SYNTHESIS PATHWAYS FOR BIOCOMPOSITES FROM VEGETABLE OILS

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ABSTRACT

Sustainable development demands productivity with future perspective from every field. Chemists need to develop products which are environmentally acceptable, maintain ecological balance and have minimum consumption of energy and raw materials. There has been an alarming increase in the use of plant and vegetable oil as a renewable source in the manufacture of various chemicals and their derivative is increasing. The vegetable oils can be chemically modified to yield useful composites which are biodegradable and hence ecofriendly and economical. This will not only reduce the burden on conventional raw material but will enhance sustainable growth. This article tries to explore the synthesis routes and pathways to produce biocomposites for a variety of applications.

Keywords: polymerization, fatty acids, triglycerides, SOMGMA, BAMA, NPGMA

I. INTRODUCTION AND SCOPE

1.1 Sustainable Development and Chemistry

Sustainable development is the only keyidea to overcome various crises exists in this world. It is the progressive and balanced gain of sustained economic development which leads to social equity and environmental quality. Sustainable development comprises of three components viz. society, environment, and economy (F45igure 1.1). If these three components are satisfied, its goals can be achieved.
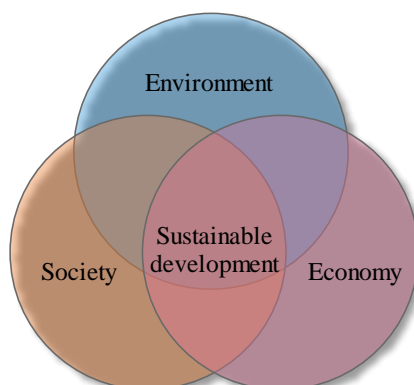

Figure 1.1.1Sustainable development.

Another major aspect for this process is the conservation and proper management of resources. At the beginning of the 19th century basic chemicals demand was fulfilled by renewable raw materials but later on there was increase in

demand of coal from the chemical industries. Mineral oil was also in demand and it was most important source of raw materials. But due to growing demand of petroleum-based products, its resulting negative effect on the environment and depletion in non-renewable resources, chemical industry began to use renewable resources as raw materials.

Due to this situationuse of renewable agricultural feedstock has been increased to produce a wide range of base chemicals and other industrial products. From the industrial application point of view natural oils and fats are very important renewable raw materials due to their high availability and versatile applications [1, 2, 3, 4].

About 80% of the global oil and fat produced from vegetable oil and 20% from animal origin. This renewable raw material is morebeneficial. It is environment friendly than fossil sources and sustainable also. Variousother renewable resources in use are starch, cellulose, sugars, and lignin[5, 6, 7]..

1.2 Vegetable Oils: Composition and Chemistry

Vegetable oils and fats are categorized under lipids type of chemical compounds. These oils aremade up of triglyceride molecules having three-armed star structure as shown in Figure 1.2. These triglycerides made up of three fatty acids and joined at a glycerol junction. Fatty acids in common oils have14 to 22 carbons in length, with 0 to 3 double bonds per fatty acid.
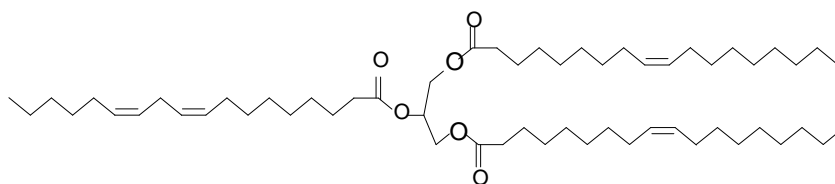

Figure 1.12Triglyceride molecule.

