

Chapter 3

Bioplastics, Biocomposites, and Biocoatings from Natural Oils

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A range of new materials can be obtained by the cationic, free radical, or thermal copolymerization of natural and modified oils with a number of petroleum-based comonomers. These novel new biobased materials possess good thermal stabilities, good mechanical properties, and good damping and shape memory properties. Unique new bioplastics have also been prepared by the ring opening metathesis polymerization (ROMP) of modified oils and fatty alcohols in the presence of strained cyclic alkenes to form rubbery to hard materials. In order to improve the performance of these new bioplastics, inorganic fillers and natural fibers have been used to reinforce the cationic, free radical, and ROMP resins. Vegetable oil-based waterborne polyurethane dispersions (PUD's) have also been synthesized from vegetable oil polyols. In order to improve their properties, the PUD's have been copolymerized with an emulsion of vinyl or acrylic comonomers to form a series of polyurethane/acrylic hybrid latexes. Core-shell latexes have also been obtained by the emulsion copolymerization of PUD's with vinyl comonomers. All of these materials exhibit properties similar to or better than related petroleum-based products.

Introduction

With the tremendous commercial importance of the plastics and coatings industries, it is obvious that the replacement of petroleum-based materials by useful new bioplastics from inexpensive, renewable, natural materials, like vegetable oils and agricultural residues, will have an enormous impact economically, environmentally, and energy-wise. The advantages of biobased materials are the ready availability of large quantities of renewable starting materials, the usually competitive price of these starting materials in comparison to currently used petroleum-based monomers, the potential of producing more bio-degradable materials than virtually indestructible petroleum-based polymers, the possibility of producing new materials with properties not presently available in commercial petroleum-based products, and the overall intrinsic low toxicity of such biobased products.

The use of renewable resources in energy and material-related applications is receiving increasing attention in both industry and academia. A range of factors contributes to frequent dramatic fluctuations in the price of oil, which is reflected in the production cost of all petroleum-based goods. This situation creates an urgent need, from an industrial point of view, for renewable starting materials and biobased products that have the potential to replace petroleum-based materials. Thus, research and development of new biopolymers is extremely important in attaining oil independence and sustainable industrial development.

Currently, the most widely used renewable raw materials are vegetable oils, polysaccharides (cellulose and starch), wood, and proteins (1). A variety of chemicals have been prepared from these starting materials. Bio-oil and syngas are obtained by the pyrolysis of wood and agricultural wastes (2). Proteins are denatured and aligned during processing to make protein-based biopolymers (3), and vegetable oils find use in paints (4), biocoatings (5–9), biofuels (10), and as building blocks for biobased polymers (11–13).

Recently, a variety of vegetable oil-based polymers, with good thermal and mechanical properties, have been developed through the cationic (14–16), free radical (17, 18), and thermal (12, 13) copolymerization of regular and conjugated natural oils with several petroleum-based comonomers. In such systems, the reactive sites in the triglyceride units are the carbon-carbon double bonds. Overall, the reactivity of vegetable oils towards these polymerization processes can be significantly increased if the carbon-carbon double bonds in the fatty acid chains are isomerized and brought into conjugation (19, 20). For the remainder of this chapter, the term “conjugated” refers to carbon-carbon double bonds that are conjugated (as in a 1,3-diene). Other polymerization methods, such as ring-opening metathesis polymerization (ROMP) (21–23) and acyclic diene metathesis (ADMET) (24), have also been recently employed to synthesize vegetable oil-based biopolymers.

Biobased materials with improved thermophysical and mechanical properties can be obtained by simply reinforcing the aforementioned polymeric matrices with inorganic fillers and natural fibers. The use of glass fiber (25) and organoclays (26) as reinforcements in biocomposites significantly improves the Young's modulus and tensile strength of the bio-materials. Along the same lines, various agricultural

residues and natural fibers, such as spent germ (27), soybean hulls (28), corn stover (29), wheat straw (30), rice hulls (31), and switch grass (32) have been added to the aforementioned vegetable oil-based resins to prepare biocomposites with up to 85 wt % of biobased content.

Promising biocoatings can also be obtained from vegetable oils. Indeed, soybean oil-based polyols have been successfully used in the preparation of anionic (6) and cationic (7) polyurethane dispersions. In order to improve the thermophysical and mechanical properties of these new soybean oil-based polyurethane dispersions (PUD's), hybrid latexes have been prepared by the emulsion copolymerization of PUD's with acrylates (8). Core-shell hybrid latexes have also been prepared by the emulsion copolymerization of PUD's from acrylated soybean oil polyols with vinyl comonomers, which results in biobased latexes with promising properties for use as coatings and adhesives (9).

The technology involved in these new natural oil-based materials is remarkably simple and should be readily adapted to the existing polymer and coating industries. The recent transition from petroleum to biobased products provides major economical advantages, and even more importantly, generates more environmentally friendly processes and products. This chapter focuses primarily on the research progress made on biobased plastics, composites and coatings derived from natural oils by the Larock group over the last 10 years and closely related work. No attempt has been made to report a comprehensive review of the development of new biopolymers.

Natural Oil-Derived Bioplastics

Natural oils are a renewable resource that can be extracted from animals and plants. Structurally, the oils consist of triglycerides with fatty acid side chains of varying length and degree of unsaturation. The general chemical representation of a triglyceride oil can be seen in Figure 1, while the fatty acid composition of the most common oils used as renewable starting materials for biopolymers is given in Table I (11, 16). The notation in parentheses ($C_{a,b}$), after the fatty acid name (Table I), denotes the number of carbon atoms (a), followed by the number of carbon-carbon double bonds (b) in the corresponding fatty acid. The carbon-carbon double bonds in these natural oils possess predominantly a *cis* configuration.

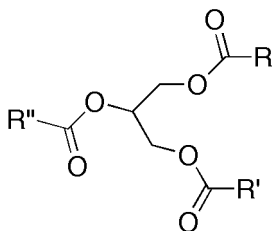


Figure 1. General triglyceride structure, where R, R', and R'' are linear alkyl chains with variable lengths and degrees of unsaturation depending on the oil involved.

