Biological Oils as Precursors to Novel Polymeric Materials

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ABSTRACT: This paper reviews a part of the rich field of oleochemicals, their synthesis and applications as precursors for polymers by referring to published data rather than discussing details of different reactions. The hope is to help readers in finding leads in the vast research area carried out over a long period of time, to avoid traps and to inspire new ideas for oil-based products and processes.

KEYWORDS: Biological oils, precursors, polymeric materials

1 INTRODUCTION

Vegetable oils and fats have been used for centuries in different non-food applications such as paints, soaps, lubricants, or as a glycerin source. Today, a wide spectrum of oleochemicals is generated from oils and fats including fatty acids, fatty esters, glycerin, fatty amines and fatty alcohols [1–4]. Oils have been studied extensively for applications in food, biofuels, cosmetics etc., but this review will cover only their use in polymeric materials.

Oils are an excellent substrate for different chemistries, with reactive sites being ester groups, double bonds and allyl hydrogens [5–8]. Catalytic cracking, like in the petroleum industry, can be applied to produce gasoline and light olefins such as propane and butane [9–12].

Biological oils and fats include triglycerides from plants, animals, fish and algae, the latter offering some new economic advantages. Utilization of oils and fats is often justified in various publications by depletion of petroleum. This is not a valid argument since only about 7% of petroleum is used for chemicals and these volumes will be available for a foreseeable future. Another argument often used is that natural products give biodegradable materials which is not always the case, since even biodegradable oils when chemically transformed, polymerized or crosslinked, lose biodegradability. Biodegradability is often touted as a desirable property, which is true if materials are used for some short-term applications such as packaging, but not if the materials are intended for long-term applications such as coatings, thermal insulation in houses, electrical insulation (transformers, insulators), etc. Utilization of vegetable oils for industrial products is warranted from the standpoint of availability, stable prices, sustainability, ecological reasons (sequestration of carbon dioxide by plants), better properties and economics.

2 NATURE OF BIOLOGICAL OILS

The composition of biological oils is discussed in many books and papers and we will not analyze it further here [1, 5, 13–16]. When considering oils and fats for designing new materials one has to bear in mind their heterogeneity. Typical edible oils (soybean, corn, canola, sunflower, peanut and palm) consist of about five major fatty acids with 0–3 double bonds and 18 carbons (stearic, oleic, linoleic and linolenic), except palmitic oil which has 16 carbons and no double bonds. Other fatty acids may be present at less than a few percent and will not be further considered here. Five fatty acids can build around 36 combinations of triglycerides even when we ignore positional isomers. For example, oleic-O and linoleic-L can give these triglycerides: OOO, OLO, LOL and LLL, but OLO is considered equivalent to OOL, and LOL is equivalent to LLO. Each combination is characterized by the number of double bonds, which may vary from 0–9. Another source of heterogeneity is the double bond position in components with the same number of

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double bonds. Variations in oil composition are also related to climate conditions. The effect of composition on properties of polyols is discussed in several papers [17, 18]. High saturated fatty acids content (usually stearic and palmitic) is characteristic for fats—they are solid at room temperature. Fish oil and algal oils are often characterized by a higher content of saturated fatty acids, some longer fatty acids with 20–24 carbons, but also with four, five or even six double bonds. One double bond in many fatty acids (oleic, linoleic, linolenic, ricinoleic) is positioned between the 9th and 10th carbon. This is significant for producing fatty acids with 9 carbons by ozonolysis, but also influences crosslinking density when functionalized oils are used to make polymer networks. Triglycerides with regular spacing of double bonds, such as triolein, give desirable network structures and better properties [17, 19].

Vegetable oils are aliphatic in nature with significant chain flexibility giving generally soft and not very strong materials even at a relatively high crosslinking density. Increasing glass transition and rigidity can be accomplished by introducing aromatics in the structure. Triglycerides do not have aromatic rings but non-triglyceride oil such as cashew nut shell liquid does, which opens new opportunities [20, 21]. When crosslinked polymers are made through crosslinks at the 9th carbon, the tail from the 10th to 18th carbon is left as the side chain. This "dangling chain" acts as a plasticizer in many applications. Saturated fatty acids from triglycerides are even longer dangling chains in crosslinked networks

Molecular weight of triglycerides can be precisely calculated from the fatty acid composition as obtained by GC/MS [22]. However, additional method is required if free fatty acids, mono- and diglycerides are present. Most edible oils with predominantly C18 fatty acids have molecular weights close to 870 (tristearin-M = 891; trilinolein M = 879). Palm oil with dominant palmitic acid is an exception with a lower value (palm kernel oil M~680). Vapor pressure osmometry is a good method for determination of M_n of oils and modified oils, but it is sensitive to low molecular weight impurities. Size exclusion chromatography (SEC) is often used for reporting molecular weights but the measurements are usually very inaccurate, especially when calibrated with polystyrene standards. Mass spectrometry allows identification of the molecular weights present, but quantification may not be satisfactory. Soybean oil has on average 4.5 double bonds per triglyceride. This is the number average value, whereas the weight average (second moment of distribution) is about 5 [18]. Most oils crystallize at low temperature but those with a significant amount of saturates are solid at room temperature. Triglycerides form coils in solution which are smaller in molecules with more unsaturated fatty acids. They are even smaller in epoxidized oils although epoxidation increases molecular weight, but larger when converted to polyols by ring opening of epoxidized oils, which is easily observed by size exclusion chromatography. Because of the presence of unsaturation, oil and oil-based products are prone to oxidation which may lead to the break-up of the fatty acid chains to off-smelling short aldehydes, acids, ketones and alcohols, which is a concern in applications [23]. Products from oils and fats have ester bonds which are sensitive to hydrolysis, especially in coating applications. Although long fatty acids shield ester bonds to a degree, it should be reckoned that long-term exposure to moisture and an alkaline environment will cause some deterioration of properties.

