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Development of Vegetable-Oil-Based Polymers

Muhammad Remanul Islam, Mohammad Dalour Hossen Beg, Saidatul Shima Jamari

Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang,
Lebuhraya Tun Razak, Gambang 26300, Kuantan, Malaysia
Correspondence to: M. R. Islam (E-mail: remanraju@yahoo.com) and M. D. H. Beg (E-mail: dhbeg@yahoo.com)

ABSTRACT: The utilization of renewable resources for the preparation of new materials is an alternative option for reducing the high demand of fossil feedstocks. Vegetable oils are potential bioresources that are renewable and abundantly available. Triglyceride-based vegetable oils, such as soybean, jatropha, linseed, sunflower, palm, castor, nahar seed, and canola oil, are being considered as precursors in the production of polymers. In this article, we attempt to summarize advancements in processes and technologies for the synthesis of polymers from various kinds of vegetable oils. The advantages and disadvantages of these biobased polymers with respect to traditional monomer-based ones are also highlighted. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40787.

INTRODUCTION

Polymers are used for various technical purposes, depending on their diversifying properties. A wide range of functional differences and behaviors has made them useful in a large variety of applications. The monomer and architectural organization of the macromolecules simultaneously decide the dominating properties of the polymers. The endless numbers of options for creating or modify polymers have made these materials attractive to researchers. Moreover, the high price of petroleum-based polymers, their nonbiodegradable nature, the significant amount of greenhouse gas emission and huge heat consumption during their processing, the scarcity of the raw materials, environmental legislations, and so on are also responsible for the search for biobased alternatives. Among biobased resources, triglyceride-based vegetable oils are important for polymer synthesis. Vegetable and modified oils have been used as main raw materials for resin preparation. Linseed and tung oil have been used for coating ingredients in oil paints and varnishes.[1] These oils are heated thermally to prepare paint ingredients through a reaction called a *Diels–Alder reaction*. Sometimes, modifications of nondrying oils by drying oils have been found to be fruitful in the preparation of polymers. For example, modified palm oil was produced by an interesterification process with tung oil for the preparation of water-reducible acrylic–alkyd resin.[2] Various polymerization reactions, including cationic, condensation, and radical copolymerization reactions, have been used to produce various types of polymers, such as polyesters, polyamides, epoxies, and polyurethanes (PUs).

In this article, we review the synthesis of vegetable-oil-based polymers of different kinds with different polymerization reactions and techniques. Generally, these polymers are environmentally friendly and inexpensive and produced from readily available raw materials. These polymers are used as coatings, adhesives, insulators, binders, medicinal sutures, and matrixes for the preparation of composites. Figure 1 shows various applications of vegetable oils in polymer sectors. The properties of these polymers are comparable to those of petroleum-based polymers and are sometimes even superior.

VEGETABLE OIL

Nature is blessed with abundant numbers of plant oils. Oils are ester compounds and consist of a glycerol molecule linked with three saturated or/and unsaturated fatty acids. Oils can be classified as drying, semidrying, and nondrying, depending on the unsaturation present on them. Drying oil, on exposure to air after a period of time, becomes a hard and solid filmlike material because of the crosslinking between fatty acid chains through the atmospheric oxygen molecule. Over many years, drying oils have been used in oil paints and as surface-coating materials because of this property. Oil properties can be measured by different parameters, including the iodine value, acid value, saponification value, and peroxide value. The degree of unsaturation in oil can be determined by the iodine value. The higher the iodine values are, the higher the unsaturation in the oils is. The determination of the acid value is important for measuring the free fatty acids or acidity present in the oil. Additionally, sometimes, the extent of the polymerization reaction or

Muhammad Remanul Islam received his Masters of Engineering in Chemical Engineering in 2012 from the Universiti Malaysia Pahang. Currently, he is studying for a Ph.D. in Chemical Engineering at the same university. His research interests include natural-fiber-based biocomposites and the synthesis of biopolymers from vegetable oils. He has published a number of research articles in various international journals.

Mohammad Dalour Hossen Beg received his Ph.D. from Waikato University, New Zealand. He is currently working for the University Malaysia Pahang as an associate professor in the Faculty of Chemical and Natural Resources Engineering. He has a numbers of publications on polymer composites in international journals.

Saidatul Shima Binti Jamari received her Ph.D. in Chemical Engineering from the University of Sheffield, United Kingdom. Currently, she is working as a senior lecturer at the University Malaysia Pahang in The Faculty of Chemical and Natural Resources Engineering.

the desired level of acidity in the sample can be monitored by the same. The chain length or average molecular weight of the fatty acids present in the oil can be determined by the saponification value. The short-chain fatty acids in oil have a higher saponification value, whereas the long-chain fatty acids have a lower value. The peroxide value is required to detect the rancidity or freshness of oil samples. The density of all oils ranges from 0.80 to 0.95 g/cm^{3}, and the specific gravity is around 0.9. All of these properties, directly or indirectly, control the characteristic profiles of polymers produced from vegetable oils. Table I shows the iodine values of some common vegetable oils.[3]

Fourier transform of infrared (FTIR) and ^{1}H-NMR spectroscopy are essential techniques for the determination of particular functional groups and the structural elucidation of oil and resin. The curing kinetics and fatty acid content can be calculated through FTIR analysis. Important absorption peaks for FTIR spectroscopy and chemical shifts for ^{1}H-NMR of vegetable oil (jatropha) are presented in Tables II and III, respectively.[4] A number of fatty acids are available in vegetable oils. These fatty acids are of different types in terms of the variation of chain

length, the number of carbon atoms, the presence of double or treble bonds, and the presence and position of these bonds. The type and content of fatty acids in vegetables oils are different and vary from oil to oil. Among the fatty acids, stearic acid, oleic acid, linoleic acid, and linolenic acids of carbon atom number 18, with an order of increasing unsaturation, are present in canola, linseed, and sunflower oil. These acids contribute more than 90% of the total acid content of the aforementioned oils.[5] A list of common fatty acids available in various types of oils is presented in Table IV. Table V represents the fatty acid percentages present in various types of vegetable oils. Fatty acid contributes 94–96% of the total weight of the triglyceride molecule.[6] Polymeric properties depend on the reactivity of vegetable oils, the properties of fatty acids, and their relative percentages.[6]

Figure 1. Applications of vegetables oils as biopolymers.

Table I. Iodine Values of Common Vegetable Oils

Name	Iodine value (g of I_2/100 g)
Castor	102.2
Coconut	15.1
Corn	123.5
Cottonseed	109.4
Linseed	180.0
Palm	43.3
Safflower	134.7
Soybean	128.7
Sunflower	120.0

Table II. FTIR Data for Vegetable Oils

Absorption band (cm^{-1})	Functionality
3468	—O—H stretching vibration
2856–2924	Aliphatic C—H stretching vibration
1744	C=O stretching vibration of triglyceride esters
1655	C=C stretching vibration
1456	C—H bending vibration
1162	C—O—C stretching vibration of esters
719	Methylene rocking vibration

For example, the dielectric properties of oleic acid based PU was assessed by Velayutham et al.,[7] and they found that the proton originating from the oleic acid determined the relaxation mechanism of the dielectric properties of PU. The authors claimed that the higher oleic acid content produced a higher amount of flexible side changes, and this resulted in a less compact polymer.

TYPES OF BIOPOLYMERS

In the following subsections, the details of the preparation methods of the biopolymers from vegetable oils, polymerization reactions, advantages and disadvantages, and properties with examples of innovative materials are discussed. Moreover, a correlation is drawn among the existing methods. A comparative discussion between the vegetable-oil-based polymers and that of traditional monomer-based polymers is also highlighted.