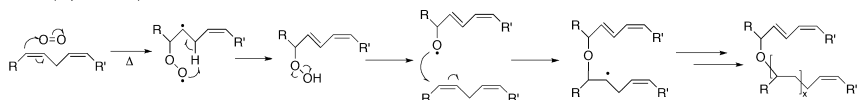
Table I. Fatty Acid Composition of Commonly Used Natural Oils in the Preparation of New Biobased Materials

Oil	Linolenic acid (C _{18:3}) content (%)	Linoleic acid (C _{18:2}) content (%)	Oleic acid (C _{18:1}) content (%)	Stearic acid (C _{18:0}) content (%)	Palmitic acid (C _{16:0}) content (%)	Double bonds per triglyceride ^a
Tung ^b	-	9	4	-	6	7.9
Linseed	57	15	19	4	6	6.6
Walnut	3	73	18	1	5	5.5
Low saturation soybean	9	57	31	1	3	5.0
Safflower	-	78	12	2	7	5.0
Sunflower	1	54	37	3	5	4.7
Soybean	8	53	23	4	11	4.6
Corn	1	60	25	2	11	4.5
Grapeseed	-	63	27	3	7	4.5
Canola	9	21	61	2	4	3.9
Sesame	1	43	41	6	9	3.9
Peanut	-	32	47	2	11	3.3
Olive	1	6	80	3	9	2.9
Castor ^c	1	4	5	1	2	2.7
Fish ^d	-	-	11-25	-	10-22	-

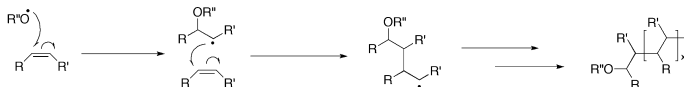
^a Average number of carbon-carbon double bonds per triglyceride. ^b Approximately 84 % of the fatty acid chains in tung oil are alpha-eleostearic acid, a naturally conjugated triene (I2). ^c Approximately 85 % of the fatty acid chains in castor oil are ricinoleic acid, a C_{18:1} acid with an hydroxyl group on carbon 12 of the fatty acid chain. ^d Fish oil presents a high percentage of polyunsaturated fatty acids, containing as many as 5-6 non-conjugated carbon-carbon double bonds (I4).

Some fatty acids bear functional groups, like ricinoleic acid, which contains an hydroxyl (-OH) group attached to carbon 12 (C₁₂) in the fatty acid chain. Structural changes in the triglyceride moiety, such as the length of the fatty acid chains, the number of carbon-carbon double bonds, the configuration (*cis/trans*) of the carbon-carbon double bonds, and conjugation of the carbon-carbon double bonds directly affect the physical and chemical characteristics of the oil, such as its reactivity towards other reagents. Thus, vegetable oils can be classified as drying, semi-drying, and non-drying oils, depending on their ability to auto-oxidize in the presence of the oxygen in air.

Thermal polymerization process:



Free radical polymerization process:



$R''O\cdot$ = Free radical initiator fragment

Cationic polymerization process:

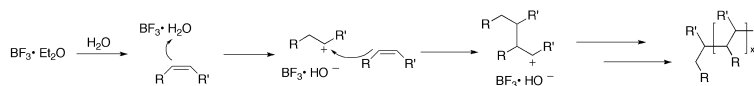
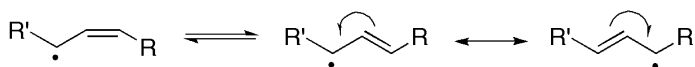


Figure 2. General reaction mechanisms for thermal, free radical and cationic polymerization.

Stabilization of a free radical:



Stabilization of a carbocation:

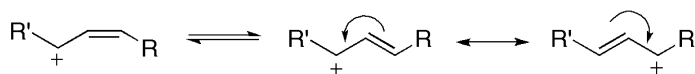


Figure 3. Resonance structures of a free radical and of a carbocation.

The carbon-carbon double bonds in triglycerides can be reacted in many different ways to form biobased polymers. The four main types of polymerizations discussed here are ROMP, cationic, free radical, and thermal polymerizations. While the free radical and thermal polymerizations of triglycerides follow essentially the same mechanism, differing only with respect to the initiation process, the cationic polymerization of triglycerides follows a different mechanism, initiated by a strong electrophile (11). The ROMP process involves still a different type of initiation process, which will be discussed in more detail later. Three out of the four polymerization mechanisms covered in this chapter are illustrated in Figure 2.

As expected thermodynamically, the intermediates formed during the free radical, thermal, or cationic polymerization of triglycerides can be further stabilized if the carbon-carbon double bonds are initially conjugated. In these cases, the intermediate free radicals and carbocations can be stabilized by the electrons on the adjacent double bonds, as shown in Figure 3. Thus, conjugated triglycerides are more readily polymerized than natural, non-modified oils.

Bioplastics from the Cationic Copolymerization of Natural Oils

As mentioned before and shown in Figure 2, a strong electrophile is required to promote the cationic polymerization of triglycerides and fatty acids. Lewis acids are the ideal species to initiate this process. Indeed, AlCl_3 , TiCl_4 , SnCl_4 , ZnCl_2 , FeCl_3 , $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, H_2SO_4 and $\text{BF}_3 \cdot \text{OEt}_2$ (BFE) have been used to initiate the cationic copolymerization of mixtures containing 50-94 wt % of regular or conjugated fish oil ethyl esters with divinylbenzene (DVB) and norbornadiene (NBD), or dicyclopentadiene (DCPD) under mild reaction conditions (33). Among the initiators tested, BFE is the most efficient (33) and is commonly used in the cationic copolymerization of natural oils with vinyl comonomers.

The cationic homopolymerization of either regular or conjugated fish oil ethyl esters affords only low molecular weight, viscous materials with limited utility (33). Therefore, the addition of reactive petroleum-based comonomers is crucial in order to obtain viable solid thermosets. The structure of the biobased starting material along with the nature and stoichiometry of the comonomers used during preparation of the bioplastics has an effect on the final properties of the polymer. The copolymerization of mixtures containing 30-60 wt % of a fish oil triglyceride, and regular or conjugated fish oil ethyl esters with various amounts of styrene (ST) and DVB affords materials ranging from soft rubbers to rigid plastics (34). It has been shown that the resulting fish oil triglyceride-containing polymeric material, due to its higher crosslink density, exhibits properties comparable to rigid plastics, while materials containing fish oil ethyl esters exhibit lower mechanical properties (34). Triglycerides have a branched structure that leads to extensive crosslinking. Each unsaturated fatty acid chain in the triglyceride can participate in the cationic reaction, thus a crosslinked, three-dimensional polymer network can be formed. Among the fish oil ethyl esters used, the conjugated esters exhibit overall better properties due to their higher reactivity (34). Likewise, the copolymerization of mixtures containing various amounts of conjugated fish oil triglycerides with DVB, NBD, or DCPD affords materials with overall better properties than the materials obtained from the cationic copolymerization of regular fish oil with the same comonomers (14). Overall, the fish oil-based bioplastics exhibit low creep-resistance at room temperature, but moduli comparable to those of conventional polyolefins (35). A comparison of the tensile properties of bioplastics made by the cationic copolymerization of various natural oils is presented in Table II (16, 34, 36, 40).