3 DIRECT POLYMERIZATION OF OILS

Some oils with conjugated double bonds (tung, calendula) self-polymerize easily when exposed to air. High linoleic oils like linseed have been used for centuries as drying paints. According to their drying abilities vegetable oils were categorized as drying (linseed, tung, poppyseed, perilla, and walnut oils) with an arbitrary iodine value of IV above 140, semi-drying (IV ~ 125–140) and non-drying (IV below 125) [1]. Direct polymerization of oils is carried out on an industrial scale to obtain specific products such as "blown oils" and "bodied oils." Crosslinking oils with sulfur (sulfur chloride) produces "factice" (or Faktis) [24, 25]. Internal 1,2 disubstituted nonconjugated double bonds have low reactivity and do not polymerize readily. Thermal polymerization (heat bodied polymerization) is carried out by simple heating of linseed or soybean oil at 290–330°C in the absence or in the presence of catalysts such as antraquinone [26–28]. The products are viscous polymeric oils accompanied by a weight loss of 20–25% due to volatile organic compounds resulting from thermal degradation [29]. The proposed mechanism involves the migration of double bonds at high temperature and formation of conjugated double bonds, which are then involved in the Diels-Alder type of reactions with neighboring chains [28, 30–34]. This mechanism was recently challenged [35]. The second industrial process for "air blown oils" [36, 37] consists of bubbling air through soybean oil at temperatures of 100–110°C for a relatively long time (30–50 hours). The result is a viscous liquid oligomer mixture. Unfortunately, the resulting oils have a range of oxidation products such as hydroxyl, carboxyl, aldehydes, ketones and hydroperoxides. The mechanism of radical oxidation of vegetable oils involves formation of highly reactive allylic hydroperoxides, which generate low molecular compounds or oligomers [2, 38–40]. Because of the 1,2 substitution with electron releasing substitutents, the internal double bonds are rich in electrons and thus susceptible to the attack of electron deficient species such as organic radicals and cations [41]. Cationic polymerization of natural oils in the presence of 2–2.8% of BF_3 is described in patents and papers [42–44]. Cationic homopolymerization of soybean oil and copolymerization of soybean, fish and tung oils with vinyl monomers, such as styrene, divinyl benzene, norbornene, dicyclopentadiene in the presence of 4–7% of $BF_3{*}Et_2O$ at 110°C, was published recently [45–51]. Polymerization of fatty acids or of fatty acid methyl esters in the presence of BF_3 was described in the literature [52–54]. Oligomerization of fatty acids to dimeric and trimeric acids catalyzed by acidic clays at higher temperatures (230–240°C) is described in several patents [55–60]. Cationic polymerization of soybean oil catalyzed by superacids (HBF_4, CF_3SO_3H, $HSbF_6$, etc.) under mild reaction conditions (temperature below 100°C, atmospheric pressure, at 1% catalyst concentration, over several hours) leads to viscous liquids or solids depending on the reaction time [41, 61]. The presence of a superacid leads to almost quantitative conversion of cis to trans double bonds. The postulated mechanism is similar to that proposed for thermal polymerization, i.e., formation of conjugated double bonds in the first step, followed by a Diels-Alder addition of diene to a double bond from a neighboring fatty acid. Viscosity of the polymerized oils increases with the reaction time and would eventually lead to a solid product. Polymerized oils were tested as plasticizers in rubbers with very good results [62]. Since retention of double bonds in polymerized oils is high, these oils are useful for printing inks [26].

4 EPOXIDIZED OILS AS A PLATFORM FOR NEW MATERIALS

Epoxidation is a controlled oxidation of double bonds to form three member cyclic ethers. Epoxidation of oils and fatty acids was widely studied because of its practical significance [63–88]. Standard systems for epoxidation of fatty acid derivatives involve oil, solvent or no solvent, an acid catalyst, an organic acid, usually acetic or formic, which are coverted to peracids when hydrogen peroxide is added [65, 89–91].

Conversion in solution is usually higher than in bulk. Mechanisms in homogeneous and heterogeneous epoxidation catalysis were treated in a book [92]. Epoxidized soybean and linseed oils are well established secondary plasticizers for PVC. Epoxidized vegetable oils (soybean and linseed) is one of the largest industrial applications of vegetable oils, with an annual production of about 200,000 tons [2].

