

Renewable functional polymers from vegetable oils: Synthesis and industrial applications

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Abstract

A growing concern about environmental issues like depletion of fossil resources, green-house gas (GHG) emissions, and large-scale polymeric waste has driven efforts toward the development of new methods to produce polymers using renewable sources. As a result, vegetable oils have been identified as an attractive feedstock due to their availability, chemical structure variety, relatively low volatility and presence of reactive functional groups. The carbon-carbon double bond found in each molecule of the triglycerides which make up vegetable oil; ester groups present on both ends of the fatty acid chains; and in some cases, hydroxyl (-OH) groups located at either or both ends of the fatty acid chain of the glycerol backbone can all undergo various chemical transformations to create polymerizable and/or crosslinkable functionality. This article provides a comprehensive overview of recent developments in the synthesis, functionalization, characteristics and industrial application of functional polymers based on vegetable oils. Modification techniques used to modify vegetable oils include epoxidation, hydroxylation, acrylation/methacrylation, carbonatation, maleination, transesterification/urethanization. Each of these vegetable oil-derived polymer families including epoxy, polyurethane, non-isocyanate polyurethane, polyester, polyamide, acrylates and thermosets will be covered along with additional focus placed upon novel functional systems including UV curable, waterborne, self-healing, dynamic covalent/vitrimeric polymers. In addition to reviewing the use of these functional polymer systems in several industrial areas (i.e., protective coatings/adhesives/composites/auto parts/packaging), we will discuss current challenges facing this technology including variability in raw material composition, lack of efficient functionalization methodologies to yield acceptable levels of mechanically and thermally stable polymers, economics/scalability issues/end-of-life management issues. Finally, we will provide suggestions regarding potential solutions to address many of the above-mentioned challenges by focusing on waste vegetable oils, multifunctional renewable monomers, dynamic polymer networks/nanocomposite systems/sustainable processing.

Keywords: Vegetable oils, renewable polymers, bio-based polymers, functionalization, epoxidation, polyurethane, non-isocyanate polyurethane, self-healing polymers, vitrimers, sustainable materials, industrial applications, bio-based coatings

Introduction

It has become evident through the recent surge in the development of synthetic polymeric materials that modern society has greatly benefited due to the many attributes of polymeric materials. Polymeric materials offer unique combinations of properties such as low densities, great durability, excellent chemical resistance, and ability to be easily processed. As a result of their advantageous combination of properties, polymeric materials have found extensive usage in many areas including; packaging, coating formulations, adhesive technologies, automotive parts and components, architectural/structural building materials, electric/electronic devices, biomedical products, and a multitude of additional applications. Despite their widespread utilization, most of the commercially available polymeric materials are synthesized from petroleum-based and/or other fossil fuel based starting materials. The continued reliance upon finite fossil resource bases, coupled with greenhouse gas emissions resulting from combustion processes, increasing energy demands, and disposal issues related to persistent polymeric wastes necessitate the development of alternative polymeric materials with decreased environmental impacts ^[1]. Thus, researchers have devoted substantial time and effort to developing novel polymeric materials utilizing renewable carbon source (i.e.,

bio-based) raw materials. In response to the need for new, environmentally friendly polymeric materials, vegetable oils have emerged as promising candidates as starting materials for the synthesis of novel polymeric materials. Vegetable oils are commonly abundant, renewable, biodegradable to some extent, and typically less expensive than traditional petrochemical-based polymeric precursor materials. Vegetable oils consist predominantly of triglyceride compounds having a variety of types of fatty acid side-chains with differing levels of unsaturation within the side-chains, varying lengths, and functionalities. There exists a broad array of vegetable oils that could potentially be employed for the synthesis of novel polymeric materials ^[2]. These include, but are not limited to: soybean oil, linseed oil, sunflower oil, rapeseed oil, castor oil, palm oil, corn oil, tung oil and others. Many of these oils contain carbon-carbon double bond(s), ester group(s) and/or hydroxyl (-OH) functionality which provide opportunities for chemical modification and subsequent formation of polymer networks. Native vegetable oils do not readily form polymers under typical conditions due to their lack of polymerizable functionality. It is necessary to chemically modify native vegetable oils to facilitate efficient conversion into high-performance polymeric materials. A number of methodologies have been developed to introduce