The conjugated carbon-carbon double bonds in tung oil are responsible for its high reactivity in cationic polymerization. Very strong materials, with storage moduli at room temperature (as determined by DMA) of about 2 GPa, are obtained from the cationic copolymerization of 50-55 wt % of tung oil with DVB (15). The gel time can be controlled by the substitution of up to 25 wt % of the tung oil with less reactive vegetable oils, such as soybean (SOY), low saturation soybean (LSS), or conjugated low saturation soybean (CLS) oils (15). Similarly, mixtures containing 35-55 wt % of corn or conjugated corn oil with various amounts of DVB and ST afford polymeric materials whose mechanical properties range from soft and rubbery to rigid plastics, depending on the stoichiometry of the comonomers used (36). The gel times can also be affected by the stoichiometry

of the comonomers, with an exponential increase in time for increasing amounts of the oil, especially beyond 40 wt % (36). The gel times for resins containing conjugated corn oil are significantly shorter than for resins made from regular corn oil, indicating the higher reactivity of the conjugated oil (36). The cure temperatures also affect the gel time of the cationic resins. For example, when a resin containing 45 wt % of corn oil, 32 wt % of ST, 15 wt % of DVB, and 8 wt % of BFE initiator is cured at room temperature, the gel time observed is 116 minutes. At 15 °C, the same resin doesn't gel completely in 24 hours (36).

Table II. Tensile Properties of Bioplastics Made by the Cationic Polymerization of Various Natural Oils

<i>Oil (wt %)</i>	<i>DVB (wt %)</i>	<i>Young's modulus (GPa)</i>	<i>Tensile strength (MPa)</i>
Fish oil (49)	15	0.82	42.6
Fish oil ethyl ester (49)	15	0.08	5.5
Conjugated fish oil ethyl ester (49)	15	0.45	18.3
Corn oil (45)	15	0.05	4.6
Conjugated corn oil (45)	15	0.07	7.0
Conjugated low saturation soybean oil (45)	15	0.23	11.5
Low saturation soybean oil (62)	30	0.06	3.0
Soybean oil (62)	30	0.05	2.5
Olive oil (62)	30	0.03	1.2
Peanut oil (62)	30	0.04	1.7
Sesame oil (62)	30	0.04	2.2
Canola oil (62)	30	0.04	1.7
Linseed oil (62)	30	0.10	5.6
Grapeseed oil (62)	30	0.05	3.0
Sunflower oil (62)	30	0.05	3.0
Safflower oil (62)	30	0.06	3.1
Walnut oil (62)	30	0.06	3.8

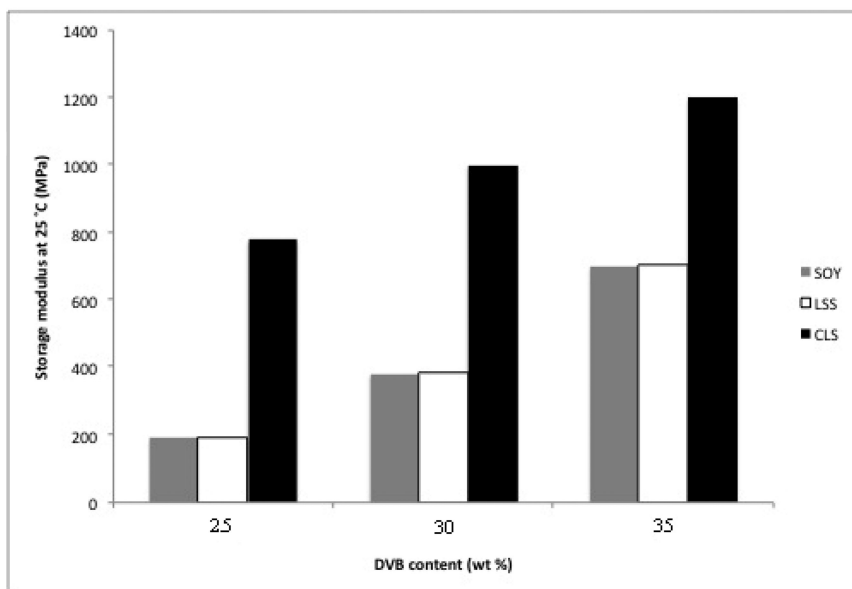


Figure 4. Storage modulus (as determined by DMA) as a function of divinylbenzene (DVB) content in soybean oil (SOY)-, low saturation soybean oil (LSS)-, and conjugated low saturation soybean oil (CLS)-based thermosets.

Extensive research has been conducted on the cationic copolymerization of SOY, LSS, and CLS with various crosslinking agents (37–45). Whenever 50–60 wt % of SOY, LSS, or CLS is copolymerized with DVB, a densely crosslinked polymer network, interpenetrated by 12–31 wt % of unreacted free oil or oligomers, is produced (37). The amount of unreacted free oil left after cure of the resin is directly dependent on the amount and reactivity of the oil initially employed in the preparation of the resin. Poor miscibility between the oil and the BFE initiator results in micro-phase separation in the SOY and LSS-based copolymers, with distinctly different crosslink densities in different parts of the bulk copolymer (37). Modification of the BFE initiator with other oils, especially with fish oil ethyl ester, helps in the homogeneous copolymerization of SOY, LSS, and CLS with DVB (37). The resulting bulk copolymers exhibit higher conversion of the oils into crosslinked thermosets than those utilizing the non-modified BFE initiator (37). With respect to the concentration of the comonomers, an increase in the room temperature storage modulus (as determined by DMA) of the final copolymer is seen when employing higher amounts of DVB in the original composition (37), as evidenced in Figure 4. For example, the storage modulus at room temperature increases from 0.78 GPa to 1.20 GPa when the DVB content increases from 25 wt % to 35 wt % in the CLS copolymers (37). The unreacted free oil or oligomers present in the final copolymers largely affects the thermal stability of the thermosets. The CLS polymers have the highest storage moduli and thermal stabilities, because they contain the least unreacted free oil (37).

To increase the structural uniformity of the crosslinked copolymers, the monofunctional monomer ST has been added to the original composition using

SOY, LSS, or CLS/DVB (38). With the substitution of 25-50 wt % of DVB by ST, the overall properties of the resulting plastics are significantly improved (38). The thermophysical properties of the thermosets are considerably affected by the crosslink density of the bulk copolymers and the yield of crosslinked material is strongly dependent on the concentration and reactivity of the crosslinking agent (DVB, DCPD, or NBD), and the reactivity of the oil used (38–40). Among the crosslinking agents used, DVB exhibits the highest reactivity and thus gives the most promising, crosslinked materials with good damping and shape memory properties (38–42). The overall properties of soybean oil-based thermosets are maximized when the concentration of the oil is equivalent to that of the other comonomers (40). An isothermal cure study of these systems established the ideal cure temperature to be in the range 12–66 °C, depending on the actual composition of the resin (43) and a DSC study of the cure of resins initiated by different concentrations of BFE revealed an optimum concentration of the Lewis acid equal to 2 wt % (45).