5 EPOXY RESINS

Epoxidized oils are biobased epoxy resins when cured with proper curing agents. They have internal epoxy groups which are not as reactive as terminal epoxy groups. As a consequence, amines, which are good curing agents for resins with terminal epoxy groups, do not work with epoxidized oils, but rather easily attack ester bonds in triglycerides. Internal epoxy groups can be polymerized directly in the presence of acid catalysts such as Lewis acids [93, 94] or superacids [95, 96] and anhydrides [97–99]. The study of polymerization of a model compound with an internal epoxy group in the presence of methyl trifluoromethanesulfonate revealed the complexity of the process and number of reaction products [100]. Cationic photoinitiated UV cured epoxidized oils were used as matrix resins for composites with relatively low glass transition and with moderate strength [74, 101]. Efficient crosslinking compounds for epoxidized vegetable oils are boron compounds [102, 103].

Anhydride-cured epoxy resins from vegetable oils are slow reacting and may require long curing times but produce strong thermoset materials [98, 104]. Sometimes they are co-cured with petrochemical epoxy resins to elevate properties [105]. They require aromatic curing agents such as phthalic anhydride in order to elevate glass transition and strength to an acceptable level [98]. Epoxidized oils cured with aromatic and cycloaliphatic anhydrides are used in the production of artificial stone [106]. Epoxidized oils with terminal epoxy groups were prepared by co-metathesis of triolein with ethylene with subsequent epoxidation of double bonds [19], or by epoxidation of triglyceride of undecenoic acid [107] or allyl modified oils and fatty acids. Epoxidized oils are generally not miscible with aromatic dianhydrides, which are required to boost T_g and properties.

6 RING OPENING OF EPOXY GROUPS TO GENERATE DIFFERENT PRODUCTS

Epoxy rings can be opened with a range of compounds. A major part of ring opening is carried out to produce polyols for polyurethanes. Opening with inorganic acid such as HCl, and HBr gives polyols with chlorine and bromine in their structure. Epoxidized soybean oil gave solid (grease) brominated and chlorinated polyols of lower reactivity [22]. Ring opening of epoxy groups is the same process used to polymerize epoxidized vegetable oils and fatty acids, but to obtain polyols of relatively low molecular weight a large excess of alcohols (methanol, ethanol) in the presence of acid catalysts must be used. Commercial polyols are also obtained by ring opening with acetic acid [108]. Polyols resulting from ring opening with formic [109], fatty [110] and lactic [111] acids have been reported. Reacting epoxidized rapeseed oil with monobutylamine at 180°C at stoichiometric ratio is claimed to produce a polyol with amine value 100–110, OH value 300–330 and viscosity of 5000–7000 mPa.s. However, partial aminolysis of ester bonds took place [112]. Ring opening of epoxy group with amides gives hydroxyalkylamides, with H_2S hydroxymercaptans, with secondary amines hydroxylamines, with HCN hydroxynitriles, with $NaHSO_3$ hydroxysulfonates [113]. Azides with vicinal OH groups are generated by ring opening of epoxidized oil with NaN_3 [8, 114, 115]. A family of monomers polymerizable by radical initiation useful for biobased polyesters is obtained by epoxy ring opening with acrylic acid and methacrylic acid [116–122]. Ring opening results in the formation of a secondary OH group and an adjacent group or hydrogen. Thus, an epoxidized oil would give a polyol with functional or nonfunctional groups which may be used in a dual curing mechanism. Epoxidized oils and fatty acids ring opened with allyl alcohol were cured with maleic anhydride using esterification and radical polymerization mechanisms to give excellent thermosetting materials [123, 124]. Polyols are the most important group of industrial products obtained from vegetable oils used for urethane foams, coatings, adhesives, sealants and elastomers [113, 125–127].

7 HYDROFORMYLATION

Hydroformylation is a high pressure catalytic reaction of carbon monoxide and hydrogen with double bonds to produce aldehydes, which can be subsequently oxidized to acids or reduced by hydrogenations to alcohols or amines by reductive amination [128–130]. Hydroformylation is catalyzed by transition metal carbnyls whose activities vary from very active rhodium to low activity iron and nickel. A generally accepted series of the activities of the unmodified metal is as follows [131]: Rh » Co > Ir, Ru > Os > Pt > Pd » Fe > Ni.

The catalysts of industrial importance are rhodium carbonyls (very efficient but expensive) and cobalt carbonyls (less efficient, requiring higher temperatures and pressures but catalyzing both hydroformylation and hydrogenation) [132]. Vegetable oils and fatty acids can be directly converted to polyols without any by-products and with high atom economy (all the reactants end up in the product without by-products). Hydroformylation of oils was studied extensively for the preparation of polyols [132–138] but even more for fatty acid derivatives [139–150]. Polyols prepared by this method have all primary OH groups and are thus very reactive unlike epoxidation polyols. Hydroformylation polyols produce softer polyurethanes than polyols by epoxidation because of higher molecular weights at the same functionality and an extra CH_2 group per double bond [18, 151].