There are various fatty acids. Figure 1.3shows common fatty acids in vegetable oil. There are also some exotic oils whichcontainsfatty acids with other functional groups such as hydroxyl, epoxy, and furanoid groups[8].
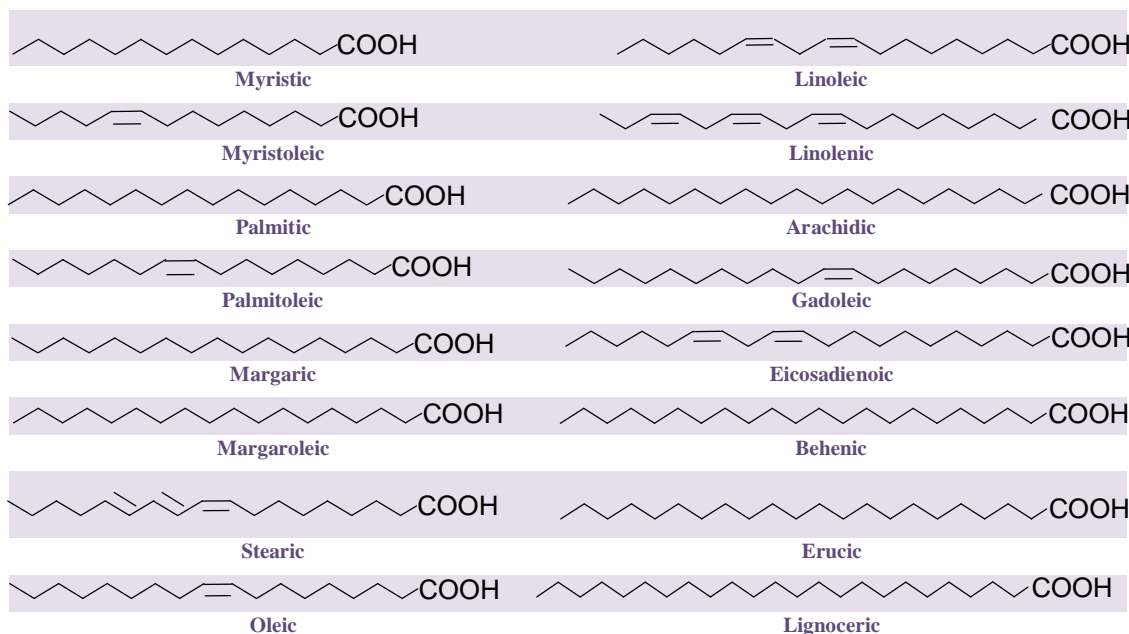

Figure 1.1.3 Structure of common fatty acids

These oils are made up of various types of triglycerides having diverse levels of saturation at the molecular level. By using newly developed genetic engineering techniques oil quality can be changed by introducing a new fatty acid. High oleic soybeans (82.6% oleic acid content) produced are the example of genetic engineering techniques developed by DuPont .There are variousreactivesites in triglycerideswhich actasstartingpointsin differentreactions. These are estergroups(a),C=Cdoublebonds(b),allylic positions(c),andtheα-position of ester groups (d).Nowadays, modification of oil-based fatty compounds providesuseful products from renewable feedstocks. Industrial oleochemistry has made use of carboxylic functionality of fatty acids and derived various useful products using basic oleochemicals like free fatty acids, methyl esters, fatty alcohols, fatty amines, with glycerol as a by-product[8].But enzymatic and microbial transformations also produce various useful products and this area of chemistry still needs tobe developed[9, 3].

II. VEGETABLE OILS: POLYMER APPLICATIONS

Today polymers are used everywhere due to their diverse applications. Many polymers are produced from fossil sources which are non-renewable sources of energy. With consumption of material and energy resources issues, another major issue is pollution which takes place due to large amount of solid waste plastics produced from fossil-fuel feedstock. Though recycling and combustion in incinerating plants are some of the remedies but have to be considered carefully from economic and ecological point of view.