functional groups onto oil molecules. Some common examples include: oxidation reactions (epoxidation); reaction of alkenes with hydrogen peroxide; reaction of alkenes with peroxy acids (hydroxylation); reaction of alkenes with acrylic acid derivatives (methacrylation); reaction of alkenes with diacid chlorides (carbonatation); reaction of alkenes with maleic anhydride (maleinization); transesterification reactions; amidation reactions; and urethanization reactions ^[3]. These methodologies convert naturally occurring oil structures into multifunctional monomers, oligomers or reactive intermediates capable of undergoing polymerization/cross-linking. Of all the methodologies listed above, epoxidation stands out since epoxide groups can undergo a very wide range of ring opening/polymer forming reactions. Functionalized vegetable oils have been successfully employed to produce a wide variety of polymeric classes including: epoxy resin systems; polyurethane systems; polyester systems; polyamide systems; acrylate systems; and thermoset systems.

Additionally, to replace petroleum derived materials in these polymeric systems appropriate molecular design may impart specific desirable properties to the resultant materials. This review aims to provide a detailed overview of the development of renewable functional polymers derived from vegetable oils with focus on the correlation between oil

structure/functionality/modifications/polymers/architecture/material properties/industrial applications. A discussion on the primary methods for transforming vegetable oils into functionally modified polymer precursors will follow. An assessment of important polymer classes/emerging functional systems (e.g.: water borne/UVC/SH/DYN/CVITRIMERS) as well as an examination of industrial application/use characteristics/performance will also be presented. A review of the key limitations/concerns regarding scaling up/sustainability-related topics/future research directions will conclude by identifying avenues leading to high-performance and industrially applicable vegetable-oil-derived polymeric materials ^[4].

Vegetable Oils as Renewable Polymer Precursors

Vegetable oils are renewable organic resources mainly composed of triglycerides, in which three fatty-acid chains are esterified with glycerol. Most vegetable oils are complex mixtures of various types of fats, known as triglycerides. Triglycerides consist of approximately three long-chain fatty-acid molecules that have been attached to a single molecule of glycerol through esterification reactions. These fatty-acids may have a variety of different lengths (i.e., numbers of carbons), and some may have multiple double-bonds (i.e., be "unsaturated"). Because each type of fat has unique physical and chemical properties, vegetable oils offer a wide range of possible chemical modifications that can produce highly variable types of polymeric materials. For example, olive oil typically includes about 70 percent oleic acid (an unsaturated fatty-acid); sunflower oil is primarily made up of linoleic acid (also an unsaturated fatty-acid); and soybean oil usually contains both saturated and unsaturated fatty-acids. Each type of fatty-acid in these vegetable oils offers the possibility of creating a distinct type of polymer. For example, polyols derived from unsaturated fatty-acids can be used as monomers to create alkyd resins, or as di-isocyanate precursors for the creation of rigid foams. Polyols that are produced from saturated fatty-acids can also be used as monomers to create alkyd

resins or rigid foams ^[5]. However, the majority of vegetable oils do not possess sufficient reactive sites to form linear polymers, so most require chemical treatment to increase their reactivity before they can be converted into polymeric materials. Chemical treatments can convert the alkene groups within unsaturated fatty acids into other functional groups (e.g., epoxide, hydroxyl, acrylate). Once treated, these modified vegetable oils can then be used as monomers to produce a wide variety of polymeric products. As mentioned earlier, the primary characteristic of castor oil is its high content of ricinoleic acid, which has both a hydroxyl group and an alkene group. The presence of the hydroxyl group makes castor oil particularly useful for producing polyurethane and similar functional polymers ^[6].

Factors Governing the Selection of Vegetable Oils

The choice of suitable vegetable oils for the development of renewable functional polymers is very important; this is due to the fact that the chemical characteristics of the chosen oil will be responsible for the potential pathways available for the functionalization and polymerization of the oil; additionally, these characteristics may also impact the overall structure of the resultant network and therefore the ultimate properties of the formed material.