The cationic copolymerization of SOY and 100 % conjugated soybean oil (CSO) with DCPD in the presence of various modified BFE initiators has been studied and the results indicate that the commonly used fish oil ethyl ester modifier is unnecessary when the polymerization involves the more reactive CSO (46). It was also found that below a DCPD content of 42 wt %, the final thermosets behave as rubbers at room temperature (47).

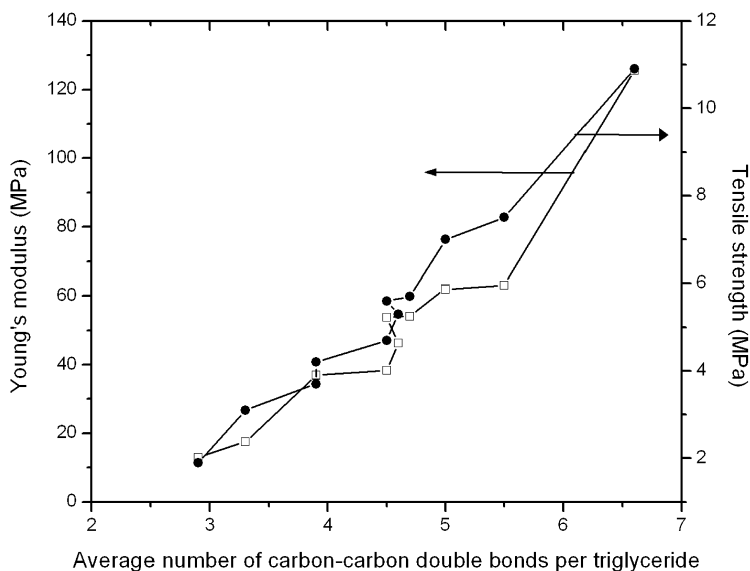


Figure 5. Young's modulus and tensile strength as a function of the average number of carbon-carbon double bonds per triglyceride in thermosets containing 45 wt % of vegetable oil, 32 wt % of styrene (ST), and 15 wt % of divinylbenzene (DVB).

A variety of other vegetable oils, including olive, peanut, sesame, canola, grapeseed, sunflower, safflower, walnut, and linseed oils have been cationically copolymerized with DVB and/or ST to form a range of thermosets with properties that can be tailored for specific applications (48). Overall, the properties of these new materials exhibit a gradual increase with the degree of unsaturation and thus increasing oil reactivity (48), as shown by the curves for the Young's modulus and tensile strength versus carbon-carbon double bond content shown in Figure 5. However, it has been found that the gelation times of these copolymers are independent of the degree of unsaturation of the vegetable oil used (48).

More recently, the products of the Diels-Alder reaction of linseed oil with cyclopentadiene (sold commercially as Dilulin), and the ene reaction between linseed oil and cyclopentadiene (sold commercially as ML189), have been copolymerized with DCPD (49). The structures of Dilulin and ML189 are represented in Figure 6. Due to the similar reactivity of DCPD and the modified linseed oils, homogenous thermosets containing 57-97 wt % of the biobased materials are obtained after their cationic copolymerization (49). As observed for thermosets prepared by the cationic copolymerization of SOY, LSS, and CLS with DVB (37, 40), the Dilulin and ML189/DCPD thermosets exhibit mechanical properties that increase with an increase in the amount of the crosslinking agent, DCPD. Overall, the cationic thermosets developed by the Larock group are dark brown in color, exhibit promising damping and shape memory properties, and may find applications in the substitution of petroleum-based plastics.

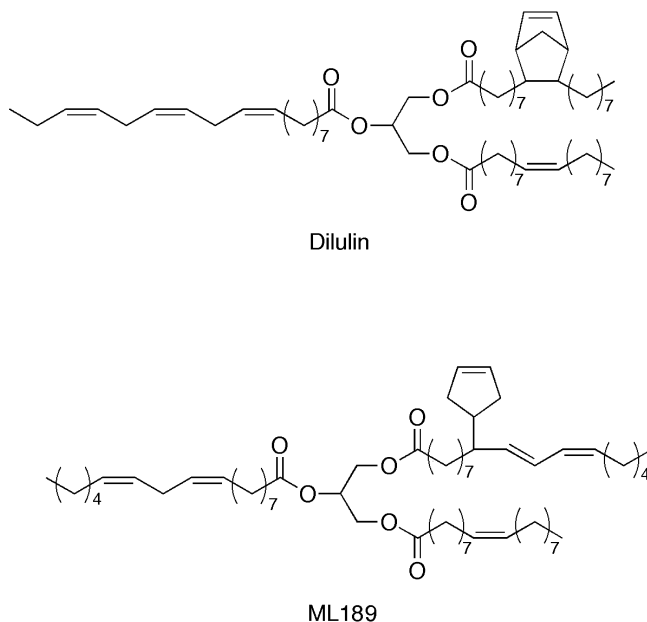


Figure 6. Chemical structures of Dilulin and ML189.

Bioplastics from the Free Radical Copolymerization of Vegetable Oils

Translucent vegetable oil-based thermosets have been obtained by the Larock group through the free radical copolymerization of reactive unsaturated triglycerides and vinyl comonomers (17, 18). The free radical copolymerization of vegetable oils with petroleum-based comonomers requires that the carbon-carbon double bonds in the oil be sufficiently reactive in order to form a homogeneous material. As discussed earlier, conjugated double bonds form more stable intermediates during free radical polymerization, suggesting that conjugated vegetable oils are better starting materials for the preparation of free radical biobased thermosets. The conjugation of a variety of vegetable oils can be easily achieved in the presence of a rhodium catalyst in a process developed by the Larock group and previously described in the literature (19, 20).

The bulk free radical copolymerization of mixtures containing 30-75 wt % of 100 % conjugated linseed oil with various amounts of acrylonitrile (AN) and DVB affords a range of materials from flexible to rigid thermosets (17). The free radical reaction, in this case, is initiated by 1 wt % of azobisisobutyronitrile (AIBN) (17). Although the materials exhibit promising thermophysical and mechanical properties, Soxhlet extraction with methylene chloride for 24 hours revealed that only 61-96 wt % of the oil, initially employed in the synthesis, is retained in the final thermoset (17). Alternatively, benzoyl peroxide has been used as a free radical initiator for the preparation of rigid thermosets containing 30-65 wt % of regular linseed oil, ST, and DVB (50). Independent of the free radical initiator used, there is a tendency for the properties to decrease when increasing the vegetable oil content in the thermosets (17, 50).