Due to these disadvantages, chemist developed interest in production ofvegetableoil-basedbiopolymers which are more advantageousthan polymerspreparedfrom petroleum-basedmonomers.Thesearebiodegradable, cheaper thanpetroleum-basedpolymers.Various vegetable oils and fatty acids are used for polymer applications such as polymer additives (e.g., epoxidized soybean oil as plasticizer), as building blocks for thermoplastic polymers (e.g., dicarboxylic acids like azelaic, sebacic, and dimer acid for polyesters or polyamides), as a basis for thermosets, polymers, adhesives, and composites with specific properties and applications [10].

III. POLYMERIC MATERIALS FROM VEGETABLE OILS

The various active sites in triglyceride molecules leads to no of chemical reactions and can be used to polymerize triglycerides directly or with polymerizable groups. Same synthesis techniques are applicablewhich are used for the synthesis of petroleum-based polymers.

3.1 Direct Polymerization

It is known[11]that double bonds C=Cpresent in triglyceride molecules can be polymerized through a free radical or a cationic mechanism. Due to chain-transfer processes to the many allylic positions in the molecule, the free-radical polymerization of triglyceride double bonds is not preferred by researchers.But vegetable oils such as linseed and tung oils have been derived as drying oils and it is due to highly unsaturated nature of these oils which leads to react with atmospheric oxygen forming a network. These oils are used in paints and coatings, inks and resins.

Larock's group [12]has studied widely direct cationic polymerization of the C=C double bonds of natural oils. They prepared various thermosetting polymers ranges from rubbers to hard plastics using cationic polymerization of a variety of oils such as fish, tung, and soybean oil with petroleum-based comonomers such as styrene,

divinylbenzene, and dicyclopentadiene and initiator boron trifluoride diethyl etherate. Thisnew thermosetting material found to have good thermal and mechanical properties comparable to industrial plastics, as well as some other useful properties, such as high damping and shape memory.

Some vegetable oils have naturally occurring functional groups such as hydroxyl and epoxide. Due to presence of these groups it is possible to make direct crosslinking with different hardeners to form polymer networks. For e.g.Castor oil is triglyceride of ricinoleic acid.(Figure 1.7a). Ricinoleic acid has 18 carbon atoms, a double bond (C9=C10), and a secondary hydroxyl group. This oil iswidely used in manypolyurethane applications[13, 14, 15]. Vernonia oil has triglycerides containing70–80% vernolic acid. It has a naturally occurring epoxide functional group. The triepoxide functionality of vernonia oil is used to get crosslinked polymers with difunctional reagents, such as dibasic acids[16. and aromatic diamines. Both oils are used to produce interpenetrating polymer networks (IPNs) which increase the toughness and fracture resistance of conventional thermosetting polymers[17, 18].

3.2 Chemical Modification and Polymerization

The internal double bonds in the triglyceride structure are sufficiently reactive for cationic polymerization only and to carry out other polymerization reactions for producing solid polymers, some modifications are necessary. These modifications are

i.   Introducing reactive groups into the aliphatic chains, which would exhibit a higher aptitude to polymerize (synthesis route A, Figure 1.4), and

ii. the reduction of the triglycerides to monoglycerides through a glycerolysis reaction(synthesis route B).
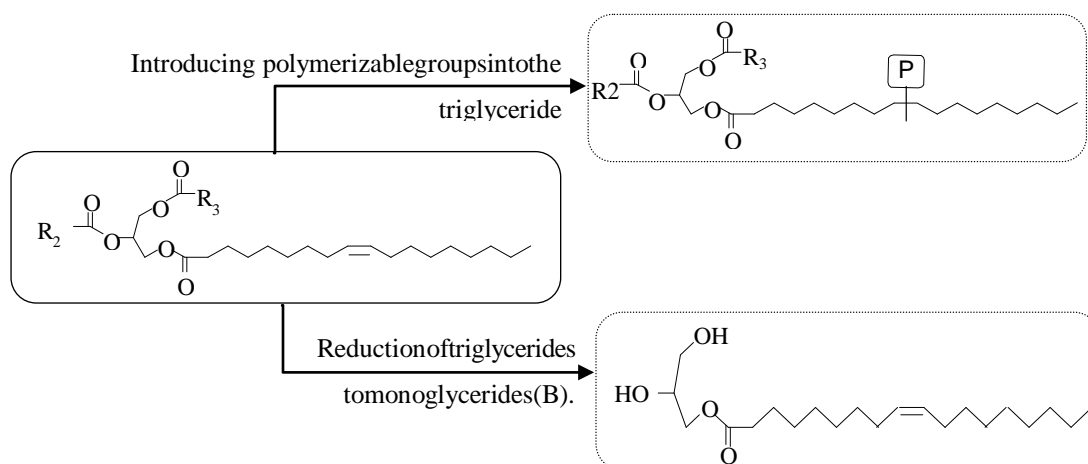