Polyesters

Polyesters have been used as a major binder since the starting of the 19th century because of their excellent auto-oxidative, chemical, and mechanical properties.[7] The general methods for preparing polyesters are (1) the polycondensation reaction of hydroxyl group (—OH) containing organic acids or diacids with a diol and (2) the ring-opening polymerization of lactones (Scheme 1).[8] Earlier, tartaric and phthalic acid were used individually to prepare polyesters by a reaction with glycerin, but the polyesters were found to be brittle and inflexible, whereas fatty acids with glycerin showed good film-forming properties. Because vegetable oils are very rich sources of various kinds of carboxylic acids, their modification through the esterification

Table III. Some Representative ^{1}H-NMR Shift Values for Vegetable Oil

^{1}H chemical shift (ppm)	protons
0.87–0.89	Protons of terminal methyl groups
1.60	Protons of internal —CH$_2$— groups
2.01–2.05	Allylic protons of CH$_2$
2.30–2.32	α protons of ester groups
2.75–2.78	—CH$_2$ of double allylic protons
4.15–4.28	Protons of glyceride moieties
5.32–5.35	Protons of the —CH=CH— moieties

**Table IV.** Common Fatty Acids, Structures, and Formulas

Name	Scientific name	Structure	Formula	CN/DB	Type
Caprylic	Octanoic acid	CH$_3$(CH$_2$)$_6$COOH	C$_8$H$_{16}$O$_2$	8:0	Saturated
Capric	Decanoic acid	CH$_3$(CH$_2$)$_8$COOH	C$_{10}$H$_{20}$O$_2$	10:0	Saturated
Lauric	Dodecanoic acid	CH$_3$(CH$_2$)$_{10}$COOH	C$_{12}$H$_{24}$O$_2$	12:0	Saturated
Myristic	Tetradecanoic acid	CH$_3$(CH$_2$)$_{12}$COOH	C$_{14}$H$_{28}$O$_2$	14:0	Saturated
Palmitic	Hexadecanoic acid	CH$_3$(CH$_2$)$_{14}$COOH	C$_{16}$H$_{32}$O$_2$	16:0	Saturated
Stearic	Octadecanoic acid	CH$_3$(CH$_2$)$_{16}$COOH	C$_{18}$H$_{36}$O$_2$	18:0	Saturated
Arachidic	Eicosanoic acid	CH$_3$(CH$_2$)$_{18}$COOH	C$_{20}$H$_{40}$O$_2$	20:0	Saturated
Palmitoleic	Hexadec-9-enoic acid	CH$_3$(CH$_2$)$_5$CH=CH(CH$_2$)$_7$COOH	C$_{16}$H$_{30}$O$_2$	16:1	Monounsaturated
Oleic	Octadec-9-enoic acid	CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH	C$_{18}$H$_{34}$O$_2$	18:1	Monounsaturated
Erucic	Docos-13-enoic acid	CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_{11}$COOH	C$_{22}$H$_{42}$O$_2$	22:1	Monounsaturated
Linoleic	9,12-Octadecadienoic acid	CH$_3$(CH$_2$)$_4$CH=CH—CH$_2$—CH=CH(CH$_2$)$_7$COOH	C$_{18}$H$_{32}$O$_2$	18:2	Polyunsaturated
α-Linolenic	Octadeca-9,12,15-trienoic acid	CH$_3$—CH$_2$—CH=CH—CH$_2$—CH= CH—CH$_2$—CH =CH(CH$_2$)$_7$COOH	C$_{18}$H$_{30}$O$_2$	18:3	Polyunsaturated
α-Eleostearic	Octadeca-9,11,13-trienoic acid	CH$_3$—(CH$_2$)$_3$—CH =CH—CH= CH—CH= CH(CH$_2$)$_7$COOH	C$_{18}$H$_{30}$O$_2$	18:3	Polyunsaturated
Ricinoleic	(9Z,12R)—12-Hydroxyoctadec-9-enoic acid	CH$_3$(CH$_2$)$_5$CH(OH)CH$_2$CH=CH(CH$_2$)$_7$COOH	C$_{18}$H$_{34}$O$_3$	18:1	Monounsaturated
Vernolic	Cis-12,13-epoxy-cis-9-octadecenoic acid	CH$_3$(CH$_2$)$_4$CH—CH—CH$_2$—CH=CH(CH$_2$)$_7$COOH	C$_{18}$H$_{32}$O$_3$	18:1	Monounsaturated

Table V. Common Vegetable Oils and Their Fatty Acid Content

Name	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic	Arachidic	Oleic	Erucic	Linoleic	Linolenic	Ricinoleic
Palm	–	–	–	1.2	41.8	3.4	–	41.9	–	11.0	–	–
Soybean	–	–	–	–	14.0	4.0	–	23.3	–	52.2	5.6	–
Coconut	6.2	6.2	51.0	18.9	8.6	1.9	–	5.8	–	1.3	–	–
Sunflower	–	–	–	–	6.5	2.0	–	45.4	–	46.0	0.1	–
Rapeseed	–	–	–	–	4	2	–	56	–	26	10	–
Castor	–	–	–	–	1.5	0.5	–	5	–	4	0.5	87.5
Linseed	–	–	–	–	5	4	–	22	–	17	52	–
Naharseed	–	–	–	–	15.9	9.5	–	52.3	–	22.3	–	–
Corn	–	–	–	–	10	4	–	34	–	48	–	–
Olive	–	–	–	–	6	4	–	83	–	7	–	–
Sesame	–	–	–	0.1	8.2	3.6	–	42.1	–	43.4	–	–
Safflower	–	–	–	0.1	6.8	2.3	0.3	12.0	–	77.7	0.4	–

reaction was found easily to produce polyesters. The common process used to prepare alkyds from plant oils is the monoglyceride method, which includes alcoholysis followed by esterification or polycondensation (Scheme 2). In this route, the oil is processed through alcoholysis to produce monoglyceride or diglyceride in the presence of an acid or base catalyst (e.g., NaOH, PdO, CaO, *para*-toluene sulfonic acid). After this, alkyds are prepared with a polycondensation reaction between monoglycerides and anhydrides (aromatic or aliphatic). Different types of anhydrides are available for preparing alkyds, such as glutaric, phthalic, maleic, and succinic anhydrides. The properties of the alkyds depend on the types and content of anhydrides and the oil length. Aromatic polyesters have high heat and moisture resistances compared to aliphatic-based polyesters because of the presence of a stable benzene ring. Additionally, the drying time decreases with increasing anhydride content, whereas maleic anhydride-based resins show minimum drying times compared to the others when the same amount is used. Alkyds with an oil content below 40% are termed *short-oil alkyds*. Those with oil contents above 60% are called *long-oil alkyds*, and those with values between 40 and 60% are called *medium oil alkyds*. Long-oil alkyds are useful for brushing enamel, whereas short-oil alkyds are useful for backed finishes on refrigerators, automobiles, washing machines, and so on. Palm, sunflower, linseed, soybean, rapeseed, jatropha, and

rubber seed oils (RSOs) were used to prepare oil-modified polyesters. A comparison between palm- and soya-oil-based alkyd resins was drawn in terms of the hardness, adhesion, and impact strength.[9] Analyses revealed a better hardness and strength for the soya-oil-based resins compared to the other. Alkyd resins from jatropha and rapeseed oil were prepared with a monoglyceride method for electrical insulation purposes.[10] The physicochemical properties were measured and compared with those of a traditional monomer-based commercial alkyd resin (Syntolocal-60). The drying times for jatropha and rapeseed-oil-based resins were 4 and 3 h, whereas that of a traditional monomer-based one was 3 h. The chemical resistivity for the jatropha-based alkyd was found to be the same as that of the commercial-based one. The nonvolatile material content was found to be 97% for jatropha-based alkyds, 70% for rapeseed-based alkyds, and 99% for commercial alkyd resins.
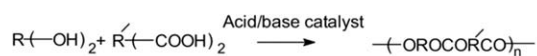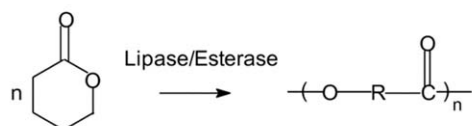
Scheme 1. Route of polyester preparation: (a) polycondensation reaction between diacids and diols and (b) ring-opening polymerization.
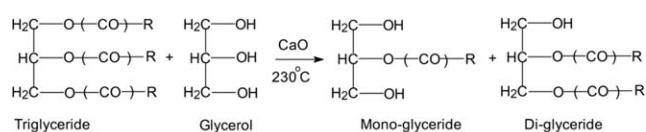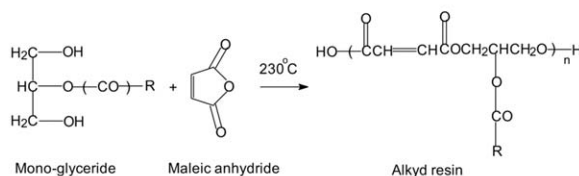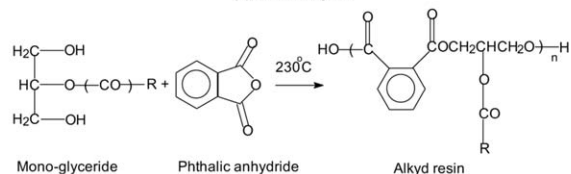

Scheme 2. (a) Alcoholysis and (b) esterification reaction of oil with acid anhydride.
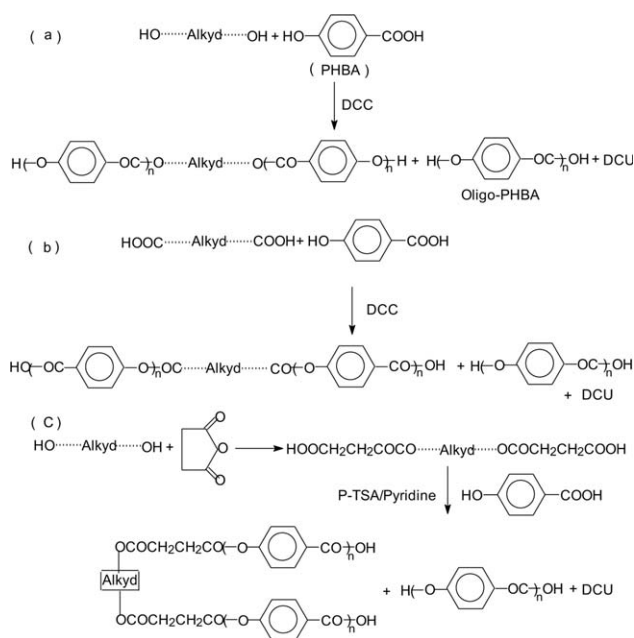
Scheme 3. Preparation of LC alkyds: (a) grafting of PHBA to hydroxyl-terminated alkyd resin, (b) grafting of PHBA to carboxyl-terminated alkyd resin, and (c) grafting of PHBA to an excess of succinic anhydride-modified alkyd resin (DCC = dicyclohexylcarbodiimide; DCU = dicyclohexyl urea; P-TSA = para-Toluene Sulfonic Acid).

