



Review

Vegetable-oil-based polymers as future polymeric biomaterials[☆]Shida Miao^{a,b}, Ping Wang^c, Zhiguo Su^a, Songping Zhang^{a,d,*}^a National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, People's Republic of China^b Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH 44325, USA^c Biotechnology Institute and Department of Bioproducts and Biosystems Engineering, University of Minnesota, St Paul, MN 55108, USA^d Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, People's Republic of China

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ABSTRACT

Vegetable oils are one of the most important classes of bio-resources for producing polymeric materials. The main components of vegetable oils are triglycerides – esters of glycerol with three fatty acids. Several highly reactive sites including double bonds, allylic positions and the ester groups are present in triglycerides from which a great variety of polymers with different structures and functionalities can be prepared. Vegetable-oil-based polyurethane, polyester, polyether and polyolefin are the four most important classes of polymers, many of which have excellent biocompatibilities and unique properties including shape memory. In view of these characteristics, vegetable-oil-based polymers play an important role in biomaterials and have attracted increasing attention from the polymer community. Here we comprehensively review recent developments in the preparation of vegetable-oil-based polyurethane, polyester, polyether and polyolefin, all of which have potential applications as biomaterials.

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1. Introduction

Biomaterials can either be derived from nature or be synthesized in the laboratory via a variety of chemical approaches including metallic components, polymers, ceramics or composite materials. Much attention is being paid to the preparation and application of bio-based polymers because of environmental concerns [1–3]. Bio-based polymers are defined here as any polymer derived from living organisms such as plants, trees and algae, while biopolymers here refer to any polymer applicable for biomaterials, though bio-based polymers and biopolymers are used equivalently elsewhere [4–7]. Due to their universal availability, inherent biodegradability and low price, vegetable oils have become an area of intensive interest for both academic and industrial research as platform chemicals for polymeric materials. Particular attention has been paid to investigating the suitability of vegetable-oil-based polymers (VOBPs) as future biomaterials [8–10]. Vegetable oils from both plants (such as soy, palm, linseed and sunflower oils) and animals (such as fish oils) are valuable resources for the preparation of a variety of polymers [11–20]. Compared to other bio-based biopolymers such as carbohydrates and proteins, VOBPs

have several characteristics that make them more attractive as biomaterials:

- (1) Although vegetable oils are not naturally present as polymers, they are precursors for monomer chains that can be used to synthesize various polymers including polyurethane, polyester, polyether and polyolefin. Therefore, the VOBP structures can be easily tuned by converting vegetable oil to different monomers.
- (2) Vegetable oils are suitable for synthesis of hydrophobic polymers and complement nicely other bioresources like carbohydrates and protein that are naturally hydrophilic.
- (3) Vegetable oils are suitable for producing monomers with structures similar to petroleum-based monomers. Therefore, petroleum-based biopolymers are possibly substituted by VOBP with identical desired properties.

The major components of vegetable oils are triglycerides – esters of glycerol with three long-chain fatty acids with varying compositions depending on the source of oil [11,21–23]. A general molecular structure of triglycerides is demonstrated in Fig. 1. The physical and chemical properties of vegetable oils are mainly determined by the fatty acids, i.e., the fatty acid chain length and the numbers and locations of double bonds in the fatty acid chains [11,23]. Usually, the length of the fatty chain is between C12 and C20, with oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3) being the most common [11,23]. The average number of double bonds per triglyceride varies in different oils. For example, soybean oil has roughly 4.5 double bonds per molecule – this

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* Corresponding author at: National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, People's Republic of China. Tel./fax: +86 10 82544948.

E-mail address: spzhang@home.ipe.ac.cn (S. Zhang).

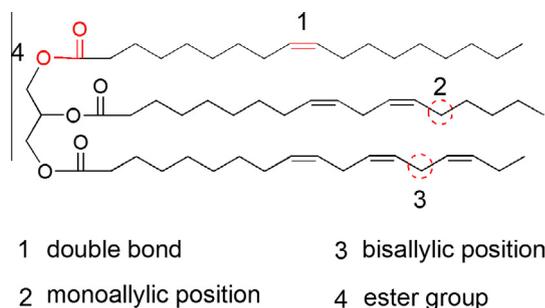


Fig. 1. Demonstration of the structure of triglyceride and reactive sites.

increases to 6.4 for linseed oil [23]. Other functional groups are also present in the fatty acid chains of some special oils.

For example, ricinoleic acid has one hydroxyl group and is the most abundant fatty acid in castor oil [24]; vernolic acid has an epoxy group and is high in vernonia oil [25]. The α -eleostearic acid has conjugated double bonds and is the major fatty acid of tung oil. When vegetable oils are utilized to derive monomers or produce polymers, double bonds, allylic positions (including monoallylic and bisallylic positions), ester groups and the other functional groups are the most important reactive sites (Fig. 1). By introducing functional groups through these reactive sites, various VOBPs can be readily synthesized. There are already quite a few nice reviews dealing with vegetable oil as a platform chemical for polymeric materials, but these focus on the synthetic route for polymer preparation [11–12,15–17,19,26–28]. In this review, we will detail recent and innovative approaches in the preparation of vegetable-oil-based polyurethane, polyester, polyether and polyolefin. Properties, including biocompatibility, shape memory effect and biodegradability that might make them more suitable for using as future biomaterials, will be emphasized.