Figure 1.1.4Generalsynthesis routes

IV. SYNTHESIS ROUTE A: INTRODUCTION OF POLYMERIZABLE GROUPS

One of the most important functionalization reaction is the epoxidation reaction which involves C=C double bonds. It increases reactivity of triglycerides byring-opening. Due to ring-opening of epoxidized vegetable oils, introduction of polymerizable groups into triglyceride is possible. Lot of work is done on the preparation of biobased epoxy resins from epoxidized vegetable oils by the researchers [19, 20, 21].

Triglyceride-based polyols suitable for polyurethane synthesis were also prepared by reaction of epoxidized vegetable oils with various chemical reagents.

Following are some reactions for conversion of epoxy groups to secondary hydroxyl groups

i. Epoxy group reaction with hydrochloric or hydrobromic acid produces halogenated polyols (Figure 1.6)

ii. An acid-catalyzed ring- opening reaction with methanol, yielding a methoxylated polyol (c), or with water, forming vicinal hydroxyl groups (d)

iii. catalytic hydrogenation (e). [22, 23].

Epoxidation of unsaturated fatty compounds [24], peracetic acid (peroxy acid) prepared from hydrogen peroxide and the corresponding acid in a separate step or in situ (Figure1.5).
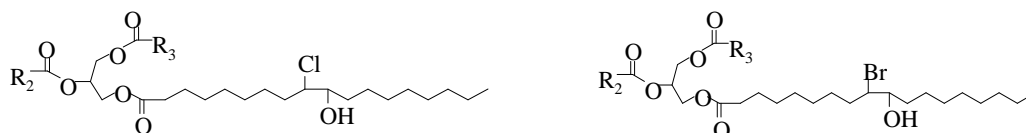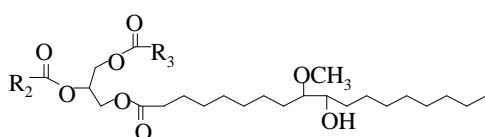

Figure 1.1.5

For better results preformed peroxy acids such as m-chloroperbenzoic acid is used on laboratory scale. In other epoxidation methods dioxiranes, various peracids from aldehydes and molecular oxygen and hydrogen peroxide and methyltrioctyl-ammonium (diperoxotungsto) phosphate as a phase transfer catalyst34 are used. In another chemoenzymatic self-epoxidation of unsaturated fatty acids, unsaturated acid or ester is converted into an unsaturated percarboxylic acid by a lipase-catalyzed reaction with H_2O_2, and in an intermolecular reaction it is self-epoxidized.