8 POLYURETHANES

Polyurethanes are the most versatile type of polymers since they allow tailoring of properties by the end user by a simple combination of components and their ratios [152–155]. Two essential components for preparation of polyurethanes are polyols and isocyanates, but major efforts in the field of renewable materials is in the area of polyols. Isocyanates for foams must be aromatic in order to have the high reactivity necessary for the process, but aliphatic isocyanates are used in coatings, adhesives and elastomers. The only commercial oil-based diisocyanate (Dimeryl@) known to us is prepared by Cognis (now part of BASF). DDI 1410 diisocyanate is prepared from dimerized fatty acids and has low viscosity at 25°C and NCO content 14.4%. One of the aplications is in coatings. A new linear saturated terminal diisocyanate derived from azelaic acid via Curtius rearrangement was synthesized and used to prepare polyurethanes [156]. Polyisocyanates from plant oil triglycerides were prepared by bromination of triglycerides at the allylic positions by a reaction with N-bromosuccinimide, and in the second step, these brominated species were reacted with AgNCO to convert them to isocyanate-containing triglycerides [157]. In a similar fashion isothiocyanate derivatives of soybean oil triglycerides were prepared, but the resulting polyurethanes displayed poor properties [158].

A number of companies produce polyols from vegetable oils [127, 159]. Several reviews on oil-based polyurethanes were published recently [15, 23, 127, 160, 161]. Oil-based polyols are prepared by methods including but not limited to epoxidation and ring opening as discussed earlier, esterification/transesterification [110, 162–167], hydroformylation [132, 136, 137, 147, 168–172], ozonolysis [173–179], hydrogenation of acids [96, 180], glycerolysis and glycolysis, and oxidation. Oxidation of oils to polyols can be carried out in the presence of osmium tetroxide. It is used mainly for the cis-hydroxylation of olefinic double bonds to give glycols. For this purpose it is the smoothest and most efficient general reagent known [181–183]. Of course, castor oil is a natural triol used widely in the polyurethane industry for various products [154, 166, 184–200].

Polyols can be multifunctional, suitable for adhesives, coatings and foams, or they can be diol prepolymers which are used in thermoplastic polyurethane elastomers. The latter are usually polyesters with molecular weights from 1000–5000 and terminal OH groups. They are synthesized from hydroxy fatty acids obtained by hydroxylation of oleic acid or ricinoleic acid, or products of ozonolysis such as hydroxynonanoic acid [179, 201–205]. A special form of polyols having hyperbranched structure were tried in foams but their natural application is in coatings [164, 165, 167, 206, 207]. Alkoxylation of monomers or oil-based polyols is often used to alter reactivity or decrease viscosity. Ethoxylation converts secondary hydroxyls to primary hydroxyls, while propoxylation may be used to increase molecular weight to the desired range and decrease viscosity [125, 208, 209]. Catalysts used are usually cationic or DMC (double metal catalyst) since anionic catalysts would destroy ester bonds [210, 211].

9 POLYESTERS

Esterification is often used for the preparation of different types of precursors for polymers [212]. Transesterification was used to obtain polyols and polyesters [162, 179, 213–216]. Enzyme-catalyzed esterification works well for low molecular compounds [217–221]. “Transesterification of Vegetable Oils: A Review” discusses acid and base catalysts [222].

An interesting esterification reaction is the preparation of estolides. Estolides are a special class of fatty acid esters in which the carboxyl from a fatty acid reacts with a double bond on a second fatty acid to form an ester. In fact, the formation of estolides is the result of the addition of carboxyl group of one fatty acid to the double bond of the second fatty acid [223–231]. Estolides are also products of self-condensation of hydroxy-fatty acids such as ricinoleic acid. They are characterized by the estolide number (EN) defined as the average number of fatty acids (n) added to a base fatty acid (EN = n + 1) [228]. Estolides are found naturally in some plant and fungus oils [229, 230]. Intense studies were carried out on estolides prepared from oleic acid in the presence of acid catalysts (H_2SO_4, $HClO_4$, p-toluene sulfonic acid, acidic clays, methanesulfonic acid, etc.) [223–228]. The best catalyst for the synthesis of estolides from oleic acid is $HClO_4$, leading at 50°C to an estolide number of n=10 in and yield of 76% (the highest from all the acid catalysts mentioned) [228]. The formation of estolides from unsaturated fatty acids and hydroxy fatty acids is catalyzed efficiently by some enzymes (lipase) [232–235]. The ester linkages of estolides are more resistant to hydrolysis than the triglyceride ester bonds. When compared to petroleum-based fluids, soy-based fluids and petroleum oils’ estolides have superior biodegradability and superior lubricating properties [228]. Estolides are used first as biodegradable lubricants. They are also used for preparation of special surfactants used in cosmetics and coatings [218, 228, 236]. Oleic acid estolides show a very good stability toward oxidation, having better oxidative stability than petroleum and vegetable oil-based fluids [237]. Hydrogenation of estolides produces saturated estolides, which are much more oxidatively stable than the unsaturated ones [228, 237]. It is interesting that the synthesis of estolides from oleic acid generates as side products two lactones: delta-stearolactone (a six-membered ring) and gamma-stearolactone (a five-membered ring) [238, 239].