1. Fatty-Acid Composition and Degree of Unsaturation

The amount and location of C-C-double-bonds in fatty acid-chains is important when considering a chemical alteration of those acids. Due to their large number of unsaturations (double bonds) highly unsaturated oils like Linseed oil, Tung oil and Soybean oil will have multiple points available for an epoxide formation or an oxidative polymerization reaction or some other form of functional group introduction. However due to their low degree of unsaturation, oils that have less saturation than typical, i.e., High-Oleic Sunflower Oil and High-Oleic Soybean Oil generally have better oxidative stability; however, they will also have less areas for further chemical modifications ^[7].

2. Natural Functional Groups

Naturally occurring functionalities within monomers also may present other opportunities for polymer formation. For instance, castor oil is a natural source of hydroxyl functionality via the ricinoleic acid contained in it. Therefore, it has potential to be used as a renewable polyol source for polyurethane synthesis. However, most petroleum-based oils contain insufficient functional group content to form polymers by themselves; they must first undergo chemical reaction to produce modified chemistry that can then be formed into a polymer ^[8].

3. Molecular Functionality

The amount of a particular group that reacts with an oil molecule is very important to what shape the polymer will have as well as how dense it will be cross-linked. Generally, higher levels of functionality tend to result in the creation of more highly cross-linked networks which then leads to greater degrees of hardening; improved thermal stability; and better overall chemical resistance. However, over-cross-linking can lead to loss of flexibility and/or impact toughness. Thus, the level of functionalization must be carefully regulated so that the final product meets the needs of its intended use ^[9].

4. Availability and Cost

Availability and cost-effectiveness in terms of raw material is a primary concern to use an industrial process. Edible oil

is widely used; however, using edible oil can be a problem from the perspective of competing against food supplies. Therefore, many researches have been done to find non-food edible oil sources, agricultural residues and waste oil as alternative polymers raw materials. The utilization of these non-conventional raw materials also allows reducing waste disposal and increasing economical viability of producing bio-based polymer ^[10].

5. Oxidative and Thermal Stability

The degree of unsaturation in an oil will influence its oxidative stability as well as that of the polymeric material that is formed from it. In general, oils with a high degree of unsaturation are more susceptible to oxidative degradation than those with lower degrees of unsaturation; while this can be beneficial when oxidative cross-linking is desired, it can lead to issues regarding longer term stability. Therefore, appropriate chemical modification or addition of stabilizers may be necessary for certain end use applications ^[11].

6. Suitability for Target Applications

Vegetable oils should therefore be selected based on their potential uses as functional polymers. As such, oils that are highly reactive will typically be used in applications that produce rigid or thermoset polymers; however, those that have lower reactivity will generally provide better toughness and flexibility. In addition to reactivity (chemical), the compatibility of the modified oil with various curing agent/solvent combinations as well as additives (nanoparticles, etc.) is critical to forming an effective functionalized polymer system. The selection of a vegetable oil therefore includes a combination of several key factors including reactivity, functionality, properties of end-use product, environmental impact (renewability) cost, and availability ^[12].

Functionalization Strategies of Vegetable Oils

Vegetable oils typically consist of triglycerides that are limited in their ability to create polymers. Therefore, chemically modifying them is typically necessary to develop functional groups within these oils so they may be considered useful for creating new polymer precursors. Through modification of native functional groups (i.e., double bonds) within the vegetable oil, by introducing additional functional groups (e.g., ester groups), and through generation of new reactive sites that are capable of undergoing polymerization reactions, cross-linking reactions, and curing reactions, a wide variety of different types of reactive sites can be generated. The selection of the appropriate approach to functionalize vegetable oils will significantly influence both the molecular architecture of the derived polymer and its associated processing characteristics. Vegetable oils can be converted to functionalized polymer precursors using several different approaches. Some of the more frequently utilized approaches include; epoxidation, hydroxylating, acrylating, methacrylate forming, carbonating, maleinating, transesterifying, amidating, and urethane forming. The individual techniques described above can be used singularly or in combination to produce intermediate products with multiple functionalities that exhibit controllable reactivity ^[13].

1. Epoxidation

Epoxy is among the most common functionalization techniques that utilize unsaturated vegetable oils. A carbon-carbon double bond is transformed into an epoxy group by

utilizing suitable oxidative systems. Upon formation of the epoxides, they then react through ring opening with alcohol, amine, acid, or another nucleophile. As such, epoxidized vegetable oils are very important as precursors to epoxy polymers; polyols; coatings; composites; and non-isocyanate polyurethane systems ^[14].