In industry, unsaturated fatty compounds are epoxidized by in-situ performic acid process. Nowadays these vegetable oils are used as plasticizers for polyvinyl chloride[25], reactive diluents[26], IPNs[27] and toughening
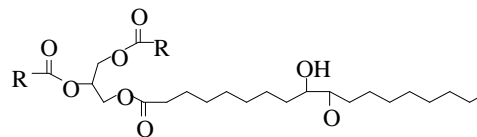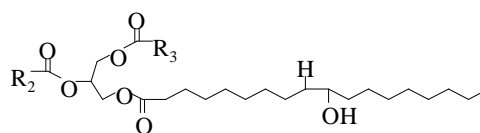

a. r ing-openingwithhydrochloricacid b. ring-openingwithhydrobromicacid

c. r ing-openingwithmethanol d. r ing-openingwithwater

e. r ing-opening b y catalytichydrogenation

materials for commercial epoxy resins[28]

Figure 1.1.6Polyols from ESO (ring opening with different chemical agents)

Carboxylic acid (–COOH group) can also react with a triglyceride structure by opening oxirane ring (Figure 1-7) and formed polymer.
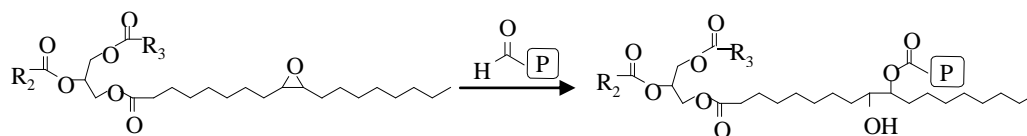
Figure 1.1.7

Many epoxidized vegetable oils and fatty acids can be modified with acrylic acid[29, 30, 31].This reaction is partially catalyzed by acrylic acid and the additional catalysts N, N- dimethylaniline and triethylamine are used. Hence the epoxy functional triglyceride incorporates polymerizable acrylate moieties onto the triglyceride (Figure 1.8).
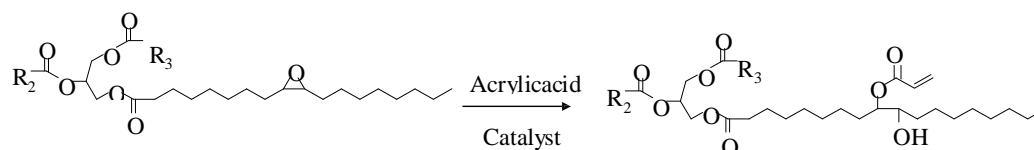
Figure 1.1.8

Acrylated epoxidized soybean oil (AESO)are used in surface coatings, urethane and amine derivatives of AESO are used for coating and ink applications[32]are some of the applications.Free-radical polymerization of AESO, and its blend with styrene is useful in structural applications[33].Pelletier et al 2006 [31], reported the polymerization of AESO with free-radical photoinitiators. lso, cyclohexane dicarboxylic anhydride, having cyclic groups which gives stiffening to the polymerreacts with epoxy groups of triglycerides to form modified resins with better mechanical properties showing improvements in the storage modulus at room temperature and the glass-transition temperature (Tg).Cinnamic acid reacts with epoxidized soybean oil using triphenyl phosphine (PPh3) as a catalyst (Figure 1.9) [34].Cinnamic acid does not free-radically homopolymerize to a high-molecular-weight polymer but it can undergo copolymerization with other alkene monomers (having electron-deficient double bonds). The copolymerization of cinnamate ester of epoxidized soybean oil with 25% (w/w) styrene, vinyl acetate, and methyl methacrylate produces insoluble thermosetting materials.
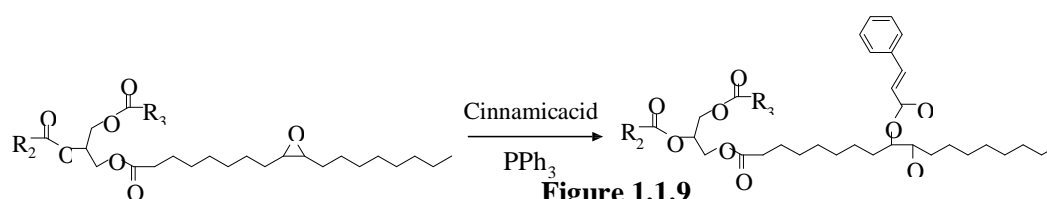
Figure 1.1.9

