the inexpensive and biorenewable characteristics of the castor oil, therefore reducing the environmental footprint of LAEs. The proposed sensor could be deployed in a large network configuration to cover large-scale surfaces, enabling monitoring of local strain over global areas.

The sensor showed to reach stability after approximately 16 days from fabrication.

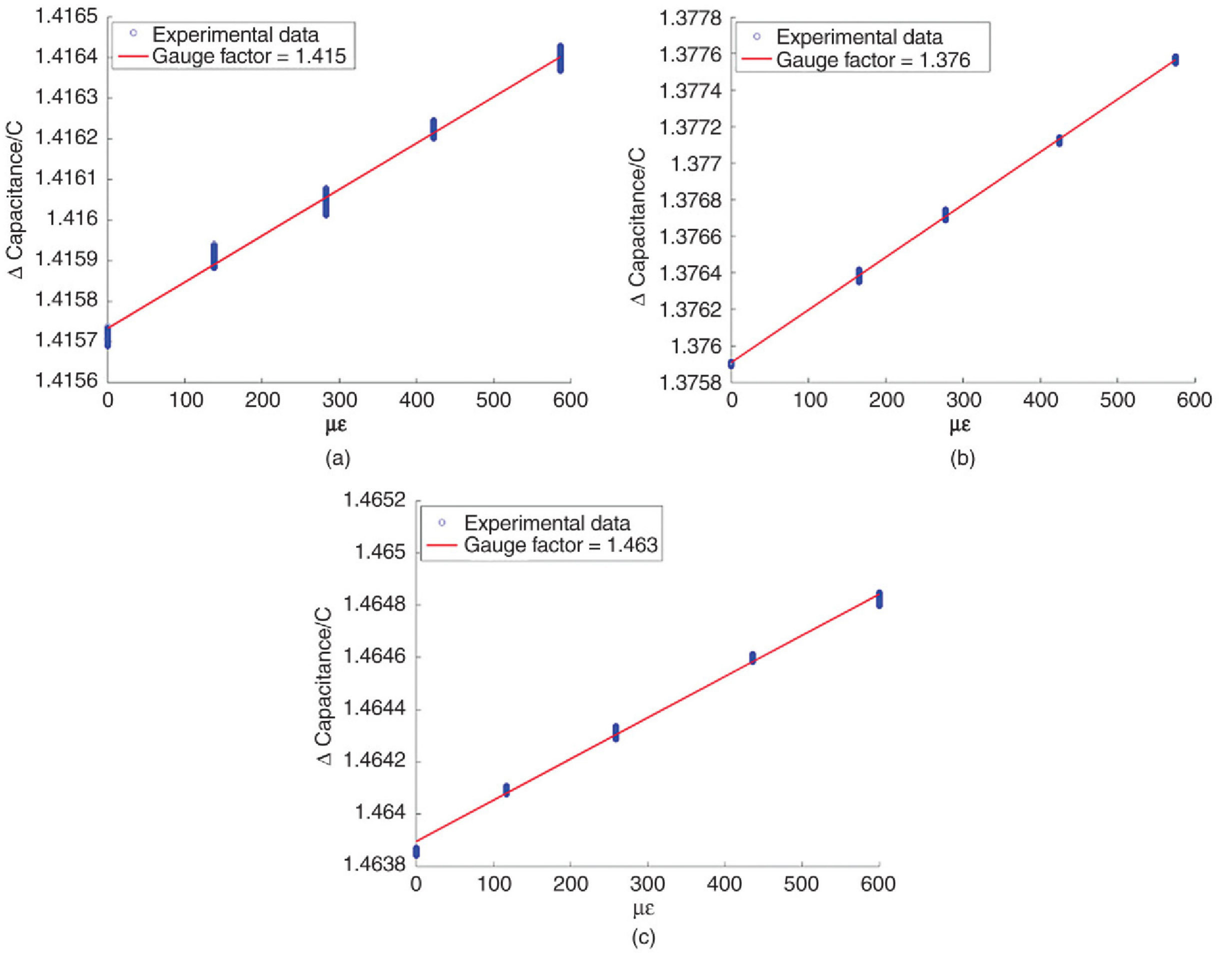


Figure 11.14 Verification of gauge factor for biobased SEC (bending plate test). (a) 5% TiO_2 content; (b) 10% TiO_2 content; (c) 15% TiO_2 content [19].

Scanning electron microscopy tests showed that all concentrations of TiO_2 (5%, 10%, and 15%) are dispersed well in the horizontal axis, but appear to have settled in the vertical axis. The TGA showed good physical and chemical properties.

Static load tests were conducted on free-standing specimens and on specimens adhered to an aluminum plate subjected to bending. Results from free-standing specimens showed that the sensor remained linear in the range 0–6% strain, and bending tests verified the theoretical gauge factor experimentally. These results confirmed the good dispersion of the particles within the castor oil PU and that the SEC can be used as a strain sensor.

The proposed castor oil-based SEC constitutes a promising sensor for monitoring of mesoscale surfaces. It demonstrates the utilization of biobased polymers in the fabrication of sensors, which can result in important environmental benefits.

Acknowledgment

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12 The Future of Essential Oils as a Pest Biocontrol Method

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12.1 Introduction

The use of synthetic pesticides has come under significant scrutiny in the last decade, with continued reliance on "conventional" insecticides and acaricides threatened by current or impending legislation being implemented at a range of geographical scales. In the EU numerous plant protection products are at risk of withdrawal under Regulation (EC) No. 1107/2009, the Water Framework Directive, and the Sustainable Use Directive. The combined impact of such legislation, coupled with reviews of substances previously approved, will be the loss of many plant protection products from the sector [1], and a need for more considered use of those that remain.