2. Hydroxylation

The incorporation of hydroxyl groups to the oil molecular structure through hydroxylation is a method by which we increase the functional character of the oil. Hydroxylated vegetable oils are capable of being used as biorenewable polyols in the syntheses of polyurethane and polyester materials. The addition of hydroxyl groups provides an additional area that can be chemically reacted upon with another component or used for a subsequent reaction ^[15].

3. Acrylation and Methacrylation

Acrylation and methacrylation of vegetable oils introduce polymerizable vinyl groups into the structure of vegetable-oil-derived materials. The functionalized vegetable-oil derivatives can undergo free-radical polymerization or UV-induced curing to produce cross-linked polymer networks. Acrylated vegetable oils are of particular interest for rapid-curing coatings, inks, adhesives, and additive-manufacturing applications ^[16].

4. Carbonation

Carbonation is another key strategy in order to develop non-isocyanate polyurethane prepolymers. Vegetable oil-based epoxides (e.g., from soybean or rapeseed) are reacted with CO₂ forming the cyclic carbonate group, which then reacts with multi-functional amines to produce poly-hydroxyl-urethanes without using traditional isocyanates. Therefore, this method provides an alternative route that may lead to safer and possibly more environmentally friendly polyurethane alternatives ^[17].

5. Maleinization

Maleinization is a process in which maleic anhydride (or functional analogues) are chemically incorporated into unsaturated vegetable oils. Chemically modified vegetable oils will have increased numbers of reactive sites and thus will be capable of participating in polyreactions, cross-linking reactions, and/or blending with various polymer systems. Vegetable oil based maleinized products have been examined as potential coating products, composite materials, adhesive products, and as precursors to thermosetting materials ^[18].

6. Transesterification and Amidation

The transesterification reaction has the capability to modify the triglyceride's chemical makeup as well as create a variety of fatty acid derivatives, polyol compounds, and various intermediates that have defined functional groups. The amidation reaction creates amide containing moieties that provide improved inter-molecular interaction as well as improvements in thermal/mechanical properties. Because both reactions allow for the creation of unique molecular architecture, they will be beneficial for synthesizing polymers ^[19].

7. Urethanization

Hydroxyl functional vegetable oils are capable of undergoing urethanes reaction in conjunction with appropriate reactive components to create a variety of polyurethane-based materials. Flexible elastomers,

thermosetting networks, coatings, adhesives and foam may be generated depending upon the desired chemical route. Additionally, there has been an increasing amount of interest in the area of non-isocyanates as an alternative method for reducing dependency on traditional isocyanate, based chemistry [3].

8. Sequential and Multifunctional Modification

A significant new area has been the integration of numerous functionalization processes to generate multifunctional renewable intermediates for polymers. For example, an oil may undergo an epoxidation process that follows the formation of the epoxy group as a cyclic carbonate and then further reacted with an amine. Similar to this methodology, epoxides generated from

epoxidated oils have also been converted to include a wide variety of functional derivatives such as hydroxy-, acrylate- or similar functionalities based upon the desired structure of the polymer.

Therefore, the choice of functionalization method will depend on how reactive, what type of function, what mechanism of cure, what form of molecular architecture and what properties are required in the final polymer. The same level of care must be exercised when controlling both the reaction conditions and the extent of functionalization as it is possible to over-modify which increases the viscosity, promotes unwanted side-reactions or impairs the flexibility and processability of the resulting polymer. The major functionalization strategies and their corresponding polymer applications are summarized in Table 1 [20].

Table 1: Major functionalization strategies of vegetable oils and their polymer applications

Functionalization strategy	Reactive group introduced	Major polymer applications
Epoxidation	Epoxy	Epoxy resins, coatings, composites, NIPUs
Hydroxylation	–OH (Hydroxyl)	Polyurethanes, polyesters, coatings
Acrylation	Acrylate	UV-curable polymers, coatings, adhesives
Methacrylation	Methacrylate	Thermosets, UV-curable materials
Carbonatation	Cyclic carbonate	Non-isocyanate polyurethanes (NIPUs)
Maleinization	Maleic anhydride functionality	Coatings, composites, adhesives
Transesterification	Modified ester/polyol structures	Polyesters, polyurethanes
Amidation	Amide	Polyamides, coatings, composites
Urethanization	Urethane	Polyurethane coatings, elastomers

These approaches to modifying chemical structures provide the basis for various types of functional polymers from renewable feedstocks based on vegetable oil. Epoxidation is also significant due to its versatility as an intermediate that can be used in multiple subsequent reactions to form polymers; accordingly, this reaction will be presented separately in the next section.