Lactones are an interesting class of compounds with many possibilities as industrial intermediates. Reacting lactones with amines produces hydroxyl amides, which serve as intermediates for biodegradable detergents [240].

Oil-based alkyd resins have been used extensively in coatings [82, 241–247]. They are a special group of polyesters, generated from mono- and diglycerides and diacids or diisocyanates (urethane alkyds) [152, 155] and will not be discussed further here.

10 CARBONATES FOR NON-ISOCYANATE POLYURETHANES

Organic carbonates (esters of carbonic acid, H_2CO_3), are an important class of compounds. Low molecular weight linear or cyclic carbonates such as dimethyl-, diethyl-, ethylene and propylene carbonate, and glycerol carbonate, are commercial products characterized by high boiling and flash points, low odor, low evaporation rates and toxicity, good biodegradability and high solvent power. They are used in a number of applications [248] as inert solvents and/or reactive intermediates [249], components in lubricants [250–252], cosmetics [253], plasticizers [254] and fuel additives [255, 256]. In contrast, oleochemical carbonates from animal- and plant-based feedstocks, are not currently used in large quantities in many commercial applications. Only in the last decade have they earnestly been examined as potentially useful materials in lubricants, cosmetics, plastics or as starting materials for new chemicals [257–259]. Hyperbranched polyglycerol containing a terminal five-membered cyclic carbonate groups was used for modification of the bisphenol A-based epoxy resin [260].

A number of different routes can be used for preparing carbonates [257, 261]. The phosgenation reaction is a very important industrial method for producing carbonic acid esters, although phosgene is a highly toxic and corrosive reagent [254]. The reaction between phosgene and hydroxy compounds proceeds readily, it can be run continuously, and provides high yields of carbonates. To avoid the toxicity of phosgenation, new environmentally friendly processes were developed, such as oxidative carbonation [262, 263]. In this process dimethyl carbonate is produced from methanol, carbon monoxide and oxygen, in the presence of a copper chloride catalyst. Dimethyl carbonate is a good starting compound for the synthesis of different carbonates by carbonate interchange reaction, i.e., transesterification between a low molecular weight dialkyl carbonate and an alcohol [258]. Reaction between alkylammonium hydrogen carbonates and halohydrins is an interesting route for cyclic carbonate synthesis. Aliphatic halohydrins react with alkylammonium hydrogen carbonate (obtained from alkylammonium hydroxide and carbon dioxide) and produce five-membered cyclic carbonate compounds [264, 265]. The reaction between epoxides and carbon dioxide under pressure in the presence of various catalysts produces five-membered cyclic carbonates, and it is of interest because of the direct use of carbon dioxide [266, 267]. This method is very well suited for cyclic carbonate synthesis from epoxidized vegetable oils, which are inexpensive starting materials. Direct reaction of CO_2 with epoxidized oils or epoxidized fatty acids can be carried out under both atmospheric and elevated pressure [268, 270]. The catalyst mixture of tin(IV) chloride pentahydrate/tetrabutylammonium bromide was found to improve conversion of epoxidized oil to the cyclic carbonate [271]. When supercritical CO_2 is used, the tetrabutylammonium bromide catalyst system shows the highest reactivity and yield of nearly 100%. Tetrabutylammonium hydroxyl, LiBr and KBr show little or no activity, probably due to their poor solubility in both ESBO and supercritical CO_2 [272, 273].

A silica-supported ionic liquid was found to be an efficient heterogeneous catalyst for solventless synthesis of cyclic carbonates from epoxides and carbon dioxide under supercritical conditions [274]. This reaction does not require organic solvents and a high purity product is obtained. One possible way for carbonate synthesis is oxidative carboxylation of olefins in ionic liquids [275]. Organic carbonates can be prepared enzymatically using lipases [276, 277].

Five-membered cyclic carbonates react relatively easily with most hydrogen donor compounds [248]. Aromatic hydrogen donor compounds, such as phenol and phenolic resins [278], thiophenols [279], and aniline [280], produce alkylated aromatics. Aliphatic hydrogen donor compounds react differently than their aromatic analogues. Alcohols produce carbonate esters as a result of transesterification carbonates [281–283]. The reaction of cyclic carbonates with amines is utilized for the synthesis of polyurethanes by a non-isocyanate route [284–289].

This reaction also forms a hydroxyl group at the ß-carbon atom of the polyurethane chain that is hydrogen bonded to the urethane carbonyl. Materials containing intramolecular hydrogen bonds display resistance to organic chemicals that is 1.5 to 2 times higher than the materials of the similar chemical structure without such bonds [286]. These materials have better thermal stability than regular polyurethanes because of the absence of thermally unstable biurets and allophanates. Due to the presence of hydroxyls, they absorb water much more than isocyanate-based polyurethanes, and may have applications where water absorption and retention is desirable. Non-isocyanate polyurethanes derived from vegetable oils have ester groups, and in a chemical sense they are polyester-polyurethane-polyhydroxyl compounds.