Another method, which is called the *fatty acid method,* is commonly used to prepare alkyds. The advantage of this method compared to the former is that there is no intermediate step involved as the polyacid, polyalcohol, and fatty acid are added and heated at the same time. Moreover, polymers prepared by this method show a high viscosity and good drying and hardness properties.

Liquid-Crystalline (LC) Alkyds. The molecules of LC alkyd resins are mutually aligned and structured (crystal), and the bulk LC polymer shows fluidity in the molten state of the polymer. These resins usually show excellent mechanical performance, low dielectric constant, and high-temperature resistivity. They are prepared by the following three methods: (1) the grafting of *p*-hydroxybenzoic acid (PHBA) to a hydroxyl-terminated alkyd resin, (2) the grafting of PHBA to a carboxyl-terminated alkyd resin, and (3) the grafting of PHBA to an excess succinic anhydride-modified alkyd resin (Scheme 3).[11] Dicyclohexylcarbodiimide was used to react with formed water and promote the esterification of PHBA with alkyd at room temperature. Pyridine was used as a solvent, and the catalytic amount of *para*-toluene sulfonic acid was added to suppress side reactions and promote esterification. The grafting efficiency was estimated to have a range of 70–95%. The character of liquid crystallinity was imparted only when at least two or more aromatic units of PHBA were connected to form the rodlike mesogenic side chain. The advantages of LC polymers are the reduced viscosity and the coating's dry-to-the-touch time, and films prepared from them show more hardness and toughness with excellent resistances to water and acid. Moreover, their excellent moldability and heat resistance are also motivational for users. On the con-
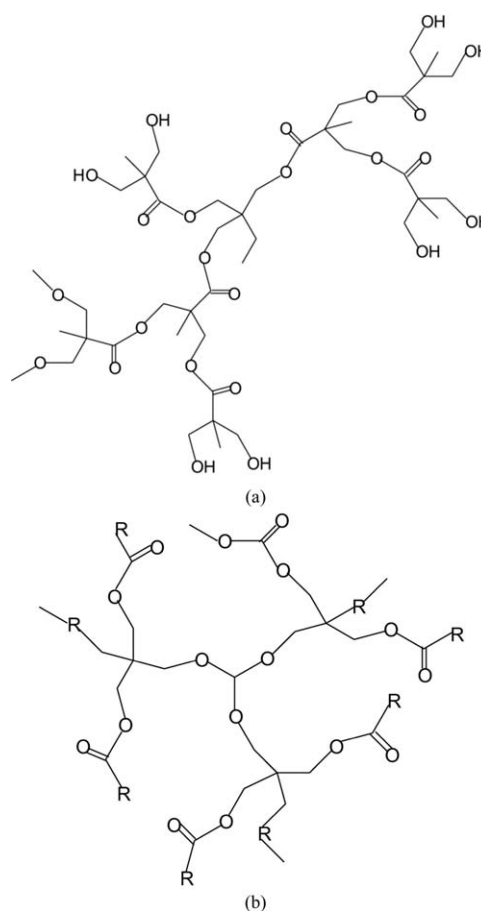
Scheme 4. Structure of (a) hyperbranched and (b) star (three-armed) architectures of polyesters.

trary, the high cost and drying required before processing are disadvantages associated with these polymers. In addition, they possess low amounts of volatile organic compounds (VOCs) compared to organic-solvent-based ones. Mahua-oil-based pentalkyds (medium oil length) were prepared and converted to LC form by copolymerization with PHBA.[12] A maximum graft efficiency (95.2%) was observed for samples prepared with a 3:1 ratio of PHBA to alkyd; this resembled the behavior of traditional LC alkyds. In traditional monomer-based LC alkyds, the
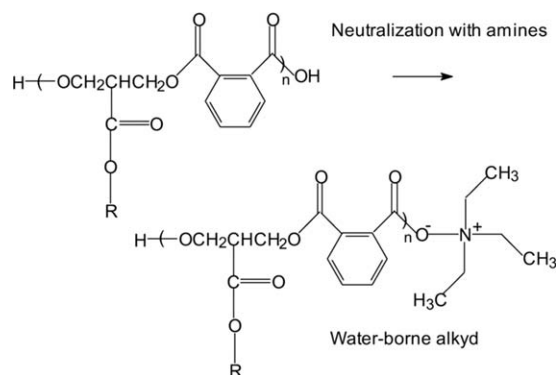
Scheme 5. Preparation of waterborne alkyds.

grafting efficiency decreases with the PHBA/alkyd equivalent ratio. The hardness and impact resistance were found to be similar to that shown by both vegetable-oil and traditional-monomer-based LC alkyds. The innovative applications of these materials include applications in the field of automobiles, advanced printed writing boards, food containers, electrical products, and packaging stuffs.

High-Solid-Content Alkyds. High-solid-content resins are attractive because of technical aspects and economic benefits.[13] They also reduce the use and emissions of volatile organic solvents; this has a negative impact in coating industries. In the development of high-solid alkyds, the major problem is the reduction of the viscosity without a deterioration of the properties. To address this problem, several theoretical options, such as a narrow molecular weight distribution and an increase in the oil length and the use of reactive diluents can be applied. Another problem, associated with high-gloss decorative paints because of decreasing solvent contents, can be mitigated by the preparation of high-solid-content alkyd resins through a decrease in the molecular weight.[14] The molecular weight can be decreased by increasing the fatty acid content or increasing the ratio of OH to COOH groups. Resins prepared in this way have a slow drying rate with weak properties, and this problem can be overcome to a great extent by the production of star and hyperbranched structures.[14] The structure of hyperbranched polyesters and star alkyds are presented in Scheme 4(a,b), respectively. High-solid alkyds have been found to be advantageous because of their better protection and greater hiding power when they are used as paints. In one study,[15] long-oil-length soybean-oil-based conventional alkyds and star and hyperbranched high-solid enamels were prepared and compared with commercial monomer-based enamels. It was found that increasing the degree of branching accelerated the curing process of the hyperbranched and star alkyds compared to that of the conventional alkyds. Otherwise, the most of the properties of commercial and conventional
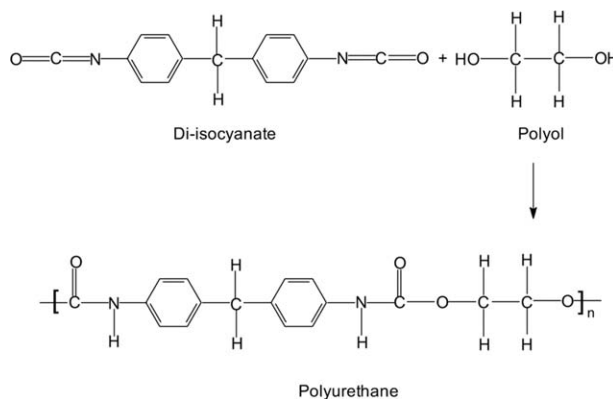

Scheme 6. Reaction between diisocyanate and polyol to form PU.

alkyds were found to be similar. The only exception, noticed for the case of highly branched alkyds, was their lower elasticity compared to that of others. This may have been due to the effect of the higher crosslinking density obtained with the higher content of fatty acids and the higher concentration of double bonds.