Vegetable-Oil-Based Polymer Classes

Chemical modification of vegetable oils offers a lot of opportunities in terms of producing large variety of new polymeric materials (with diverse structure) and properties. Vegetable oil's potential as a precursor for different types of polymeric materials such as epoxy, polyurethane, non-isocyanate polyurethane, polyester, polyamide, polyolefin, acrylic polymer and hybrid material depends on both reactive group(s) that are attached to it and chemical method used for its polymerization. As a result of their use in synthesis of various polymeric materials; they have also shown to be capable of forming highly flexible elastic materials and highly rigid thermosets [21].

1. Vegetable-Oil-Based Epoxy Polymers

Epoxides represent one of the most popular methods to convert unsaturated vegetable oils to polymerizable intermediates. The presence of carbon-carbon double bond within the fatty acid chain of vegetable oil enables the epoxide group (oxirane) to form on these molecules; this allows for subsequent ring opening during the cure process. Therefore, many researchers have looked at using epoxidized versions of soybean, linseed, sunflower, corn and other vegetable oils as potential renewable sources of epoxy intermediates. Vegetable oil epoxies may be cured with various types of curing agents including amines, anhydrides, acids, etc., to create cross-linked thermostable network structures. In addition to providing adhesion,

chemical resistance, and dimensional stability, the cross-linking structure also imparts high thermal resistance while the flexible nature of the fatty acid portion of the molecule imparts toughness and flexibility [22].

2. Vegetable-Oil-Based Polyurethanes

Vegetable-oil-polyurethanes (PUs) are one of the most widely researched renewable polymers. Vegetable oil may be transformed by a number of different processes such as hydroxylation, epoxide ring opening, transesterification, hydroformylation or other similar chemical reactions into polyols. Polyol precursors that contain hydroxyl functional groups can then undergo reaction with either diisocyanates or polyisocyanates to create PU networks. Properties of PU materials derived from vegetable oil are dependent upon various parameters including hydroxyl function, fatty acid composition, the relative proportion of hard- and soft-segments in the material, and degree of cross-linking. Flexible elastomers, rigid materials, foams, adhesives, and coating systems may be produced based on appropriate molecular design. In fact, reviews have been published indicating that PUs derived from vegetable oils range from flexible foams to rigid plastic and are potentially applicable to many commercial uses [23].

3. Vegetable-Oil-Based Non-Isocyanate Polyurethanes

Non-Isocyanate Polyurethanes (NIPUs), have emerged as one of the most important new categories of renewable polymers. The reason for their importance is that they provide a means to generate polyurethane type networks without using traditional isocyanate chemistry. One of the most commonly used methods to prepare NIPUs from Vegetable Oils has involved converting the Epoxides in these oils into Cyclic Carbonates via ring opening of the epoxide with either secondary or tertiary amines. Subsequent ring opening of the Cyclic Carbonates by

Primary Amines results in the formation of Polyhydroxyurethane Networks which contain both Urethane Groups and Hydroxyl Functionality that were formed during the Ring Opening Reaction of the Carbonate by the Amine. It has been shown that these additional hydroxyls can form hydrogen bonds and therefore may improve Adhesion Properties, Mechanical Strength and Thermal Stability of the Network ^[24].

4. Vegetable-Oil-Based Polyesters

Vegetable oils can also be used as a renewable resource for the synthesis of polyester. Fatty acids (hydroxylated) derivatives and modified triglycerides are all capable of participating in esterification, transesterification or other condensation reactions with di-acids, anhydrides or multi-functional monomers. As a result of these reactions flexible aliphatic segments derived from fatty acids can be formed which are typically located alongside esters. These regions influence polarity, mechanical behavior and thermal properties. Materials ranging from thermoplastic polyesters to thermosets can be produced depending on monomer functionality and cross link density.