Non-isocyanate polyurethanes prepared from carbonated SBO and aliphatic diamines: 1,2-ethylenediamine, 1,4-butylene-diamine, and 1,6-hexamethylenediamine, had tensile strength in the range of 0.5–6 MPa and elongation at break of 71–219% [24]. One of the possible ways to increase strength and rigidity is to utilize diamines with rigid aromatic or cyclic structures. The samples prepared with carbonated soybean oil and m-xylylene diamine, p-xylylene diamine, and isophorone diamine displayed tensile strength up to 11.1 MPa, and elongation up to 433% [290]. Triglyceride or fatty acid cyclic carbonates are relatively stable and the reaction with amines is slow, limiting their application in polyurethanes. Lithium salts were among the most effective catalysts, but their insolubility in vegetable oil carbonate systems and solvent requirement make their application inconvenient. Tin and titanium organic compounds showed a catalytic effect and improved reactivity of amines [270]. Linseed and soybean oil-based polyurethanes, prepared via the non-isocyanate route by reacting the seed oil carbonates with 1,2-ethane diamine (EDA), 1,4-butane diamine (BDA) and isophorone diamine (IPDA), displayed glass transition temperatures from 17°C to 60°C. Polyurethanes obtained from linseed oil had higher crosslink density, higher stiffness and reduced water swelling and toluene uptake [291]. A terpene-based, cyclic limonene dicarbonate does not contain ester groups. It is an interesting starting material for different applications and for non-isocyanate polyurethane synthesis. With increasing amine functionality of the curing agent, it was possible to increase both stiffness and glass transition temperatures [292].

11 OZONOLYSIS

Ozonolysis was already mentioned as an oxidative method for precise cutting of double bonds and generating ozonides, which can be further oxidized to carboxylic acids or reduced to aldehydes or alcohols [175, 293, 294]. Cutting fatty acids with one double bond would give two components, one being hydroxy acid or aldehyde-terminated acid after reduction, or diacid after oxidation. The second component under the same conditions would be a monol, monoaldehyde or mono acid. Fatty acids with two double bonds would in addition generate a diol, dialdehyde or diacid. Fatty acids with three double bonds would generate one more diol, dialdehyde and diacid, which are useful components for a range of new polymeric products [175]. The beauty of ozonolysis is that it is a fast and precise, low temperature process. However, because the reaction is highly exothermic, it must be run slowly to maintain low temperature. Ozonolysis is a rather expensive process and the size of the reactors is limited because of the explosive nature of the process. The applicability for large-scale industrial products is limited to high value products such as azelaic acid or hydroxynonanoic acid. Dilactone from hydroxynonanoic acid was polymerized to a high molecular weight polyester [205]. The main factor in the price of the products is the cost of electricity for ozone generation. Triglycerides of unsaturated fatty acids are produced by ozonolysis and reduction of ozonides, solid triols and by-products [176]. Oxidation of trglyceride ozonides would give triacids as well as useful by-products. Triacids can be very good flexibilizing curing agents for epoxy resins. Aldehydes generated by this process are intermediates for other products. Ozonolysis of oils in the presence of diols and NaOH leads to aldehydes and acids, which after esterification, result in terminal OH groups [295]. Ozonolysis was used to prepare 9-aminononanoic acid from soybean oil in four steps [296].

12 VINYL PRECURSORS FOR RADICAL POLYMERIZATION

As was stated earlier, direct polymerization of oils in the presence of cationic initiators is not fast enough for many applications and requires strong acid catalysts. Oils are often used for electrical insulation because of their high dielectric strength, low dielectric constant and low dielectric losses. However, they tend to deteriorate with time due to oxidation and partial polymerization. Instead, polyurethanes are used as casting and embedding compounds for solid insulation transformers, but the reactive systems are sensitive to moisture producing bubbles in the cured materials [188]. Preparation of solid electrical insulation by radical polymerization would solve many of these problems. The process can be carried out at room temperature or slightly above, the compounds are stable in storage for a long time, they are insensitive to moisture and the material would retain a low dielectric constant and dielectric losses. Such compounds should have terminal double bonds as obtained by allylation, cross-metathesis with ethylene, ring opening of epoxidized oils with acrylates, or simultaneous addition of bromine and acrylate to the double bonds [297] or maleinization [298, 299] of oils. Only acrylated oils have sufficient reactivity for radical polymerization due to the presence of carboxyl groups. Allyl double bonds and higher olefins have low reactivity due to the presence of allyl hydrogens which are good transfer agents. However, copolymerization of terminal olefins with maleic anhydride (MA) is viable because of the absence of homopolymerization of MA. The degree of polymerization of allyl groups in allylated oils was low and the product was very soft [123]. Hard polymers were obtained with MA participating in radical copolymerization and esterification reactions with hydroxyls, resulting from the epoxy group ring opening with allyl alcohol [123, 124]. Radical copolymerization of acrylated oils with styrene is used for the production of unsaturated polyesters and composites [122, 300–306]. The amine derivatives of acrylated epoxidized soybean oil, which is the reaction product of epoxidized soybean oil with acrylic acid or methacrylic acid, are produced by the reaction of acrylated epoxidized soybean oil with an organic amine. They are useful alone or in conjunction with a photosensitizer and/or a pigment as inks and coatings. The compositions can be cured by UV radiation [117, 307]. Compositions of urethane derivatives of acrylated epoxidized soybean oil, which are the reaction products of an organic isocyanate with the reaction product of epoxidized soybean oil with acrylic acid or methacrylic acid, and an acrylic compound, are useful as coatings and inks. Photosensitizers and/or pigments can optionally be present. The compositions can be cured by UV radiation [120, 308]. Acrylated urethanized oils were prepared by reacting castor oil with acryloil chloride, ring opening of epoxidizd soybean oil with acrylic acid [309]. The authors have also introduced terminal double bonds reacting castor oil with an isocyanate derivative of α-methyl styrene. Both acrylated ansd styrenated oils were successfully cured with UV radiation.