Waterborne Alkyds. Environmental legislation on volatile organic solvent utilization in traditional coatings and their high costs has helped to develop more environmentally friendly and comparatively low-cost coating materials, such as waterborne alkyds. These have been used widely in the past several decades for coating applications. Some other advantages of these materials also have been documented, such as their good resistance to chemicals, heat and abrasion, excellent adhesion, very low VOCs, lower required amount during application (compared to solvent-based materials), easy application and cleaning, and the lack of further additives needed during their use. They exhibit the same properties as organic-solvent-based ones after the evaporation of water from the coating system.[16] This type of resin contains water-reducible binders. Alkyd resins with high acid values, upon neutralization of their carboxylic acids with

Table VI. List of Diisocyanates Available for Polymer Synthesis

Name	Code	Structure	Contributing properties
Toluene diisocyanate	TDI		Flexibility
Methylene diphenyl diisocyante	MDI		Rgidity
Naphthalene-1,5-diisocyanate	NDI		–
Isophorone diisocyanate	IPDI		Abrasion and degradation resistivity
Hexamethylene diisocyanate	HMDI		Abrasion and degradation resistivity

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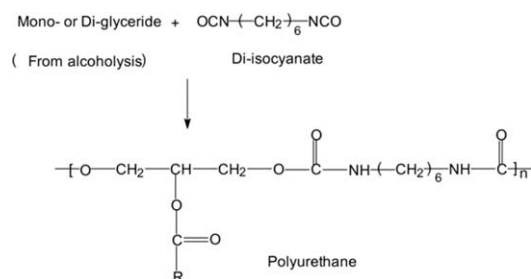
**Scheme 7.** Synthesis of PU from partial glyceride and diisocyanate.

amines, act like water-reducible binders. Scheme 5 illustrates the preparation of waterborne alkyds. Because of the introduction of carboxylic groups, alkyd resins were found to be waterborne.[17] The disadvantages of these kinds of resins include slow drying and tackiness. This problem can be mitigated by the incorporation of melamine or urea formaldehyde during backing at 150°C for 2 h.[16] Maleinized RSO was used to prepare waterborne alkyd emulsions.[18] Alkyds prepared from RSO were neutralized with triethylamine and mixed with maleinized RSO in isopropyl alcohol, and 70% w/w water of the prepared alkyd was added to formulate the emulsions. Changes in the physicochemical properties and low VOCs with high chemical resistance were shown by the alkyd emulsions. An inadequate hydrolytic stability is another shortcoming associated with waterborne alkyd resins, and this limits its storage stability.[19] Waterborne alkyd resins were prepared with a high storage stability from the reaction between acrylic copolymers and monoglycerides formed from soybean oil and trimetylol propane.[19] Analyses revealed that after 9 months of storage, excellent stability was reported with a 10% change in the acid number. In another study, linseed oil was used to produce a sulfonate-based waterborne alkyd resin.[20] With a relatively small amount (3 wt %) of sodium sulfonate groups, a good water dispersity and short drying time with good water-resistance performance of the coating were obtained. In a recent study,[21] soybean oil was used to prepare waterborne alkyd resins by neutralization with triethylamine, and these were modified by butylated melamine formaldehyde. The results reveal antibacterial properties in the resin, and the resin could be used in food packaging applications. Although waterborne alkyds emit low or zero VOCs and cause minimum hazardous air pollution, they also possess some disadvantages compared to traditional solvent-based alkyds. Because of the presence of water, they are responsible for corrosion in storage tanks and transfer pipes. Because of their high surface tension, they show poor flow characteristics. They also required special arrangements or equipment for electrostatic applications, and they are sensitive to humidity.

PUs

PUs are polymers made from the reaction of diisocyantes and hydroxyl-functional-group-containing compounds or polyols. This kind of polymer was discovered for the first time by Bayer in 1937 through a reaction between a polyester diol and a diisocyante.[22] Modified oils or triglycerides can be used as polyols to produce a partial glyceride, which may be used in the formulation of PUs. The reaction mechanism between methylene-4,4′-diphenyl diisocyanate and a diol produces the PU polymer, as

shown in Scheme 6. The diisocyanates used to prepare PUs can be aromatic or aliphatic in nature. A list of these diisocyanates is presented in Table VI. Polymers belonging to this category show a wide range of variations in properties, including density, flexibility, and rigidity; this makes them useful in many application-based products, including foams, varnishes, paint ingredients, adhesives, glues, and matrixes for composites. For example, toluene diisocyantes (TDIs) and methylene diphenyl diisocyantes (MDIs) have been used for flexible and rigid PU products, respectively. Basically, two physical chemical processes are responsible for these wide ranges of properties, that is, phase separation between hard and soft segments and hydrogen bonding between the urethane or carbamate bonds. In addition, the high reactivity of isocyanate, even in a viscous system or at low temperatures, is also responsible for the variations of the properties. A number of research studies, including those of vegetable-oil-based PUs, have been performed in the last few decades. Castor, canola, soybean, sunflower, neem, palm, nahar seed, tung, karanja, and *Prosopis juliflora* have been used to produce PU-based polymers. The types of isocyanates and the polyol used in the preparation have the major controlling roles in determining the properties of the formulated PUs. The only disadvantage of these PUs is the inherent toxicity, which is due to isocyanates.

A vegetable-oil-based PU network is a heterogeneous composition. The evaluation of the structure and concentration of an elastically active network chain of PUs was done by rubber elasticity theory.[23] Its structure–property relationship was examined by Zlatanic et al.[24] A model PU network, through the reaction between triolein (triglyceride of oleic acid) and MDI, was prepared by the authors. According to them, because of crosslinking, the middle of the fatty acid chains remained in the structure as a hanging part. The swing part of the chain in another PU structure was removed with the help of metathesis. Analyses revealed that the PU structure without a dangling chain showed a decreased viscosity and glass-transition temperature (T_g). The dangling chain acted as a plasticizer, and the removal of that part increased the solvent resistivity of the model PU structure.
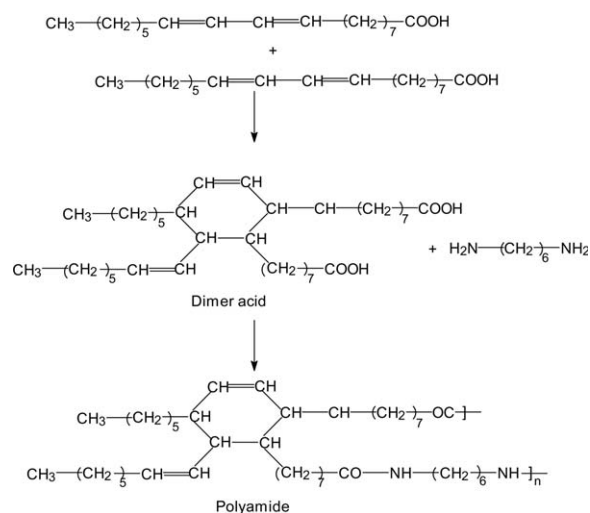
**Scheme 8.** Preparation of polyamides.

Organic-Solvent-Based PUs. Organic-solvent-soluble PUs can be prepared by the reaction between hydroxyl-containing oil or their partial glyceride and diisocyanates. The reaction mechanism is shown in Scheme 7. The fatty acid content in the polyol and the isocyanate (NCO)/OH ratio contributes to the variation of properties of the PUs. To assess their contributions to the dielectric constant and the loss mechanism, palm-oil-based PU was analyzed by Velayutham et al.[7] A γ-relaxation process was proposed as the probable mechanism for the dielectric behavior. The dielectric properties were found to be in the range 2.0–3.0 for the real permittivity and 0.02–0.08 for the imaginary permittivity. At the same OH/NCO molar ratio, a higher T_g, better tensile properties, and a longer elongation break could be achieved because of the introduction of a mild solvent (ethyl acetate) and zinc as a reductive reagent onto the higher triol content canola-oil-based PU.[23] In addition, the hydroxyl functionality (which ranged from 2.4 to 4) also contributed to the good film properties of the PU resin.[25] Additionally, hyperbranching in the PU resins was found to be facilitating in terms of the thermal stability and other film properties compared to the conventional linear-based one.[26]

The development of new PUs with different properties is based on modified polyols and their hybridization with other compatible functional groups of different compounds.[27] Rapeseed oil was functionalized to prepare a polyol by thiol-ene coupling for the preparation of PU based on 1,6-hexamethylene diisocyanate (HMDI) and methylene diphenyl-4,40-diisocyanate. The produced elastomeric product showed comparable thermal properties to commercially available polyol-based PUs. In another work, castor oil was modified through —Si—OCH$_3$ groups in the backbone chain with isophorone diisocyanate (IPDI) and was used to prepare PU/urea–silica-based hybrid coatings.[27] Improved mechanical and viscoelastic properties were claimed by the authors. The hydrophobic character of the hybrid coating and T_g were found to increase with increasing NCO/OH ratio. The swelling properties and contact angle were also found to be dependent on that that ratio.

Linear saturated diisocyanate was derived from fatty acids, and different types of PUs were prepared with canola oil.[28] For comparison, canola-oil-based polyol and prepared diisocyanates and petroleum-based polyol and commercially available HMDIs were used to prepare different kinds of PUs. The comparative properties of the resulting canola-oil-based PU with acceptable tolerance were reported by the authors.