Soybean oil-based thermosets have been prepared by the copolymerization of mixtures containing 40-85 wt % of CLS with various amounts of AN, DVB, and/or DCPD in the presence of AIBN (18). The copolymers obtained exhibit 100 % incorporation of the CLS when the amount of oil initially added ranges from 40 wt % to 65 wt %, especially for the DCPD-containing thermosets (18). This higher oil incorporation in DCPD-containing thermosets is related to the similar reactivity of both components. When the oil content exceeds 70 wt %, a large amount of unreacted oil is recovered from the final thermoset after Soxhlet extraction with methylene chloride (18). A wide range of thermal and mechanical properties have been obtained by simply changing the stoichiometry of the resin components.

Bioplastics from the Thermal Copolymerization of Vegetable Oils

Drying oils undergo auto-oxidation in the presence of oxygen, and form peroxides, which then undergo crosslinking through free radical recombination to form highly branched polymeric materials. This characteristic of drying oils makes them very useful biorenewable materials for the coatings industry. It has been shown that vegetable oil-based free radical macroinitiators can be formed by a similar process using linseed and soybean oils (50-52). Such free radical macroinitiators have been used to initiate the polymerization of methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA) to form polymeric linseed (52) and soybean oil (51) grafted copolymers, respectively. One of the advantages

of these new materials is their partial biodegradability and biocompatibility when compared to standard PMMA and PnBMA (51, 52).

In 1940, a tung oil-styrene copolymer was produced by simply heating these two compounds at 125 °C for 3 days (53). However, tung oil constituted only 0.1-2.0 % of the copolymer in that work (53). Thermosets containing 30-70 wt % of tung oil (TUN) have been prepared by the Larock group through the thermal copolymerization of TUN with various amounts of ST and DVB at temperatures ranging from 85 °C to 160 °C (12). The materials prepared range from rubbery polymers to tough and rigid plastics (12). These fully cured thermosets, initiated by simply heating the mixture, exhibit higher crosslink densities and overall better properties when metallic salts of Co, Ca, and Zr are added as catalysts during the cure (12). Similar materials have been prepared using 30-70 wt % of a commercially available 87 % conjugated linseed oil (13). Once again, materials ranging from rubbers to hard plastics are obtained by simply varying the stoichiometry of the comonomers (13). The use of a less reactive oil, compared to TUN, resulted in the appearance of two distinct glass transition temperatures (T_g 's), which indicates a microphase separation into oil-rich and DVB-rich phases (13). A scanning electron microscopy (SEM) analysis of solvent extracted samples of such thermosets revealed that the soluble components consist mainly of unreacted oil, which is well distributed throughout the polymer matrix, leaving evenly distributed nanopores after extraction (13). As observed for the TUN-based thermally produced thermosets (12), the use of increasing amounts of cobalt drying catalysts, during the cure, results in increasingly higher crosslink densities (5).

Bioplastics from the Ring Opening Metathesis Polymerization (ROMP) of Modified Vegetable Oils

In the ROMP process, strained, unsaturated cyclic molecules are opened at the carbon-carbon double bond, by interaction with a ruthenium carbene catalyst. Subsequent coordination of a new molecule of the strained ring and metathesis of the carbon-carbon double bonds results in an unsaturated polymer (54) that can be additionally crosslinked through thermal reaction of the remaining carbon-carbon double bonds. A step-wise illustration of the ROMP process is provided in Figure 7, using norbornene as an example of a strained, unsaturated ring. If more than one type of strained, unsaturated ring is present in the reaction medium, a copolymer is formed.

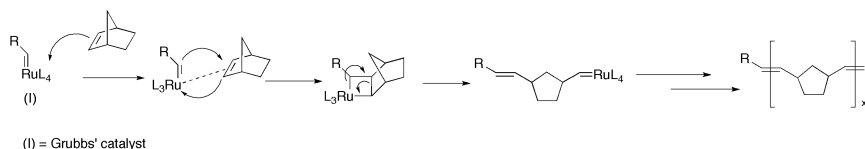


Figure 7. Step-wise ring opening metathesis polymerization (ROMP) mechanism using norbornene as an example.

In order for vegetable oils to participate in ROMP, modification of the fatty acid chains is necessary. As mentioned earlier, the Diels-Alder reaction of cyclopentadiene and linseed oil produces a commercially available product, Dilulin, which has been used, by the Larock group, in ROMP with a norbornene-based crosslinking agent (22). As the content of the crosslinking agent increases from 0 wt % to 50 wt %, increases in the thermal stability and the crosslink density of the resulting thermosets are observed (22). Quantitative incorporation of Dilulin in the polymer network is attained even in the presence of lower amounts of the crosslinking agent (22). DCPD has also been employed as a crosslinking agent in ROMP with Dilulin, but unlike the results obtained with the norbornene-based crosslinking agent (22), the maximum oil incorporation was only 80 wt % (55). The 20 wt % of unreacted free oil acts as a plasticizer in the final thermoset (55). Decreasing the DCPD content in those thermosets results in materials with lower T_g 's (55).

Castor oil, where approximately 90 % of the fatty acid chains bear an hydroxyl group on C12, has also been modified for use in ROMP reactions (21). It has been reacted with bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride to give a norbornenyl-functionalized triglyceride, referred to as BCO and represented in Figure 8. Varying amounts of this modified oil (55-85 wt %) have been copolymerized with cyclooctene in the presence of 0.5 wt % of the 2nd generation Grubbs catalyst to afford transparent rubbery thermosets (21). An increase in the thermal stability of such thermosets has been observed when increasing the oil content (21). It has been shown that the thermal stability of ROMP thermosets is closely related to the presence of unreacted triglycerides in the final material (21).

A different approach to the preparation of biobased ROMP thermosets involves the use of vegetable oil-derived functionalized fatty alcohols (23). Norbornenyl-functionalized fatty alcohols from soybean oil (NMSA), Dilulin (NMDA), ML189 (NMMA) and castor oil (NMCA) have been prepared and polymerized in the absence of other comonomers (23). These fatty alcohols are represented in Figure 9. The number of norbornenyl groups appended to the fatty acid alcohols and their viscosity affect the final properties of the thermosets. Polymers obtained from the ROMP of NMDA and NMMA exhibit Young's moduli and ultimate tensile strengths comparable to HDPE and poly(norbornene), and show promise as high performance bioplastics (23). In order to avoid the problems associated with viscosity during the ROMP of biobased systems, novel norbornenyl-functionalized castor oil (NCO) and fatty alcohol (NCA), were developed by reacting castor oil and its fatty alcohol with norbornene carbonyl chloride (56). The chemical structures of NCO and NCA are shown in Figure 10. The ROMP of NCO and NCA results in rubbery to rigid transparent thermosets with increased crosslink densities and good thermophysical and mechanical properties, and thermal stabilities (56).