The acrylamide derivative of SBO and sunflower oils was obtained by the Ritter reaction with acrylonitrile in the presence of sulfuric acid. Free-radical copolymerization of the product with styrene produced semi-rigid polymers [310]. Since vegetable oils are rich with allyl hydrogens, considerable chain transfer is expected during radical polymerization of acrylated oils. The extent of chain transfer in radical co-polymerization of vegetable oil macromonomers with butyl acrylate and methyl methacrylate in solution has been determined [311]. Acrylated high oleic sunflower oils with 2.5 acrylate groups per triglyceride were prepared by esterification of polyols by acryloyl chloride in the presence of triethylamine [312]. The products were polymerized in the presence of dicumylperoxide and copolymerized with pentaerithritol tetraacrylate to give soft products with glass transitions up to 31°C. Copolymer networks of acrylated oils and styrene with different crosslinking density were analyzed [313]. It was found that 0.5 acrylates per triglyceride were lost to intramolecular cyclization for homopolymerized triglyceride-acrylates and 0.8 for triglycerides copolymerized with styrene. T_g of networks varied from −50°C to 90°C.

13 PHENOLATION OF VEGETABLE OILS AND OF UNSATURATED FATTY ACIDS

It is well known that phenols are easily alkylated with olefins in the presence of strong Bronsted or Lewis acids [314–319]. By analogy, the double bonds of unsaturated vegetable oils can alkylate the aromatic rings of phenols in the presence of strong acids as catalyst, generating oils containing phenolic rings chemically linked to the fatty acid chains of the triglyceride structure [320–323]. These compounds are called phenolated oils. The phenolation of oils in the presence of strong protonic acids is carried out in three steps. In the first step, organic cations are formed in the reaction of catalyst protons with the double bonds of fatty acid chains. In the second step, the formed cations react with the most nucleophilic group in the reaction system, the phenolic group, generating phenyl ethers. In the third step, the phenyl ethers isomerize to alkylated phenols (Claisen rearrangement) [314–316, 318, 319]. Phenolation of soybean oil with superacids as catalysts (including HBF_4 [321, 323], CF_3SO_3H [324]) generates as products phenolated triglycerides, cationic polymerized oils with chemically attached phenolic rings, phenyl esters of fatty acids by transesterification of phenol with triglyceride ester bonds (< 10%) and unreacted oils (<30%). The study of the phenolation of model compounds (9-octadecene, methyl oleate, methyl linoleate and triolein) leads to the conclusion that the best fatty acid for phenolation reactions is oleic [321]. Fatty acids containing two double bonds (linoleic acid) and three double bonds (linolenic acid) predominantly generate polymeric oils and are less active for phenol alkylation [321]. This behavior is explained by the transfer reaction of cations with *bis* allylic hydrogens of linoleic and linolenic acids generating stable allyl cations (conjugated hybrids with positive charge distributed on three carbon atoms), which are much less reactive cations in alkylation reactions [321, 323]. Propoxylation of phenolated soybean oil in the presence of coordinative catalysts affords hybrid aromatic-aliphatic polyols. Further reaction with isocyanates (MDI) leads to polyurethanes with high tensile strength and hardness [320]. Phenolated oil can be converted to biobased phenol formaldehyde resins after the reaction with paraformaldehyde or hexamethylenetetramine, for applications in laminates with excellent electrical properties [325]. Significant attention was paid to phenolation of oleic acid [325–329]. The carboxyl is a tolerant group and does not interfere negatively with alkylation. Alkylation of phenol with oleic acid in the presence of methane sulfonic acid leads to phenyl ethers, alkylated phenol (major compound-82–88%), small quantities of phenyl ester (~2%) and estolides (7–12%) [12]. It is interesting that in the same reaction carried out with thiophenol the only product is the phenylthioether [325, 326]. Cresols (ortho and meta) react more efficiently than phenol, due to the higher electron density of the nucleus resulting from the presence of electron releasing substituents (methyl groups) [327–329]. In phenolation of soybean oil around 30–33% of double bonds participated in the alkylation reaction while around 65% were involved in the alkylation of triolein [321]. The phenolated oils are suitable for the preparation of polyols for polyurethanes, phenol formaldehyde resins and special antioxidants with fatty acid structure [322].