Potential applications exist for vegetable oil-based polyesters in coatings adhesives composites packaging and biomedical materials. Additional modification is possible through the use of functional components such as bio-based monomers nanocellulose lignin inorganic fillers, etc ^[25].

5. Vegetable-Oil-Based Polyamides

Vegetable oil-based polyamides are derived from fatty acid-based monomers which contain both amino- and carboxylic functional groups. Vegetable oils provide a basis for the production of long chain fatty acid derivatives that can be converted into diamines (or other di-functional compounds), dicarboxylic acids, amino acids or other intermediate chemicals for producing polyamides. Vegetable oil-derived polyamides possess good combinations of toughness, flexural properties, chemical resistance and high temperature stability due to their ability to form hydrogen bonds through the amide groups in addition to possessing flexible chains formed by long aliphatic moieties.

Therefore, they may find utility in various industrial applications including coatings, adhesives, engineering thermoplastics, fibers and composite materials ^[26].

6. Vegetable-Oil-Based Polyolefins and Metathesis-Derived Polymers

The C=C double bonds that are inherent to all unsaturated vegetable oils can similarly be utilized through metathesis (olefin) chemistry as well as polymerizations. The metathesis process allows for the redistribution of the unsaturated carbon chain units of the original fatty acids and generation of structurally defined monomers from them. These monomers may then be further reacted by way of a number of polymer forming methods including but limited to condensation and/or metathesis type polymerization. In addition, such methodology offers an additional method of functionalizing the ester groups of triglycerides with greater control over molecular structure than through direct functionalization of the triglyceride ester group. Olefin-metathesis chemistry has significant potential due to its ability to convert natural occurrence of unsaturation into useful chemically reactive entities ^[27].

7. Vegetable-Oil-Based Acrylate and Methacrylate Polymers

Acrylation and methacrylation are two of the most common methods that have been used to produce oil derived materials that have a rapid polymerization rate. Vegetable oils can be epoxidized which allows them to react with either an acrylic or methacrylic derivative to open the epoxy ring forming a new polymerizable C-C bond (double bond). Once the vegetable oil is converted into either an acrylated or methacrylated oil it can be cured by free radical polymerization or photopolymerization to form a cross linked network. This process lends itself very well to the production of UV curable coatings, adhesives, inks, sealants and even additive manufacturing resin. Vegetable oils as renewable photo-polymerizable monomers have recently been studied as possible feedstock for sustainable 3D printing applications ^[28].

8. Comparative Overview

The major vegetable-oil-based polymer classes differ in their functionalization requirements, polymerization mechanisms, properties, and applications. Epoxy systems are particularly attractive for thermosetting coatings and composites, whereas polyurethane systems provide a broad range of mechanical properties. NIPUs provide an important isocyanate-free pathway, while acrylate systems offer rapid UV curing. Polyesters and polyamides provide additional opportunities for renewable engineering and functional materials.

Table 2: Major vegetable-oil-based polymer classes and their characteristics

Polymer class	Main oil modification	Polymer-forming chemistry	Important properties	Representative applications
Epoxy	Epoxidation	Epoxy ring-opening curing	Adhesion, hardness, chemical resistance	Coatings, adhesives, composites
Polyurethane	Hydroxylation/polyol synthesis	Isocyanate-hydroxyl reaction	Flexibility, toughness, durability	Coatings, foams, adhesives
NIPU	Epoxidation + carbonatation	Cyclic carbonate-amine reaction	Isocyanate-free, adhesion, tunable network	Coatings, adhesives, packaging
Polyester	Hydroxylation/transesterification	Esterification/condensation	Flexibility, tunable crosslinking	Coatings, composites, packaging
Polyamide	Fatty-acid-derived amino monomers	Condensation/polyaddition	Strength, hydrogen bonding, durability	Engineering materials, coatings
Polyolefin/metathesis polymers	Utilization of C=C bonds	Olefin/metathesis polymerization	Tunable chain structure	Specialty polymers, elastomers
Acrylate/methacrylate	Acrylation/methacrylation	Radical/photopolymerization	Rapid curing, surface functionality	UV coatings, inks, adhesives, 3D printing

9. Structure–Property Considerations

Polymer properties are determined by the relationship between functional group density, molecular structure, cross-linking chemistry and the composition of the vegetable oil used. Higher degrees of unsaturation allow greater opportunity for chemical modification; however, the use of vegetable oils that contain natural functionality (e.g., Castor Oil) allows direct synthesis of hydroxy-functionalized polymer precursors. The length and flexibility of the fatty acid chains determine the glass transition temperature and toughness of the polymer. Increased functionality typically increases cross-linking and creates a more robust network. Therefore, vegetable oil-based polymer systems require optimization, rather than just an increase in renewable content ^[29].