Recent developments in the production of non-isocyanate-based polyurethane (NIPU) have motivated the researchers because of the scope of preventing toxic isocyanates in the PU structure.[28] NIPU can be prepared by the reaction between cyclocarbonates and amines. Commercially available amines, such as ethylene diamine, hexamethylene diamine, and tris(2-aminoethyl)amine, were used to prepare NIPU.[29] Improvements in the porosity, water absorption, and chemical and thermal resistivity were found for NIPU compared to isocyanate-based PUs.

Water-Based PUs. Waterborne PU is environmentally friendly. Nowadays, researchers have shown interest in water-based PUs because traditional organic-solvent-soluble PUs pollute the
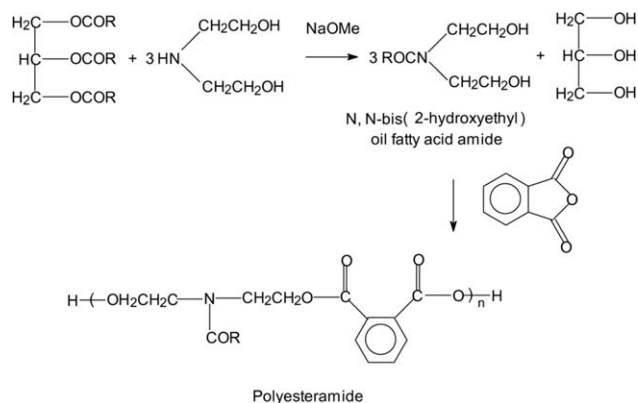
Scheme 9. Synthesis of PEA (NaOMe = Sodium methoxide).

environment through VOC emission during their application and formulation by evaporation processes. Toxic and expensive volatile organic solvents have been replaced by water as an environmentally benign solvent in the formulation of polyurethane dispersions (PUDs), and this has resulted in minimal VOC contents.[29] Waterborne PUDs can be used in various purposes, including in coatings for various fibers, adhesives for alternative substrates, primers for metals, caulking materials, emulsion polymerization media for different monomers, paint additives, defoamers, associate thickeners, pigment pastes, and textile dyes. Novel biorenewable, waterborne, castor-oil-based PUDs were successfully synthesized via homogeneous solution polymerization in methyl ethyl ketone followed by solvent exchange with water.[30] A detailed rheological behavior of PUD as a function of the angular frequency, solid content, and temperature were evaluated through small-amplitude oscillatory shear flow experiments. The solid content and temperature were significantly affected the rheological behavior of the PUDs. The composition dependency of the complex viscosity was found to be well described by the Krieger–Dougherty equation. Although the viscoelastic behavior of the PUD was well described by the time–temperature superposition principle in a temperature range lower than the gel point, but the time–temperature superposition principle failed to represent the behavior of the PUD at temperatures near the critical gel point.

Interpenetrating Polymer Networks (IPNs). IPNs are polymer blends and can be prepared by permanent entanglement between two or more distinctly crosslinked polymers. They possess excellent properties because of the interlocking of polymer chains.[31] There are many kinds of IPNs, among which sequential IPNs and simultaneous IPNs are the two most important types.[32] Castor-oil-based PUs and styrene monomers were used to prepare IPNs with tough elastomeric properties.[33] Sequential IPNs were prepared with PU synthesized from canola-oil-based polyol with terminal primary functional groups and poly (methyl methacrylate).[34] The mechanical properties of the IPNs were found to be superior to those of the constituent polymers. In addition, soya bean, canola, and castor oils were also studied for the preparation of IPN-type PUs. The new IPN material covered a broad spectrum of useful properties, such as sound and vibration damping, and found to be valuable substitutes for existing materials.[34]
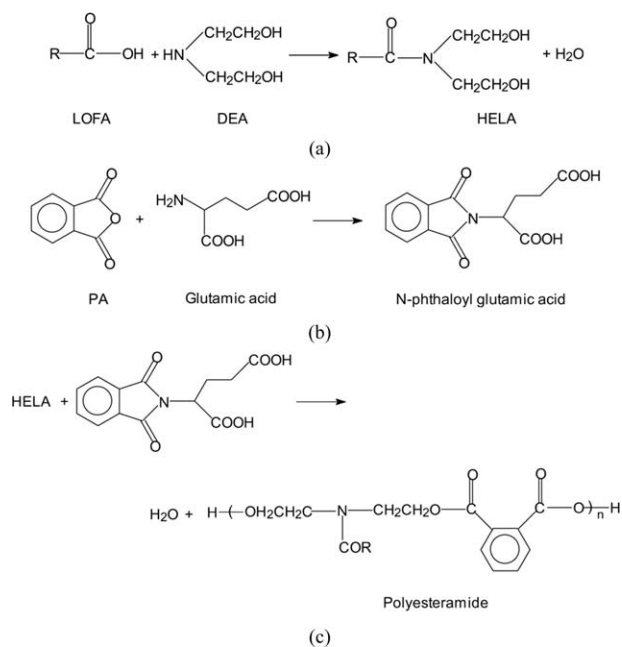
Scheme 10. Syntheses of (a) HELA, (b) *N*-phthaloyl glutamic acid, and (c) PEA (LOFA = Linseed oil fatty acid; DEA = Diethanolamine).

Polyamides

To prepare polyamides, monomer dimer acids (DAs), obtained by the condensation of the C18 acids, such as oleic and linoleic acids of vegetable oils, are required.[35] DAs are environmentally friendly, reactive, nontoxic, biodegradable, and liquid at room temperature and soluble in hydrocarbons.[36] They have higher molecular weights compared to conventional diacids. The preparation of polyamide is illustrated in Scheme 8.[37] DA-based polyamides are often compared with traditional monomer-based nylons 6-6 (poly(hexamethylene adipamide)) and have been found to be more flexible, to be more soluble in alcohol, to have a lower melting point, and to possess an average molecular weight. They also show better compatibility with other resins and modifiers.[36] They are useful in many applications, for example, as binders in painting ink, varnishes, and heat-seal coatings. In paint systems, thixotropes are prepared from DAs from soybean and tall oil to modify the flow of the paint.[37] Thixotropy is an outcome of weak intermolecular forces in hydrogen bonds.[38] Because of thixotropy, the viscosity of the phthalic anhydride (PA) was found to increase in a state of rest and decrease in constant shear stress.[39]

Poly(ester amide)s (PEAs)

PEAs are regular copolymers of polyester and polyamide, and they have a combination of their properties, including good mechanical properties, high melting temperatures, fast crystallization, excellent solvent resistance, and low water absorption. They usually show better properties in terms of drying time, hardness, and chemical resistivity than polyesters made from the same source.[40] In the preparation of vegetable-oil-based PEAs, pongamia glabra, coconut, linseed, cottonseed, castor, soybean, neem, nahar seed, and albizia benth have been studied extensively. PEAs can be prepared from different monomers and with different synthetic routes; this leads to materials with ran-

dom, blocky, and ordered microstructures.[41] In one study, different types of PEAs were prepared with PA, maleic anhydride, and adipic acid from *N,N*-bis(2-hydroxyethyl) *Mesua ferrea* fatty amide, obtained from methyl ester of the oil (nahar seed) by treatment with diethanol amine.[40] A three-step reaction with sodium methoxide and PbO was found to be helpful and quite easy in the formation of the resin compared to other existing processes. The steps are presented in Scheme 9. Ester linkages are considered to be responsible for the biodegradability, whereas amide linkages are responsible for the thermal and mechanical strengths. They have both commodity and specialty applications because of their engineering plastic and thermoplastic elastomeric nature. For example, they are suitably applicable for biomedical purposes, including controlled drug-delivery systems, hydrogels, tissue engineering, anticorrosive or high-performance primers, and surface-coating applications.[41]

Nondrying oils, such as pongamia glabra, are used to prepare PEAs for anticorrosive coatings, which are claimed to be biologically safe materials.[42] Furthermore, a successful study with the same oil with the incorporation of zinc acetate (4 wt %) made this PEA an antibacterial room temperature-cured coating, which could sustain at high temperature (300°C).[4] The authors suggested the use of a nondrying oil, such as coconut oil or an oil having an iodine value less than 120, for the same purpose.