14 SULFUR CONTAINING MONOMERS AND POLYMERS DERIVED FROM VEGETABLE OILS

Sulfur derivatives of vegetable oils were synthesized by two main methods: a) photochemical addition of hydrogen sulfide or mercaptans to the double bonds of oils [330], and b) ring opening of epoxy groups of epoxidized oils with hydrogen sulfide [331]. Chevron Phillips produces on an industrial scale three derivatives of vegetable oils containing thiol groups [331, 332]. The first compound, having only thiol groups, is obtained by the addition of hydrogen sulfide in the presence of UV light to the double bonds of soybean oil [330]. The resulting product (Polymercaptan 358) has around 2.9 thiol groups per triglyceride [331]. By the addition of hydrogen sulfide to the double bonds of castor oil, under the same conditions, an interesting compound having both hydroxyl and thiol groups (Polymercaptan 805) is obtained [331]. Ring-opening addition of hydrogen sulfide to epoxidized soybean oil produced a polymercaptan, having on average, four hydroxyl groups and four thiol groups per triglyceride (Polymercaptan 407). Thiol groups react with isocyanates leading to thiourethanes. One application of all three compounds is in the preparation of polyurethanes (foams, coatings). All three compounds with –SH groups are excellent biobased hardeners for epoxy resins. New monomers based on vegetable oils containing sulfur were obtained by thiol-ene "click chemistry." The reaction carried out under mild conditions involves the addition of thiols to unsaturated oils. It is initiated photochemically with UV light or thermally in the presence of radical initiators (most often with AIBN) [7, 214, 333–336]. The addition of 2-mercaptoethanol to soybean oil affords in one step a vegetable oil polyol, with around three hydroxyl groups per mole [7, 335, 336]. Cast polyurethanes obtained with this polyol and diisocyanates have good mechanical properties. The polyol can be used in polyurethane foams, coatings and adhesives. The addition of 2-mercapto ethanol to epoxidized soybean oil in the presence of perchloric acid as a catalyst, results in a highly functional polyol [334]. This compound is a potential monomer for rigid polyurethane foams. Due to the presence of thioether groups, it has a superior thermo-oxidative stability and excellent lubricity [334]. Thioether groups tend to decompose hydroperoxides resulting from the oxidation of hydrocarbon chains and transform them to inert sulfoxides or sulfones in a way that stops the degradation chain reactions. It has been proven that all derivatives of vegetable oils containing sulfur are more resistant to oxidation than the initial oil, possibly as a result of the addition of thiol groups to double bonds, and thus reduced unsaturation [334].

15 MONOMERS AND POLYMERS BY CLICK CHEMISTRY

It was mentioned that thio-ene reactions, which belong to the group of click chemistry, are utilized for preparing some oil-based monomers and polymers. The other important reaction in this group involves azides and alkynes in Huisgen cycloaddition, resulting in the formation of triazoles [337–339]. Azide-containing oils (azidated oils) were prepared by ring opening of epoxidized oils with NaN_3 [114, 115, 340, 341] or by the addition of bromoazide to the double bonds [342]. Acylazides were prepared by reacting ricinoleic acid with NaN_3 in the presence of triethylamine [343]. Alkynated oils or fatty acids can be obtained by ring opening of epoxides with propargyl alcohol or by transesterification of fatty acids methyl esters with propargyl alcohol [115, 344]. The reaction of azidated oils with propargylated oil without catalysts produces relatively soft polymer networks, but short aromatic azides with alkynated vegetable oils give glassy polymers [345].

16 METATHESIS PRECURSORS

Metathesis is a very useful method for creating new compounds from olefinic raw materials [346]. Ring-opening polymerization has been successfully used on a commercial scale for reaction injection molding of dicyclopentadiene (DCPD) [347]. However, conversion of vegetable oil and fatty acids to useful products on a large scale was limited by the catalyst cost. Direct metathesis (acyclyc diene metathesis) of vegetable oils utilizing Grubbs' catalyst produced a mixture of low molecular and polymeric species [348]. When high oleic sunflower oil was polymerized via acyclic triene metathesis (ATMET) it produced highly branched and functionalized polyesters [349]. Useful precursors with terminal double bonds are prepared by co-metathesis with ethylene [350–353]. Cross-metathesis of fatty acid methyl esters with allyl chloride was used to make α,ω-difunctional chemical intermediates [354]. Cross-metathesis of oils and fatty acids or their methyl esters with unsaturated diols and unsaturated diacids or vinyl acids introduces functional terminal groups useful as precursors for polymers [355–357]. Self-metathesis of fatty acids can be used to make unsaturated diacid [358, 359] or polyhydroxy compounds [360]. Technological and economical aspects of the metathesis of unsaturated esters were analyzed [361]. Attaching DCPD to castor oil and ricinoleic alcohol generated compounds which could be polymerized by ring-opening metathesis [362]. Ring-opening metathesis polymerization (ROMP) of oil-DCPD was carried out in the presence of the Grubbs' 2nd generation catalyst. The resulting materials that were produced were rubbery with oil-DCPD and glassy with fatty alcohol-DCPD. In a similar fashion a commercial adduct of DCPD to linseed oil was polymerized by ROMP to obtain rubbery materials [363]. Several reviews cover metathesis of oils and fatty acids [364–366].

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