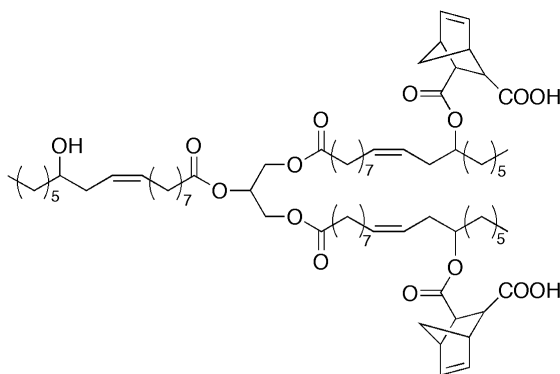


Figure 8. Chemical structure of BCO.

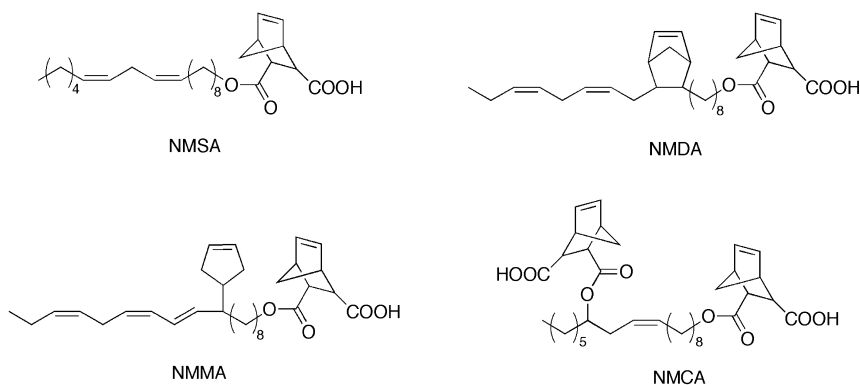


Figure 9. Chemical structures of NMSA, NMDA, NMMA, and NMCA.

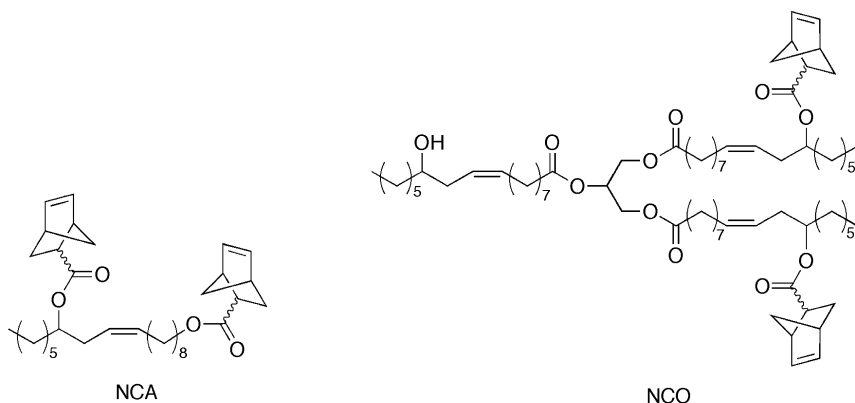


Figure 10. Chemical structures of norbornenyl-functionalized castor oil fatty alcohol (NCA) and norbornenyl-functionalized castor oil (NCO).

Biocomposites

In order to improve the thermophysical and mechanical properties of the biobased thermosets developed by the Larock group, the biobased polymeric matrices have been reinforced with inorganic fillers and natural fibers. The use of such fillers in the preparation of biocomposites significantly improves the Young's modulus and the tensile strength. Using natural fibers, high biobased content biocomposites, with a biorenewable content of up to 85 wt %, have been prepared.

Vegetable Oil-Based Biocomposites Reinforced with Inorganic Fillers

Particularly stiff materials have been obtained by reinforcing the cationic corn oil-based copolymers described previously (36) with continuous glass fibers (25). It has been shown that significant improvements in Young's modulus and tensile strength can be attained by using up to 45 wt % of glass fibers (25). Indeed, the Young's modulus increases from 4.1 MPa to 874 MPa and the tensile strength increases from 1.7 MPa to 8.4 MPa, when the glass fiber content is increased from 0 wt % to 45 wt % (25). Changes in the resin composition also affect the final properties of the composites (25). As discussed previously (36), increases in the DVB content of the resin result in an increase in the crosslink density of the thermoset, which has a positive effect in the thermophysical properties of the material. Also, the replacement of regular corn oil by conjugated corn oil results in a material with slightly better properties due to the higher reactivity of the conjugated system.

In similar work, soybean oil-based cationic resins have been reinforced with continuous glass fibers (57). SOY and LSS have been copolymerized with ST and DVB, in the presence of 0-50 wt % of continuous glass fibers, in a cationic process initiated by fish oil ethyl ester-modified BFE (57). As a result, significant increases in the Young's modulus from 0.15 GPa to 2.73 GPa, and in the tensile strength from 7.9 MPa to 76 MPa, have been obtained (57). The thermal stabilities and mechanical properties can also be improved by increasing the crosslink density of the matrix. Such materials have promise for use in housing and automotive applications.

Glass fibers have also been used as a reinforcement for Dilulin/DCPD ROMP resins, producing promising composites (58). Such resins have been described previously by the Larock group (55). They exhibit an increase in T_g values for the higher crosslink densities obtained by increasing the DCPD content in the original formulation (55). Since the presence of glass fibers has no effect on the crosslink density, no changes in either the T_g values or the thermal stability are detected when the pure resin is compared to the glass fiber composite (58). Although the presence of 40 wt % of glass fibers results in an increase in the Young's modulus from 29 MPa to 168 MPa, SEM revealed a weak interaction between the fibers and the matrix (58). Nevertheless, the ability of the fibers to reduce crack propagation and fracture results in an overall improvement in all of the mechanical properties (58).

A different class of biocomposites has been prepared by reinforcing cationic thermosets with a functionalized organoclay (26). The cationic thermosets have been prepared by the copolymerization of either conjugated soybean oil (CSO) or CLS with ST and DVB. The resin has been reinforced with a reactive organomodified montmorillonite clay (26). The filler has been prepared by the cationic exchange of sodium montmorillonite with (4-vinylbenzyl)triethylammonium chloride in aqueous solution (26). Wide angle X-ray (WAX) and transmission electron microscopy (TEM) experiments have revealed the nanocomposite character and the morphology of the composites prepared (26). The latter greatly depends on the amount of nanofiller added, with an intercalated and exfoliated morphology at organoclay loadings ranging from 1 wt % to 2 wt % (26). That loading range also results in the best overall properties, especially thermal stability (26). The use of the more unsaturated CLS oil over CSO results in even better composites (26).

The same organoclay filler has also been used as a reinforcement for corn oil-based cationic resins (59). The resin consisted of a copolymer of conjugated corn oil, ST, and DVB. In this system, optimum, intercalated composites have been obtained for clay loadings between 2 wt % and 3 wt % (59). Changes in the crosslink density result in an improvement in the mechanical properties (59).