Nearly 2 decades ago, the modification or functionalization of PEAs was taken into consideration to incorporate the amine, hydroxyl, and carboxyl pendant groups or carbon–carbon double bonds in their backbone chain or pendant groups. This strategy was followed to develop innovative materials for new applications. In a recent study, modified PEAs were prepared for anticorrosive coating applications.[41,43,44] PEAs were synthesized with condensation polymerization between *N,N*-bis(2-hydroxyethyl) linseed oil fatty acid amide (HELA) and PA, which was partially replaced with pyromellitimide acetic acid (PAA) and *N*-phthaloyl glutamic acid (NPGA), individually as a new dibasic acid source.[41,44] First, linseed oil fatty acids and diethanolamine were used to prepare HELA. After that, HELA and PA were used in the presence of xylene at 140°C to prepare PEA. Modifications were carried out during the preparation of PEA with PAA and NPGA. The reactions are shown in Scheme 10. The physicomechanical properties and chemical resistivity were evaluated, and the enhancement of the properties was claimed to be due to the modification by PAA and NPGA. The formulated resins were incorporated within the primer to evaluate the anticorrosive properties. The improvement of corrosion resistance was due to the combination of amide–imide groups, the presence of ester and amide repeating units, and the high molecular weight of the modifier. All of these factors decreased the permeability of the coating to water, oxygen, and chlorine.[44] In another study, the modification of PEAs were performed by a postreaction with a vinyl acetate monomer with various ratios of 4:1, 3:1, and 2:1 in the presence of *t*-butyl hydroperoxide as an initiator.[45] Earlier, cottonseed oil fatty amide was prepared in the laboratory by the base-catalyzed aminolysis of cottonseed oil. Furthermore, it was reacted with phthalic acid to obtain PEA. The modification of PEA improved the curing and mechanical and chemical performance of the PEA films. It was
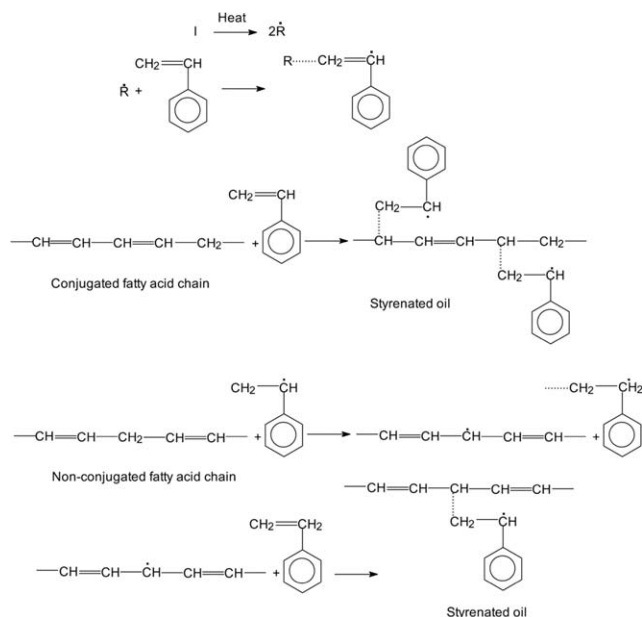
**Scheme 11.** Styrenation of conjugated and nonconjugated fatty acids.

found that among the PEA/vinyl acetate ratios, 2:1 exhibited the best results. Modification was also carried out with melamine to improve the physicomechanical properties of linseed-oil-based PEA.[46] Castor oil was used to prepare hyperbranched PEA for the formulation of polyaniline-based nanofiber-incorporated nanocomposites, which are useful for antistatic purposes.[47] Maleinized albizia benth oil (ABO) PEA was prepared with maleinized hydroxyethyl amide derivatives of ABO, obtained by the appending of maleate half esters onto the hydroxyethyl amide derivative of ABO and PA.[48] It was revealed that maleic anhydride could successfully be used to modify PEAs to improve its properties, such as its drying, flexibility, scratch hardness, impact resistance, chemical resistance, and lower curing temperature. Boron-filled PEA prepared from soybean oil was used to formulate PEA urethane for the preparation of antimicrobial coating materials. In a different study, urethane-modified soybean-oil-based PEA was evaluated for anticorrosive purposes.[49,50] In an improved study, neem-oil-based PEA was used to prepare PEA urethane by the incorporation of poly(amido amine)-based polyurea microcapsules (3–4%) containing a natural self-healing agent for self-healing anticorrosive coatings.[51] Coconut oil was used to prepare poly(ester amide urethane) to make conducting semi-interpenetrating network polymer with polypyrrole. Thus, the prepared materials showed flexibility, stiffness, and satisfactory conductivity in the range 2.9×10^{-4} to 6.8×10^{-6} S cm^{-1}.[45] The miscibility of two different types of PEAs made from two different oils (linseed and castor) with poly(vinyl alcohol) were analyzed to obtained improved water sensitivity.[52] The result analyses revealed lower moisture absorption by all of the compositions compared to that of the pure poly(vinyl alcohol).

Vinyl Polymers

Classical Process. Various oils, including drying and semidrying oils, have been polymerized with vinyl monomers because of the easier synthetic process of polymerization. These types of

polymers have very good film-forming properties. Drying oils, such as tung oil and low-saturated soybean oil, were used individually with divinyl benzene and polystyrene to prepare polymers as a function of the crosslinking density by a cationic mechanism to evaluate the tribological behavior.[53] Different percentages (10–40 wt %) of concentrations of divinyl benzene were used, and a lower adhesive strength was found due to the higher crosslinking density. In addition, an increased abrasive resistivity was observed because of both the highest and lowest crosslinking densities. Li et al.[54] developed a variety of novel polymeric materials, ranging from elastomers to tough polymers. Rigid plastics were prepared by the cationic copolymerization of regular soybean oil, low-saturation soybean oil, and conjugated low-saturation soybean oil.[54] The reactions are heterogeneous in nature; thus, the densities were found to be dissimilar in different parts of the resulting polymer. The reaction mechanisms for conjugated and nonconjugated oils were proposed earlier by Hewitt and Armitage[55] (Scheme 11). Maleic anhydride modified soybean- and castor-oil-based monomers, prepared via the malination of the alcoholysis products of the oils with various polyols, such as pentaerythritol, glycerol, and bisphenol A propoxylate, were copolymerized with styrene to give hard rigid plastics.[55] Recently, the effects of phase separation and crosslinking density on the mechanical properties of newly developed tung oil pentaerythritol glyceride maleates, cured with different percentages of styrene-based polymer, were evaluated.[56] These effects were used to correlate the microstructure factors with the obtained thermomechanical and mechanical properties of the tung-oil-based resins. It was found that the phase-separation effect was the dominating factor, which affected the mechanical properties rather than other factors. The structure–property analysis made by a combination of the phase separation and the crosslink-density effects organically may also be referenced by analogous thermosetting polymer systems, such as epoxy resins, polyester resins, and phenolic resins. The common uses of vinyl polymers include paints and biopolymer manufacturing. The various properties, such as the transparency, rigidity, toughness, and thermal stability (ca. 300°C), of these biopolymers were found to be acceptable compared to those of traditional monomer-based polymers.

Macroinitiator or Macromonomer Processes. Macroinitiator and macromonomer techniques were found to be two alternative methods for preparing vinyl polymers. In the macroinitiator method, a low-molecular-weight azo initiator was incorporated into the oil part into two steps, and then, in the presence of
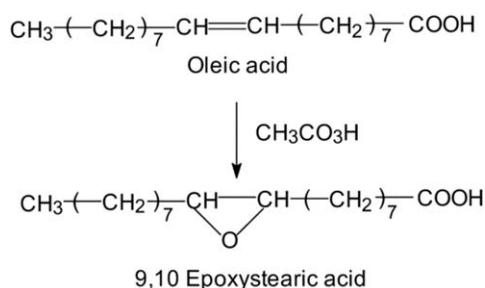
**Scheme 12.** Epoxidation of oleic acid.
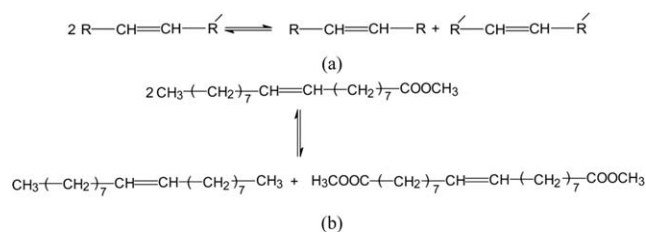
Scheme 13. Catalytic metathesis reaction.

Scheme 14. Synthesis of the (a) crosslinked polymer and (b) polyphenol.

styrene, free radicals were generated by the thermal decomposition of the azo groups to prepare oil–styrene copolymers.[57] Semidrying oils could be polymerized without any pretreatment or additional initiator. In the second method, the macromer was prepared by the reaction of a hydroxyl-containing oil and vinyl monomer followed by the homopolymerization or copolymerization with styrene.[57] Thus, the prepared polymers showed good film-forming properties with excellent water, alkali, and acid resistivity compared to polymers prepared from classical styrenated oil samples. This technique was found to be inapplicable for the drying oils.