Functional and Smart Polymer Systems from Vegetable Oils

The most recent studies of vegetable oil-based polymers have gone from simply replacing petrochemical-based materials, to creating intelligent (smart) polymer systems. The chemical modification of vegetable oils allows for the addition of functional groups, and dynamic linkages which can create properties such as self healing, reprocessable, quick curing time, hydrophilicity and corrosion protection. Protective coatings made from self-healing vegetable oil-based polymers are especially interesting. Flexible fatty acid segments allow for molecular movement, whereas reversible interactions, or dynamic covalent bonds like those found in imine, disulfide and boronic ester linkages can provide a method to repair damaged polymer networks. Thus, it is theoretically possible to maintain coating integrity even when there are scratches or micro-cracks present, extending the service life of the system. Vitrimeric polymers include dynamic covalent bonds within their cross-linked structure, allowing for potential stress relief, reformulation, repair and recycling. Vegetable oil-based polymers may be combined with nanocellulose, lignin, silica, metal oxides and carbon-based nanomaterials to produce hybrid systems possessing multiple functions including increased mechanical strength, heat stability, barrier properties against moisture vapor and gases, increased UV light resistance and improved anti-corrosion performance. Protective coatings created using renewable resources, incorporating both corrosion resistant and self-healing capabilities along with being waterborne processed appear to be especially promising ^[30].

Industrial Applications of Vegetable-Oil-Based Functional Polymers

The unique combination of being made from a renewable source (i.e., vegetable oils), having highly-tunable chemical functionalities, and offering the versatility of various polymer chemistries makes it possible that vegetable oil-based polymers could be used in a wide variety of industrial fields. Chemical modifications, cross-linking, blending, and incorporation of functional additives allow for tailoring of the final material properties (e.g., coatings, adhesives, composites, packaging, automotive materials) for specific applications or needs. Protective coatings may possibly be the largest category for the use of vegetable oil-based polymers. A number of different types of epoxy, polyurethane, polyester, acrylate, and NIPU-based systems can provide adhesion; flexibility; hardness; hydrophobicity; and chemical resistance. They can protect a variety of

surfaces (including metals and woods) by limiting the penetration of moisture and/or aggressive environmental conditions. Some of the most interesting areas of research using vegetable oil derived coatings involve self-healing and anticorrosive technologies which potentially could increase the durability and longevity of coatings by recovering damage. Vegetable oil-derived polyurethanes, epoxies, polyesters and acrylates can provide good adhesive and sealing properties when used in adhesives and sealants ^[31].

Vegetable oil-based polymers are beginning to be explored for use in polymer composite materials. Natural fiber reinforcement, cellulose, lignin, silica metal oxide fillers and a host of other nanomaterials can increase the mechanical properties (strength, stiffness, toughness); thermal properties; barrier properties; and surface properties of polymer composite materials. Use of vegetable oil-based polymers can decrease the amount of petroleum-derived material found in traditional composite materials. Emerging applications for vegetable oil-based polymers include UV-cured coatings and printing inks; electrical insulation; flooring; medical devices; and additive manufacturing resins. High value functional materials like intelligent coatings; self-repairing systems; and UV curing materials offer performance advantages that would justify the increased costs associated with incorporating bio-based functionalization. Finally, successful industrial adoption of vegetable oil-based polymers will depend not just on their ability to replace non-renewable resources with renewable ones but also on their performance; durability; ease-of-processing; feedstock availability; cost; safety and scale-up feasibility ^[32].