Vegetable Oil-Based Biocomposites Reinforced with Agricultural Residues

Composites with a high biobased content have been prepared, by compression molding, using a variety of ligno-cellulosic fillers. Spent germ, the co-product of wet mill ethanol production, has been used, at different particle sizes, to reinforce a tung oil-based free radical resin, initiated by *t*-butyl peroxide (27). The resin consists of a copolymer of tung oil (50 wt %), BMA, and DVB (27). When compared to the pure resin, the reinforced thermosets exhibit higher storage moduli (as determined by DMA), and thermal stabilities compared with the filler and the resin alone (27). The use of shorter particles and higher DVB content results in better properties (27). When the filler load is increased from 40 wt % to 60 wt %, agglomeration and formation of micro-voids in the composite cause a decrease in the properties and an increase in the wear depth against diamond (27, 60). This phenomenon can be compensated for by an increase in the molding pressure (27). An increase in the DVB content reduces the wear depth caused by a diamond probe (60). It was also found that residual corn oil from the spent germ acts as a plasticizer in the composite and if it is removed prior to preparation of the composite, better mechanical properties are obtained (27, 60).

In similar work, a CSO-based free radical resin has been reinforced with soybean hulls (28). The concentration of the resin comonomers, BMA, DVB, and DCPD, has been varied, as well as the filler particle size, the filler load (50-60 wt %), and the molding pressure (28). The concentration of CSO in the resin has been kept constant at 50 wt % (28). An optimum cure sequence of 5 hours at 130 °C, followed by a post-cure of 2 hours at 150 °C, has been established by differential scanning calorimetry (DSC) (28). Whenever BMA or DVB are substituted by DCPD, the mechanical properties are compromised (28). In this particular system, a decrease in the properties was observed when an excessive

molding pressure of 368 psi was applied (28). As previously observed by the Larock group, when studying resins composed of comonomers with different reactivities, the appearance of two distinct T_g 's implies that the resin is phase separated (28, 37).

Free radical resins containing 50 wt % of either CSO or conjugated linseed oil (CLO), and various amounts of DVB and BMA have been reinforced with 20-80 wt % of corn stover (29). Increasing the amount of corn stover and decreasing the length of the fiber results in an overall improvement of the mechanical properties and a decrease in the thermal stability of the biocomposites (29). As expected, water uptake experiments have confirmed that water absorption increases with the fiber content of the composite (29).

Wheat straw has also been used as a natural filler in the preparation of a CLO-based biocomposite (30). The resin consisted of a copolymer containing 50 wt % of CLO and various amounts of DVB, BMA, and maleic anhydride (MA) (30). MA acts as a compatibilizer between the hydrophobic matrix and the hydrophilic resin, and incorporation of 5-15 wt % of MA in the composites' structure results in significant improvements in the mechanical properties (30). As noticed with other natural fillers studied by the Larock group, an increase in the filler load from 50 wt % to 90 wt % results in improvements in the mechanical properties and a decrease in the thermal stability (30).

A free radical resin composed of 50 wt % CLO, 35 wt % BMA, and 15 wt % DVB has been used to determine the optimal conditions for the preparation of rice hull biocomposites (31). The mechanical properties were optimized when a cure sequence of 5 hours at 180 °C under 600 psi of molding pressure was applied, followed by a post-cure of 2 hours at 200 °C under ambient pressure (31). Also, 70 wt % of dried rice hulls, at a particle size smaller than 1 mm diameter, afford the best composite properties (31). SEM along with X-ray mapping of the fractured composites revealed the presence of significant amounts of silica in the rice hulls, which may account for the high mechanical and thermal properties obtained (31). With the optimum parameters established for the preparation of rice hull biocomposites (31), changes in the resin composition were evaluated (61). It has been observed by SEM that the addition of MA to the resin significantly improves the filler-matrix interactions (61). Composites made from CLO exhibit better overall properties than those prepared from CSO, due to the higher degree of unsaturation of the CLO (61).

The same CLO-based free radical resin has been reinforced with switch grass (32). Improvements in the mechanical properties of the composites have been observed when increasing the load of the filler up to 70 wt % (32). Beyond that point, excessive agglomeration of the filler compromises the composites' properties.

Finally, a thorough study has been carried out of the effect of different natural oils and different natural fillers on the properties of cationic composites (62). Cationic resins made from CSO, CLO, conjugated corn, and fish oils have been reinforced with corn stover, wheat straw, and switch grass (62). The resins all possessed 50 wt % oil, while the concentrations of ST and DVB were varied. The oils with a higher degree of unsaturation resulted in composites with better

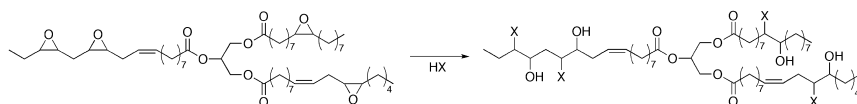
properties (62). With respect to the different fillers studied, wheat straw afforded composites with the most promising properties (62).

Vegetable Oil-Derived Biocoatings

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 (63). The epoxidized triglycerides can be reacted with various molecules to append different functional groups and increase the reactivity of the oil. Acrylated epoxidized soybean oil (AESO), synthesized from the reaction of acrylic acid and epoxidized soybean oil, has been extensively studied in polymers and composites (64) and is commercially available under the trade name of Ebecryl 860. Recently, AESO has been used to produce thermosetting foams with a high biobased content and mechanical properties comparable to semi-rigid industrial foams (65). Besides soybean oil, epoxidized methyl oleate has been acrylated and polymerized to afford pressure-sensitive adhesives (66). Only the work developed by the Larock group, related to the preparation of polyurethanes and latexes from epoxidized vegetable oils, will be covered in this section.

Polyurethane Dispersions from Vegetable Oil Polyols

Epoxidized vegetable oils can be converted into polyols by the ring opening reaction of the epoxide groups in the triglyceride. Such polyols can react with diisocyanates to give vegetable oil-based polyurethanes. Figure 11 illustrates the ring opening reaction of epoxidized soybean oil. Castor oil and ricinoleic acid, both of which contain hydroxyl groups, have been used in the preparation of polyurethanes directly or after modifications (67–69). Polyols based on a variety of epoxidized oils (sunflower, canola, soybean, corn, and linseed oils) have been polymerized with methylene diphenyl diisocyanate (MDI) to give polyurethanes (70). It has been found that the differences in the properties of these polyurethane networks results primarily from different crosslink densities, and less from the position of the reactive sites in the fatty acids.



X = Cl, CH₃O, H₂C=CHCO₂

Figure 11. Ring opening reaction of epoxidized soybean oil.