Grafting Processes. The polymer–polymer grafting reaction with functionalized polymers are another method for preparing vinyl polymers from vegetable oils. A simple blending of two immiscible polymers cannot give good properties. In that case, graft or block copolymers are usually added as compatibilizers. In this process, oils are converted, first, to crosslinked polymeric peroxide through peroxidation, epoxidation, and/or perepoxidation under atmospheric conditions at ambient temperature. The polymeric oil peroxides are soluble, and the graft copolymerization is initiated by them through a free-radical polymerization. Soybean oil and methyl methacrylate, styrene, or *n*-butyl methacrylate were used to prepare graft copolymers for biomedical purposes.[58] The result analysis revealed polymeric oil as a plasticizer in the reduction of T_g of the graft copolymer. Moreover, bacterial adhesion was found to be improved in the case of the graft copolymer. Commonly used monomers for the preparation of functionalized polymers are glycidyl methacrylate, methacrylic acid, and acrylic acid through graft copolymerization.

Epoxies
Vegetable oils can be transformed into useful polymerizable oxygenated monomers; this is commonly done by Prileshajev epoxidation, catalytic epoxidation with an acidic ion-exchange resin, chemo-enzymatic epoxidation, or metal-catalyzed epoxidation.[59] Among these epoxidation methods, chemo-enzymatic epoxidation has achieved considerable interest nowadays because this method is safe and environmentally friendly and the conversion rate of epoxidation usually exceeds 90%.[59] Through chemical oxidation, monounsaturated and diunsaturated fatty acids and their esters can be converted to epoxy (oxirane) derivatives. The reaction takes place at the double bond of the fatty acid chain. The epoxidation process of oleic acid with peracetic acid is illustrated in Scheme 12. Epoxidized oils have been used as plasticizing and stabilizing materials for poly(vinyl chloride) (PVC). *Mesua* L. seed oil–nondrying oil was modified to produce epoxidized *Mesua* L. seed oil and was used to plasticize PVC
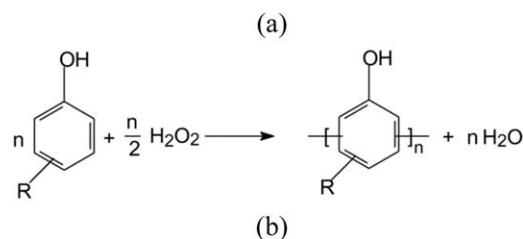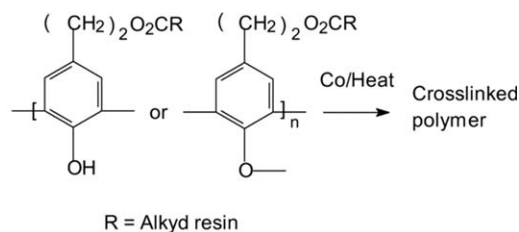
with different weight ratios.[60] The purpose of this research was *in vitro* biodegradation by the alteration of the structures by *Pseudomonas aeruginosa* and *Achromobacter* sp. bacteria. In a different study, epoxidized *Mesua* L. seed oil was also used as diluent with bisphenol-A-based epoxy resin.[61] Acrylated and epoxidized vegetable oils can be used as reactive diluents instead of styrene to produce vinyl esters. For example, acrylated epoxidized soybean and linseed oils were used to produce a bulk molding compound.[62] The applications of these epoxy resins include surface coatings, primers for car and steels, electrical insulation, adhesives, glues, and PVC products.

Metathesis of Oil
Metathesis is one kind of conversion reaction of olefins to shorter or longer chain oligomers. For instance, the conversion of olefins into new olefins through an exchange of alkylidene groups (Scheme 13). Sometimes, this process has been found to be the easiest to produce oligomers from the fatty acid esters. The effects of metathesis are the reduction of the drying time and the decrease of the melting temperature.[63] For example, the metathesis of unsaturated oils (olive, soybean, linseed, etc.) leads to the formation of high-molecular dicarboxylic acid glycerol esters with improved drying properties.[64] In a study, metathesized soybean oil was used to prepare epoxide polymer by thermal polymerization and in the presence of air.[65] Methyl trioxorhenium (VII) and pyridine were used as a catalyst system with hydrogen peroxide as an oxidant. The produced polymer was found to be a yellow, brittle gel with a high molecular weight. In another method, soybean oil was metathesized with tungsten hexachloride (WCl_6) and tetramethyl tin (Me_4Sn) in chlorobenzene as a solvent.[63] Refvik et al.[66] reported a cost-effective and environmentally friendly metathesis process with Grubbs' ruthenium catalyst for soybean oil. The produced polymer can be used as ink vehicles, photocurable coatings, and commercial additives. In another technique, the conversion of methyl oleate into an equimolar amount of 9-octadecene and dimethyl ester of 9-octadecene dioic acid was carried out in the presence of $WCl_6(CH_3)_4Sn$. The use of the $WCl_6(CH_3)_4Sn$ catalyst system had a drawback because its responsive nature to

moisture and oxygen and was found to have a disposal problem because of the solvent.[5] Analysis showed that a definite amount of metathesized oil could be used as a coupling agent for the oil molecule with a reduced drying time.[63] The drying time of soybean oil was significantly reduced from 312 to 210 min after 2 h of metathesis. The analyses revealed that the small amount of metathesized oil acted like a coupling agent among the oil molecules, whereas an increased amount may have resulted in polymerization among metathesized oils without reaction with the unmodified oil.

Polynaphthols

The Japanese lacquer (Urushi), a natural product, has been applied as a protective and decorative coating for a huge variety of objects since the Jomon period (10,000–300 B.C.E.) in Japan.[67] The major components of urushi are the urushiols and catechol bearing a C15 unsaturated hydrocarbon chain. For the preparation of the artificial urushi, the plant-oil-derived C18 unsaturated hydrocarbon chain was connected with the catechol group through an ester linkage.[68] In another example, a crosslinkable polymer was prepared from cashew nut shell liquid, whose main component was cardanol (phenol derivative). Cardanol had a metasubstituent of a C15 unsaturated hydrocarbon chain (Scheme 14).[69] It was found that cardanol and its polymers had interesting structural features for chemical modification and polymerization into specialty polymers. The prepared polyphenol was cured readily with excellent dynamic viscoelastic properties and had a high-gloss surface. The uses of these kind of lacquers were excellent for decorative designs on various surfaces, such as metal, leather, wood, bamboo, and paper.

CONCLUSIONS

Vegetable oils are an abundantly available bioresource, which can be used at relatively lower cost for biopolymer synthesis. Because synthetic polymers create various problems, biobased polymers are expected to be used to partially reduce the high demand for traditional monomer-based polymers. The ample chances to modify triglyceride-based oils and their low-cost and easy availability have allowed these raw materials to be used fruitfully for the preparation of biopolymers. The reported properties of various types of biopolymers have already shown their novelty, and this has attracted investigators and researchers to work more on them. Various types of polymers, such as polyesters, PUs, polyamides, and vinyl polymers, can be produced with different types of polymerization reactions. These biobased polymers are important for various kinds of applications, such as adhesives, paints, printing inks, surface coatings, foams, and binders, for composite preparation. Investigations of these materials have found them to be comparable to traditional monomer-based ones in terms of their physicochemical, thermal, mechanical, anticorrosive, antimicrobial, and other related properties. Although a few drawbacks and challenges are associated with these vegetable-oil-based polymers, extensive studies on them may open a wide scope for potential use in advanced material sectors. Moreover, improvements in the processes and end properties of these materials with cost feasibility analysis are essential to draw attention from other possible scopes of vegetable oils, such as biodiesel and lubricant preparation, because they are considered potential competitors of biopolymers from the same source of raw materials.

REFERENCES

1. Samadzadeh, M.; Boura, S. H.; Peikari, M.; Ashrafi, A.; Kasiriha, M. *Prog. Org. Coat.* **2011** *70*, 383.

2. Saravari, O.; Phapant, P.; Pimpan, V. *J. Appl. Polym. Sci.* **2005**, *96*, 1170.

3. Hendl, O.; Howell, J. A.; Lowery, J.; Jones, W. *Anal. Chim. Acta* **2001**, *427*, 75.

4. Boruah, M.; Gogoi, P.; Adhikari, B.; Dolui, S. K. *Prog. Org. Coat.* **2012**, *74*, 596.

5. Guner, F. S.; Yagci, Y.; Erciyes, A. T. *Prog. Polym. Sci.* **2006**, *31*, 633.

6. Stenberg, C. Influence of the Fatty Acid Pattern on the Drying of Linseed Oils. http://kth.diva-portal.org/smash/get/diva2:7720/FULLTEXT01.pdf. Last accessed 28 October, 2013.

7. Velayutham, T. S.; Abd Majid, W. H.; Gan, S. N. *J. Oil Palm Res.* **2012**, *24*, 1260.

8. Yang, Y.; Yu, Y.; Zhang, Y.; Liu, C.; Shi, W.; Li, Q. *Process. Biochem.* **2011**, *46*, 1900.

9. Issam, A. M.; Cheun, C. Y. *Malaysian Polym. J.* **2009**, *4*, 42.

10. Patel, V. C.; Varughese, J.; Krishnamoorthy, P. A.; Jain, R. C.; Sing, A. K.; Ramamoorthy, M. *J. Appl. Polym. Sci.* **2008**, *107*, 1724.