When vernonia oil reacts with a conventional phenolic antioxidant, DHTB [3-(3, 5-di-tert-butyl-4-hydroxyphenyl) propionic acid], forms a monomer which then combines with polystyrene and polyurethanes to form a macromolecular antioxidant [35].Soybean phosphate ester polyol can be synthesized by acid hydrolysis of epoxidized soybean oil in the presence of phosphoric acid, and is used in the preparation of polyurethane formulations. Other synthesis routes are also there to introduce polymerizable groups into the aliphatic chainexcluding epoxidation reaction.

Acrylate group can attach to triglyceride structures by addition of bromide and acrylate groups to a C=C double bond. It is one step reaction. Soybean and sunflower oils are bromoacrylated in the presence of acrylic acid and NBS (N- bromosuccinimide; Figure 1.10).
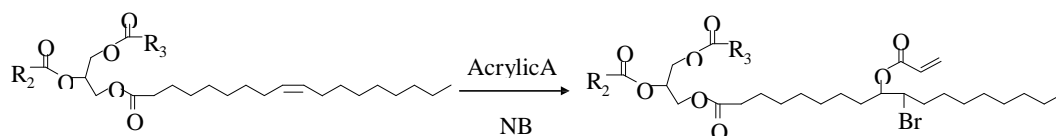
Figure 1.1.10

The free-radical homopolymerization of the bromoacrylated triglycerides is carried out in the presence of methyl ethyl ketone peroxide and AIBN [2, 2'-azobis (isobutyl nitrile)]. These bromoacrylated soybean- and sunflower-based polymers possess good flame-retardant properties due to bromine in the structure. Acrylate and bromine can be added to the C=C double bonds of castor oil. This bromoacrylated castor oil reacts with toluene diisocyanate (TDI) forming polyurethane prepolymer containing acrylate functional groups. This prepolymer finally copolymerize with styrene, 2-hydroxyethyl methacrylate, and 3-(acryloxy)-2-hydroxypropyl methacrylate, which forms IPNs.

In Ritter reactionsoyabean and sunflower oils react with acrylonitrile in the presence of sulfuric acid (Figure 1.11)[36] to produce acrylamide derivative of triglycerides .It is a free-radical copolymerization which produces semi-rigid polymers.
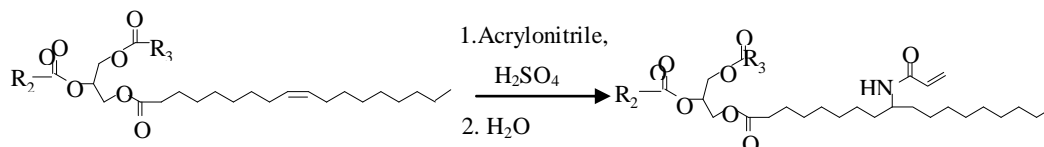

Figure 1.1.11 Ritters Reaction

In hydroformylation, C=C double bonds of a vegetable oil are converted to primary alcohols using rhodium or cobalt as a catalyst and then hydrogenation by Raney nickel[37]. In ozonolysis reaction, different vegetable oils (triolein, low-saturated canola oil, and soybean oil), produces polyols with terminal primary hydroxyl groups and different functionalities [38].When soybean oil reacts with paraformaldehyde in the presence of a catalyst Lewis acid yields a hydroxymethylated soybean oil derivative [39]A reaction of epoxidized triglyceride with water yields hydroxylated triglycerides with vicinal diols.