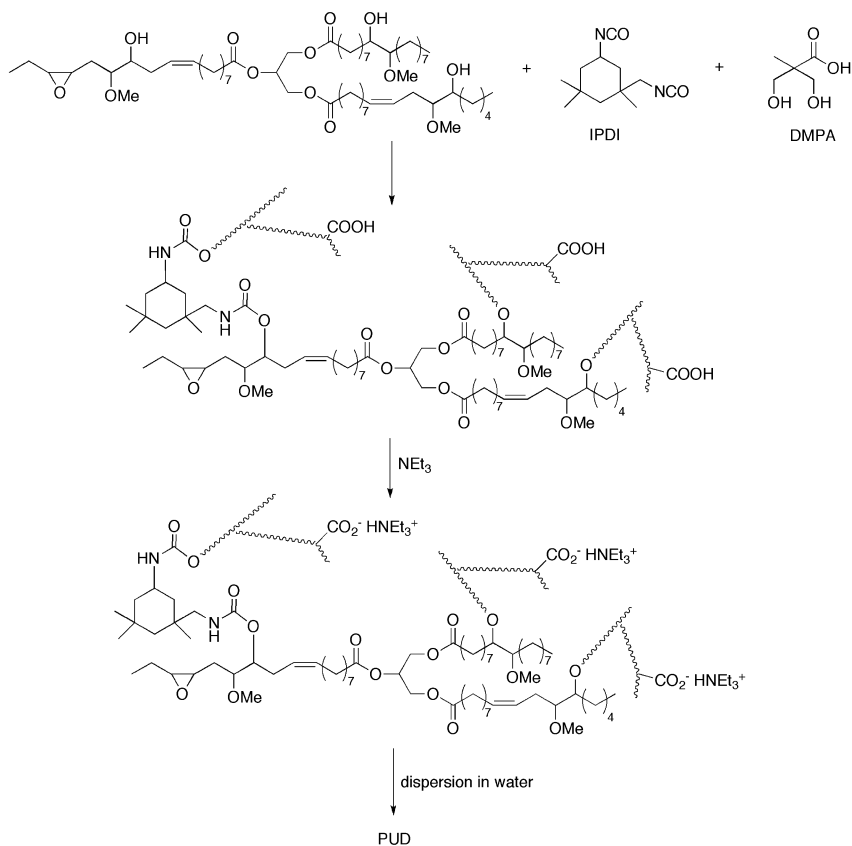


Figure 12. Preparation of a soybean oil-based anionic waterborne polyurethane dispersion (PUD).

Environmentally friendly, waterborne polyurethane dispersions (PUD's), containing no volatile organic compounds (VOCs), have found wide applications as coatings and adhesives, and related end uses. Methoxylated soybean oil polyols (MSOLs), prepared by ring opening epoxidized soybean oil by methanol, with hydroxyl numbers per triglyceride ranging from 2.4 to 4.0, have been used to prepare anionic PUD's with uniform particle sizes and biobased content ranging from 50 wt % to 60 wt % (6). These soybean oil-based waterborne PUD's have been obtained by the reaction of MSOLs with isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA), followed by neutralization with triethylamine and then dispersion in water (6). The reaction scheme is shown in Figure 12. Increased OH numbers in the MSOLs significantly increase the crosslink density of the polyurethanes, while increased hard segment content improves the interchain interactions caused by hydrogen bonding. Therefore, the structure and the properties of the resulting biorenewable polyurethanes greatly depend on these two factors (6).

Recently, the preparation of vegetable oil-based cationic PUD's with uniform particle sizes has been reported in the literature (7). Castor and methoxylated and

acrylated epoxidized soybean oil-based polyols have been reacted with *N*-methyl diethanol amine (MDEA) and MDI to form biobased polyurethanes containing tertiary amines (7). Hydrophilic groups were then formed by the addition of acetic acid and the resulting polyurethanes have been dispersed into water to give cationic PUD's (7). Compared to anionic PUD's, cationic PUD's exhibit very high adhesion to a variety of anionic substrates, such as leather and glass, which suggests wide application of these new materials as adhesives and coagulants.

Vegetable Oil-Based Hybrid Latexes

In order to increase the mechanical properties of the biobased polyurethanes developed by the Larock group, soybean oil-based anionic PUD's have been allowed to undergo emulsion copolymerization with acrylic comonomers, resulting in polyurethane-acrylic hybrid latexes with 15-60 wt % biobased content (8, 71). The polyurethane dispersions employed in such hybrid latexes have been prepared from either a soybean oil-based polyol or AESO (71), toluene 2,4-diisocyanate, and DMPA. Butyl acrylate and methyl methacrylate have been grafted onto the soybean oil-based polyurethane network by the free radical reaction of the carbon-carbon double bonds in the fatty acid chains and the acrylates (8, 71). The resulting hybrid latexes exhibit properties comparable to those of polypropylene glycol-based polyurethane/acrylic hybrid latex films indicating their potential application in the coatings industry.

Vegetable Oil-Based Core-Shell Latexes

Surfactant-free, core-shell hybrid latexes have been synthesized by seeded emulsion polymerization of 10-60 wt % vinyl monomers (styrene and butyl acrylate) in the presence of a soybean oil-based PUD as seed particles (9). The soybean oil-based PUD, synthesized by reacting IPDI with methoxylated soybean oil polyols and DMPA, forms the latex shell, and serves as a high molecular weight emulsifier, while the vinyl polymers form the core (9). The core-shell hybrid latex films show a significant increase in thermal stability and mechanical properties when compared to the pure polyurethane films, due to grafting and crosslinking in the hybrid latexes (9).

Conclusions

The technology developed in the Larock group over the last decade involves the use of natural oil-based materials in the preparation of diverse green products, such as bioplastics, biocomposites and biocoatings. The progress made in the last 10 years on the development of these new natural oil-based products has been substantial and is expanding rapidly. Biobased thermosets ranging from rubbery to hard plastics have been synthesized by the cationic, free radical, thermal, and ring opening metathesis copolymerization of a variety of natural oils with numerous petroleum-based comonomers. In general, a similarity in the reactivities of the

comonomers used in the preparation of the thermoset resins is of great importance in maximizing the oil incorporation and the homogeneity of the products obtained.

The biobased cationic, free radical, and ROMP resins have been reinforced with continuous glass fibers, functionalized organoclays, and a variety of natural fillers to afford high biobased content biocomposites. In comparison to the pure resins, significant improvements have been obtained in the mechanical properties by the addition of the fillers.

The preparation of anionic and cationic vegetable oil-based waterborne PUD's with uniform particle sizes has been achieved. Significant improvements in the thermophysical and mechanical properties have been attained by emulsion copolymerization of the PUD's with acrylates and vinyl comonomers, forming hybrid and core-shell latexes, respectively.

Current research in the Larock group on biobased materials includes improvements in the current processes, examination of other naturally occurring oils and commercially available comonomers, exploration of other polymerization processes, development of appropriate processing procedures, and examination of the new materials in various industrial applications.

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