11. Chiang, W. Y.; Yan, C. S. *J. Appl. Polym. Sci.* **1992**, *46*, 1279.

12. Tiwari, S.; Tiwari, S. *J. Appl. Polym. Sci.* **2008**, *111*, 2648.

13. Chen, D. S.; Jones, F. N. *J. Coat. Technol.* **1988**, *60*, 39.

14. Lindeboom, J. *Prog. Org. Coat.* **1998**, *34*, 147.

15. Manczyk, K.; Szewczyk, P. *Prog. Org. Coat.* **2002**, *44*, 99.

16. Murillo, E. A.; Lopez, B. L.; Brostow, W. *Prog. Org. Coat.* **2011**, *72*, 292.

17. Wang, C.; Jones, F. N. *J. Appl. Polym. Sci.* **2000**, *78*, 1698.

18. Aigbodion, A. I.; Okieimen, F. E.; Obazee, E. O.; Bakare, I. O. *Prog. Org. Coat.* **2003**, *46*, 8.

19. Wang, C.; Lin, G.; Pae, J.-H.; Jones, F. N. *J. Coat. Technol.* **2000**, *72*, 55.

20. Rokicki, G.; Lukasik, L. *Surf. Coat. Int. Part B: Coat. Trans.* **2001**, *84*, 169.

21. Pathan, S.; Ahmad, S. *ACS Sustainable Chem. Eng.* **2013**, 1, *1246*. http://pubs.acs.org/doi/abs/10.1021/sc4001077. Last accessed 28 October, 2013.

22. Delebecq, E.; Pascault, Jean-Pierre; Boutevin, B.; Ganachaud, F. *Chem. Rev.* **2013**, *113*, 80.

23. Kong, X.; Yue, J.; Narine, S. S. *Biomacromolecules* **2007**, *8*, 3584.

24. Zlatanic, A.; Petrovic, Z. S.; Dusek, K. *Biomacromolecules* **2002**, *3*, 1048.

25. Lu, Y.; Larock, R. C. *Prog. Org. Coat.* **2010**, *69*, 31.

26. Das, B.; Konwar, U.; Mandal, M.; Karak, N. *Ind. Crop. Prod.* **2013**, *44*, 396.

27. Allauddin, S.; Narayan, R.; Raju, K. V. S. N. *ACS Sustainable Chem. Eng.* **2013**, *1*, 910.

28. Hojabri, L.; Kong, X.; Narine, Suresh, S. *Biomacromolecules* **2009**, *10*, 884.

29. Wilkes, G. L.; Sohn, S.; Tamami, B. U.S. Pat. 0230009-A1 (**2004**).

30. Madbouly, S. A.; Xia, Y.; Kessler, M. R. *Macromolecules* **2013**, *46*, 4606.

31. Sperling, L. H. Interpenetrating Polymer Networks and Related Materials; Plenum: New York, **1981**.

32. Nayak, R. R.; Ray, G.; Lenka, S. *Polym.-Plast. Technol. Eng.* **2009**, *48*, 503.

33. Das, T. K.; Lenka, S. *Polym.-Plast. Technol. Eng.* **2011**, *50*, 481.

34. Kong, X.; Narine, S. S. *Biomacromolecules* **2008**, *9*, 2221.

35. Grishchuk, S.; Karger-Kocsis, J. *J. Mater. Sci.* **2012**, *47*, 3391.

36. Hablot, E.; Tisserand, A.; Bouquey, M.; Avérous, L. *Polym. Degrad. Stab.* **2011**, *96*, 1097.

37. Oldring, P. K. T.; Turk, N. Polyamides: Resins for Surface Coatings; Wiley: New York, **2000**; Vol. *III*, p 131.

38. Mewis, J. *J. Non-Newtonian Fluid Mech.* **1979**, *6*, 1.

39. Barnes, H. A. *J. Non-Newtonian Fluid Mech.* **1997**, *70*, 1.

40. Mahapatra, S. S.; Karak, N. *Prog. Org. Coat.* **2004**, *51*, 103.

41. Rodriguez-Galan, A.; Franco, L.; Puiggali, J. *Polym.* **2011**, *3*, 65.

42. Ahmad, S.; Ashraf, S. M.; Naqvi, F.; Yadav, S.; Hasnat, A. *Prog. Org. Coat.* **2003**, *47*, 95.

43. Zafar, F.; Zafar, H.; Sharmin, E.; Ahmad, S. *Prog. Org. Coat.* **2010**, *69*, 517.

44. El-Wahab, H. A.; EL-Fattah, M. A.; Ghazy, M. B. M. *Prog. Org. Coat.* **2011**, *72*, 353.

45. Ashraf, S. M.; Ahmad, S.; Riaz, U.; Dua, R. *J. Macromol. Sci. Pure Appl. Chem.* **2004**, *42*, 521.

46. Ahmad, S.; Ashraf, S. M.; Alam, M. *J. Macromol. Sci. Pure Appl. Chem.* **2004**, *43*, 773.

47. Pramanik, S.; Hazarika, J.; Kumar, A.; Karak, N. *Ind. Eng. Chem. Res.* **2013**, *52*, 5700.

48. Akintayo, C. O.; Akintayo, E. T.; Azeez, M. A. *ISRN Polym. Sci.* **2012**, Article ID 708520, 9 pages. http://www.hindawi.com/ journals/isrn.polymer.science/2012/708520/. Last accessed 28 October, 2013.

49. Ahmad, S.; Haque, M. M.; Ashraf, S. M.; Ahmad, S. *Eur. Polym. J.* **2004**, *4*, 2097.

50. Alam, M.; Sharmin, E.; Ashraf, S. M.; Ahmad, S. *Prog. Org. Coat.* **2004**, *50*, 224.

51. Chaudhari, A. B.; Tatiya, P. D.; Hedaoo, R. K.; Kulkarni, R. D.; Gite, V. V. *Ind. Eng. Chem. Res.* **2013**, *52*, 10189. http://pubs.acs.org/doi/abs/10.1021/ie401237s.

52. Sharma, H. O.; Alam, M.; Riaz, U.; Ahmad, S.; Ashraf, S. M. *Inter. J. Polym. Mater. Polym. Biomater. 56*, 437.

53. Bhuyana, S.; Holden, L. S.; Sundararajan, S.; Andjelkovic, D.; Larock, R. *Wear* **2007**, *263*, 965.

54. Li, F.; Hanson, M. V.; Larock, R. C. *Polym.* **2001**, *42*, 1567.

55. Hewitt, D. H.; Armitage, F. *J. Oil Colour Chem. Assoc.* **1946**, *29*, 109.

56. Can, E.; Wool, R. P.; Kusefoglu, S. *J. Appl. Polym. Sci.* **2006**, *102*, 1497.

57. Liu, C.; Dai, Y.; Wang, C.; Xie, H.; Zhou, Y.; Lin, X.; Zhang, L. *Ind. Crop. Prod.* **2013**, *43*, 677.

58. Güner, F. S.; Usta, S.; Erciyes, A. T.; Yagci, Y. *J. Coat. Technol.* **2000**, *72*, 107.

59. Tan, S. G.; Chow, W. S. *Polym.-Plast. Technol. Eng.* **2010**, *49*, 1581.

60. Das, G.; Bordoloi, N. K.; Rai, S. K.; Mukherjee, A. K.; Karak, N. *J. Hazard. Mater.* **2012**, 209–210, 434.

61. Das, G.; Karak, N. *Prog. Org. Coat.* **2009**, *66*, 59.

62. Grishchuk, S.; Karger-Kocsis, J. *J. Mater. Sci.* **2012**, *47*, 3391.

63. Erhan, S. Z.; Bagby, M. O.; Nelsen, T. C. *J. Am. Oil Chem. Soc.* **1997**, *74*, 703.

64. Nicolaides, C. P.; Opperman, J. H.; Scurrell, M. S.; Focke, W. W. *J. Am. Oil Chem. Soc.* **1990**, *67*, 362.

65. Refvik, M. D.; Larock, R. C. *J. Am. Oil Chem. Soc.* **1999**, *76*, 99.

66. Refvik, M. D.; Larock, R. C.; Tian, Q. *J. Am. Oil Chem. Soc.* **1999**, *76*, 93.

67. Salvemini, F.; Grazzi, F.; Agostino, A.; Iannaccone, R.; Civita, F.; Hartmann, S.; Lehmann, E.; Zoppi, M. *Archaeol. Anthropol. Sci.* **2013**, *5*, 197.

68. Kobayashi, S.; Ikeda, R.; Oyabu, H.; Tanaka, H.; Uyama, H. *Chem. Lett.* **2000**, *10*, 1214.

69. Ikeda, R.; Tanaka, H.; Uyama, H.; Kobayashi, S. *Polymer* **2002**, *43*, 3475.