Hydroxylated oil synthesized from the unsaturated oil reacting with hydrogen peroxide and formic acid[40]Also, hydroxybrominated triglyceride derivatives synthesized using an NBS/acetone/H_2O mixture[41]

These hydroxylated vegetable oils are used in polyurethane formulations. However, These oils are also modified with different reagents such as cyclic anhydrides maleic anhydride.Thismaleate half-ester derivative or maleinized triglyceride then copolymerized with styrene to produce a rigid polymer. Other type of maleate half-ester derivative, maleinated hydroxylated soybean oil, Hydroxylated triglyceride, triglyceride with maleate half-esters are also there. It is observed that after completion of maleinization reaction, the monomer resin radically polymerized and copolymerized with styrene to form homopolymer having better dynamic mechanical properties than AESO polymers.

Maleic anhydride can react with unsaturated compounds. Eren et al., 2003 [42] converted soybean oil to succinic anhydride-modified soybean oil (Figure 1.12) following polymerization with different alcohols and produced soft and tacky polymers which could not be used as structural polymers but these new polymers are used as adhesives,
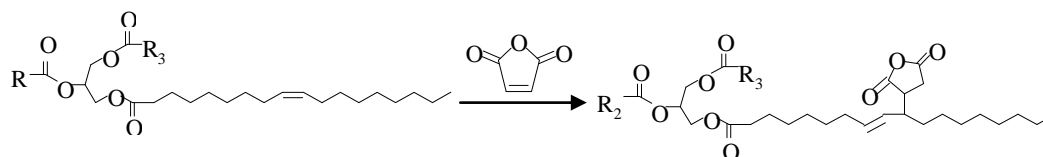
film formers, and textile and paper sizes.

Figure 1.1.12Synthesis of maleinated soybean oil

Maleinated oils are also used as an anhydride functional curing agents of epoxy resins, such as bisphenol-A (BA)-diglycidyl ether and epoxidized vegetable oils.Diels-Alder reaction is also used for modification of vegetable oils. Linseed oil was modified by reacting it with cyclopentadiene at high temperatures .It formed a partially norbornylized product (Dilulin®) (Dilulin® contains an average of only one norbornyl group per triglyceride molecule). Chen et al.2002 [43], synthesized highly norbornylized linseed oil via a high-pressure, high-temperature Diels-Alder reaction (Figure 1.13).
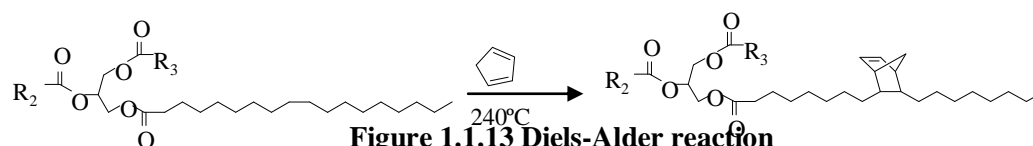

Figure 1.1.13 Diels-Alder reaction

Then this compound was epoxidized and photopolymerized. It is observed that curing rate is higher for norbornyl epoxidized linseed oil than for epoxidized linseed oil and norbornylized linseed oil can be used in the formulation of UV-curable hybrid films.ω-Unsaturated fatty compounds are obtained by catalytic metathesis with ethylene. Olefins are converted into new olefins via an exchange of alkylidene groups in metathesis reactions.

These ω-unsaturated esters are prepared from unsaturated fatty acid methyl esters by metathesis with ethylene using heterogeneous rhenium or homogeneous ruthenium catalysts. Another method is pyrolysis to get ω-unsaturated fatty compounds.
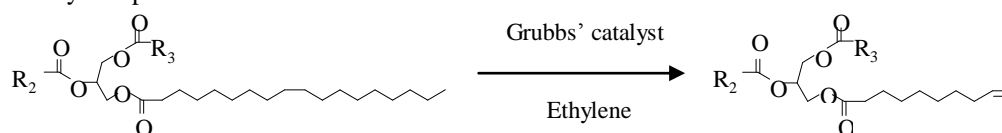

Figure 1.1.14

Pyrolysis of ricinoleic acid produces 10-undecenoic acid.5 Bis(tricyclohexylphosphine) benzylidine ruthenium (IV) dichloride [(Cy3P)2Cl2RuCHPh] (Grubbs' ruthenium catalyst) are used in the metathesis of vegetable oils. 9-undecenoyl triglyceride is obtained by reaction of triolein and ethylene in the presence of Grubbs' catalyst (Figure 1.14).