Sustainability, Challenges and Scale-Up

Replacing a portion of the traditional fossil-fuel-based feedstock for vegetable oil-based polymers offers sustainability benefits. Additionally, using waste or non-food-grade oils may also enhance the amount of material that is being utilized as feedstocks. However, depending upon the type and origin of the oil; the level of chemical modification of the oil (processing); the method used to produce and purify the final product; and how it will be disposed at the end of its useful life, the actual environmental savings achieved through the use of these types of materials depend on many factors. Significant barriers exist in the development of vegetable oil-based polymers including variability in the oil composition; low efficiency in functionalizing the various components within an oil; multi-step synthesis; high costs associated with processing and obtaining physical properties similar to those found in conventionally produced polymers. To produce large quantities of this type of material efficiently, new catalyst systems are needed that have consistent activity and produce products that have a very low variance in their physical properties. In order to create economically viable and scalable manufacturing processes for vegetable oil-based polymers, there are several key areas that need to be evaluated. These evaluations include conducting life cycle assessments; performing techno economic analyses; and optimizing all phases of each individual process ^[33].

Future Perspectives

Future research in vegetable oil based functional polymers will include the creation of new "high-performance" materials containing a larger proportion of renewable

resources along with enhanced functions. There is substantial potential for the use of "non-food" and waste oils as cost-effective and sustainable sources of raw materials. Additionally, through highly selective and efficient catalytic methods of functionalizing vegetable oils, energy consumption (heating/cooling), solvents and processing conditions can all be reduced. The most promising areas of application for such vegetable oil derived functional polymers appear to be in the development of self-healing, vitrimeric, water borne, UV curable and multi-functional polymers used for specialized coatings or other premium products. In addition to these emerging technologies, researchers have also shown significant interest in using bio-based multifunctional monomers; green catalyst systems; nano-composite formulations; and recyclable polymer networks which could enhance both the mechanical properties and processibility of vegetable oil derived polymers [34].

Conclusions

Vegetable oils have emerged as versatile and renewable platforms for the development of functional polymeric materials with potential to reduce dependence on fossil-derived resources. Their triglyceride structure, fatty-acid composition, degree of unsaturation, and naturally occurring functional groups provide diverse opportunities for chemical modification and polymer synthesis. Functionalization strategies including epoxidation, hydroxylation, acrylation, methacrylation, carbonation, maleinization, transesterification, and amidation enable the conversion of vegetable oils into reactive polymer precursors. These modified feedstocks have been successfully utilized in the preparation of epoxy polymers, polyurethanes, non-isocyanate polyurethanes, polyesters, polyamides, acrylate-based polymers, and metathesis-derived materials.

Beyond conventional polymer applications, recent developments have focused on functional and smart systems, including self-healing, vitrimeric, UV-curable, waterborne, anticorrosive, and multifunctional hybrid polymers. Such materials offer opportunities to combine renewable content with improved durability, repairability, reduced solvent use, and application-specific performance.

Despite significant progress, challenges remain in controlling feedstock variability, functionalization efficiency, molecular structure, mechanical and thermal performance, production cost, and industrial scalability. The environmental advantages of these materials must also be evaluated through complete life-cycle considerations rather than renewable content alone. Greater utilization of non-edible and waste oils, efficient catalytic processes, low-energy functionalization, bio-based multifunctional monomers, and recyclable dynamic networks could further improve sustainability. Overall, the future development of vegetable-oil-based polymers should focus on achieving an appropriate balance between renewability, functionality, performance, durability, economic feasibility, and recyclability. Integration of green chemistry, advanced polymer design, life-cycle assessment, and industrial scale-up can accelerate the transition of vegetable-oil-based

functional polymers from laboratory research toward commercially relevant sustainable materials.

Credit authorship contribution statement

Virendra M. Parmar: Writing–Original draft, review & editing

Punam D. Bagul: Formal analysis and Data curation.

Prafulla S. Patil: Project administration, Conceptualisation.

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List of Abbreviations

PU – Polyurethane; NIPU – Non-Isocyanate Polyurethane; NIPUA – Non-Isocyanate Polyurethane-Acrylate; EP – Epoxy Polymer; PE – Polyester; PA – Polyamide; UV – Ultraviolet; WPU – Waterborne Polyurethane; SH – Self-Healing; DCN – Dynamic Covalent Network; TGA – Thermogravimetric Analysis; DSC – Differential Scanning Calorimetry; VOC – Volatile Organic Compound; CNC – Cellulose Nanocrystal; CNF – Cellulose Nanofiber; SiO₂ – Silicon Dioxide; ZnO – Zinc Oxide.

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