Even where synthetic pesticides remain in use, their effectiveness may be compromised by development of pest resistance. Resistance has, for example, been observed in lice [2], mites [3,4], and ticks [5] of medical/veterinary significance, and is now widespread among agricultural pests. The peach potato aphid (*Myzus persicae*) is perhaps the most well studied example, being considered one of the world's most strongly resistant pests [6].

To develop alternative methods of pest control research has turned to plant essential oils, many of which display complex and highly pesticidal chemistries [7–9]. Essential oils are generally considered "lower risk" than many synthetics, having short persistence times and typically, though not universally,

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displaying low vertebrate toxicity [7]. The high volatility of many of these products also lends itself well to the use of essential oils as pest repellents, including against major disease vectors such as mosquitoes [10,11], for example, recently demonstrated the repellent effect of several essential oils to *Aedes aegypti* mosquitoes.

12.2 Range of Use

The potential of essential oils, and/or their chemical components, is beginning to be realized in virtually every sector in which pests pose a threat to health and/or production. In agriculture, the commercial development of botanically based products (along with other "biopesticides") now far exceeds that of synthetic pesticides, with a CAGR of 16% (Markets and Markets, 2014) [12]. Commercial products are also becoming more widely available for use against parasites of companion animals, supported by a wealth of research over the last 20 years (e.g., [13–16]). Evidence supports that they are similarly effective against an array of other pests of veterinary, as well as medical, significance [7,17]. Thymol, the primary chemical component of thyme essential oil, has been found to kill *Varroa* mites [18,19] as is now widely used in apiculture, as are several essential oil-based feed supplements (e.g., Vita Gold™ and Green™).

12.3 Mechanisms

Within the majority of sectors essential oils are primarily researched and developed as pesticides for direct topical or spray application. Their use as mosquito repellents in the medical sector is an exception, with the repellent potential of essential oils also recognized against other veterinary/medical ectoparasites [20–22]. Use or potential of essential oils as pest attractants is rarer, though had been documented (Kraus et al., 1994) [23].

The mode of action of essential oils on arthropods is not always clear, and for many products has yet to be fully studied. In addition to attacking the arthropod cuticle directly, essential oils have been generally described as having toxic, antifeedant, and antioviposition properties, also exerting developmental effects on pests (Koul et al., 2008) [24]. Those studies that have considered biochemical responses have shown essential oils to express their effects through a variety of routes, primarily acting upon GABA, tyramine and octopamine receptors/synapses, and the inhibition of AChE [7].

A potentially attractive attribute of at least some essential oils is that a single product may target pests in a multitude of ways, thus reducing the possibility of pests developing resistance to them. Thymol, for example, may block octopamine receptors and also act upon the GABA-gated chloride channel [25]. However, essential oils may not be immune to pest resistance [7], especially as arthropods possess a diverse array of detoxification pathways, as well as other resistance "strategies."

12.4 Future Research

Essential oils are often relatively volatile compounds and remain on treated surfaces for only short periods. Though rapid dissipation could be considered beneficial in some circumstances (e.g., when looking to release biological control agents shortly after treatment), in others prolonged residual activity is likely to be preferred. To this end, new research is working on the encapsulation of essential oils to maintain longer lasting exposure times. Recently, Kraus et al. [23] demonstrated that encapsulation on a chitosan–benzoic acid gel increased the half-life and antifungal properties of thyme essential oils. Similarly, Koul et al. [24] showed that zein/casein complex nanoparticles delivered a more controlled release of thymol and eugenol over 24 h. For details of further methods, and comparison between them, De Oliveira et al. [25] recently reviewed different carrier systems used for botanical compounds such as azadirachtin, rotenone, carvacrol, thymol, eugenol, and curcumin.

Issues with such an approach include maintaining sufficient efficacy of the bioactive compounds during mass production, whilst keeping particle chemically stable, though overcoming such problems may produce further benefits in addition to prolonged efficacy. Controlling the reactivity of particles through encapsulation could theoretically limit their toxicity to nontarget organisms, such as beneficial arthropods, livestock, humans, and crop plants. Though generally considered “safer” alternatives to synthetics, some essential oils may nevertheless produce cytoplasmic, cytotoxic, and phytotoxic effects [8,26], so minimizing nontarget exposure should still be considered important.

It appears that essential oils extracted from plants can produce a vast number of compounds, though not all of them being active against arthropod pests, diluting sometimes the effect of the more potent compounds. The chirality of some molecules also influences the level of bioactivity and should be investigated further to understand better how to produce the right essential oil molecules in mass.

12.5 Conclusion

Essential oils are already being used successfully against a broad range of arthropod pests and, through research and development, it is likely that more essential oil-based products will penetrate pest control markets in multiple sectors in the near future. Essential oils display many favorable characteristics as pesticides and repellents, with shortcomings that are currently being addressed through R&D. Future research should be encouraged to better clarify modes of action, molecular activity, and further means to prolong efficacy, whilst also reducing production costs. As with any new pest management product, assessing the potential for development of pest resistance to essential oils would also be beneficial, as an inability of pests to overcome essential oil chemistries should not be automatically assumed.

Overall, the future of essential oils in pest management seems relatively assured. The available evidence supports that in many sectors these, and other biopesticides (such as microbials), offer a potential alternative to conventional pest control. At worst they are a viable, and potential vital pest management solution wherein synthetic pesticides fail or are unavailable.

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