Olefin metathesis is used as a polymerization reaction. By using cross- metathesis of soybean oil sticky to rubbery polymers [44]are obtained. Polymerizable acrylic, styrenic, and glycidylic groups can be attach to naturally occurring hydroxyl groups present in castor oil by reacting castor oil with acryloyl chloride [45] 3-isopropenyl-α,α'-dimethyl benzyl isocyanate and epichlorohydrin. Castor oil glycidylicetheris used in formulations of cationic UV-curable coatings.

V. SYNTHESIS ROUTE B: REDUCTION OF TRIGLYCERIDES TO MONOGLYCERIDES

Monomers can be synthesized by reducing triglycerides using a glycerolysis reaction.In this reaction triglycerides

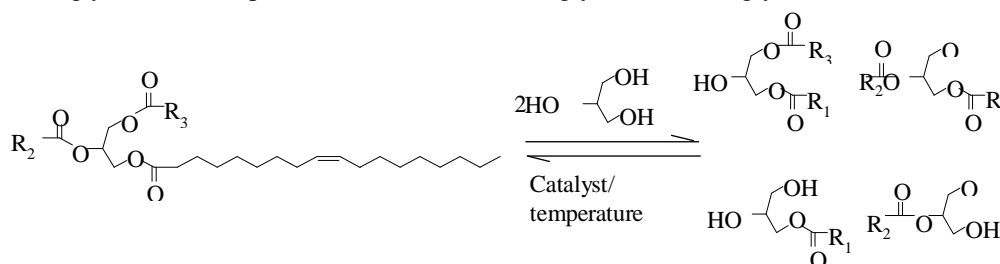reacts with glycerol and the product is a mixture of monoglycerides and diglycerides, as shown inFigure 1.15

Figure 1.1.15 Glycerolysis reaction

Plant oil triglycerides are converted to monoglycerides which areused as the diol component in polyesterification reactions with various diacids and anhydrides to produce alkyd resins. Alkyd resins are well known oldest polymers having good economy and easy for use [46].

Using monoglycerides mixtures derived from tallow oil, Friedman and Garti, 1983 [47], prepared monoesters of maleic acid. Then these monoesters were sulfonated and used as wetting agents and surfactants. Wool's groupsynthesized and polymerized soybean oil monoglyceride maleates (SOMGMA) to produce rigid thermosetting polymers.91 They maleinized mixtures of soybean oil monoglycerides, BA, and neopentyl glycol (NPG) under the same reaction conditions, and obtained maleates [SOMGMA, BAMA), and NPGMA . These maleates then copolymerized with styrene [48].Addition of NPGMA to SOMGMA increases the Tg. and modulus of the final polymer and addition of BAMA had small effect on Tg. and was slight increase in the modulus.

Nowadays castor oil is in use at place of soybean oil in alcoholysis reactions with several alcohols: glycerol, pentaerythritol, and BA propoxylate to reduce plasticizing effect. This alcoholysis product then reacts with maleic anhydride to form maleate half-esters and finally copolymerized with styrene. It is observed that the polymers prepared from castor oil have   improved modulus, strength, and Tg.values than soybean oil-based polymers [49].

VI. CONCLUSION

As discussed the synthesis routes for processing a particular vegetable oil is different and varies with the operation condition and choice of the catalyst. Depending upon the biocomposites application and desired properties,the synthesis routes must be carefully selected in order to functionalize particular group in the tryglycerides.The type of vegetable oil for synthesis of these biocomposites depends on the geographical location, yield and availability.

VII. ACKNOWLEDGEMENT

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