2. Vegetable-oil-based polyurethane

2.1. Synthesis of multi-isocyanates

Polyurethanes are among the most important polymeric materials and have versatile properties suitable for medical applications due to their good biocompatibility and mechanical properties [29,30]. Polyurethanes are synthesized by reacting polyols with petroleum-derived multi-isocyanate, both of which could be derived from triglycerides and their derivatives [22,31–35]. Currently, the most viable and industrially used method for multi-isocyanate production is the reaction of highly toxic gaseous phosgene with amines or their corresponding salts. Health and safety concerns associated with isocyanate chemistry motivate the search for non-phosgene routes for diisocyanate preparation.

With triglycerides or fatty acid as starting materials, different chemical approaches have been explored to synthesize novel multi-isocyanate. By reacting double bonds in soybean oil triglycerides with iodine isocyanate, soybean oil iodo isocyanate was synthesized (Fig. 2a) [36]. The number of isocyanate groups per triglyceride was approximately three. Soybean oil triglycerides were also brominated at the allylic positions with N-bromosuccinimide followed by reacting with AgNCO to synthesize soybean triglyceride multi-isocyanates (Fig. 2b) [37]. Approximately 60–70% of the bromine was replaced by NCO groups, and the yield increased upon increasing the amount of AgNCO.

Fatty acids (derivatives of triglycerides) were also good starting materials for multi-isocyanates. Oleic acid was used to produce 1,7-heptamethylene diisocyanate and 1,16-diisocyanatohexadec-8-ene [38–40]. Oleic acid was first converted to diacids that were then converted to diisocyanates (Fig. 2c). Polyurethanes based on

1,7-heptamethylene diisocyanate have similar physical properties as those made from petroleum-derived 1,6-hexamethylene diisocyanate [38]. Polyurethanes based on 1,16-diisocyanatohexadec-8-ene exhibited an even higher tensile strength than those commonly derived from petroleum-based 1,7-heptamethylene diisocyanate [39]. This improvement was possibly due to the higher degree of hydrogen bonding associated with the longer alkane chains. The long-chain diisocyanate polyurethanes also had a lower Young's modulus and higher elongation. This improvement was presumably due to the improved flexibility of the long diisocyanate chain. Fatty-acid-based diisocyanate was also synthesized starting from diesters (Fig. 2d). Dimethyl sebacate was hydrazinolysed in absolute ethanol to form diacyl hydrazide, which was then converted into diacyl azide. Diisocyanate was synthesized by the Curtius rearrangement of diacyl azide [31]. The determining step is the formation of diacyl azide from diacyl hydrazide because the side reaction – formation of secondary amide – was observed in this process.

2.2. Synthesis of polyols

There are many routes to synthesize vegetable-oil-based polyols, and the most widely studied reactions are summarized in Fig. 3. Thiol-ene coupling reactions can directly introduce hydroxyl groups through double bonds by reacting with 2-mercaptoethanol (Fig. 3a). Generally, thio-ene coupling reactions are very fast under mild reaction conditions [41–44]. Lligadas et al. [27] recently reviewed the “click” chemistry approach to obtain monomers and polymers from vegetable oil; thiol-ene addition reactions of fatty acids and derivatives have been successfully adopted to synthesize diols suitable for polyurethane technology. This group has also applied the thiol-ene additions to 10-undecenoate and oleate derivatives to obtain monomers for producing thermoplastic polyurethanes [45]. Rapeseed oil was also photo-chemically reacted with 2-mercaptoethanol via a thiol-ene coupling reaction [46]. The obtained polyols had an average hydroxyl functionality of 3.6 (the number of hydroxyl groups per molecule). Neither solvents nor photo-initiator was needed, and the product was easily purified. The number of double bonds per chain in the vegetable oil had a marked effect on the reaction, and several side reactions were observed such as disulfide formation and intermolecular combinations.

Ozonolysis is an important route to synthesize polyols (Fig. 3b) [47–49]. In this process, double bonds are oxidized into aldehyde groups that are further reduced to hydroxyl groups. One unsaturated fatty acid chain could only generate one hydroxyl group. Saturated fatty acid chains would be left as pendant chains. Therefore, the average hydroxyl number of the obtained polyols was less than three. The hydroxyl functionality obtained from a soy polyol was 2.5, and that of a canola polyol was 2.8 [47]. The unsaturated double bonds were cleaved in the ozonolysis process, and the byproducts were evidently formed. Thus, the molecular weight of the polyols was lower than that of the vegetable oils.

Vegetable oils can also be converted to polyols via hydroformylation (Fig. 3c). In this approach, double bonds were reacted with hydrogen and carbon monoxide to form aldehyde groups that were then hydrogenated to hydroxyl groups. Since one double bond could generate one hydroxyl group, the hydroxyl functionality of the polyol was usually higher than 3.0. Soy polyols obtained with hydroformylation had a hydroxyl number of about 5.0, and the hydroxyl functionality of the polyols could be adjusted from 2.5 to 5.0 by reacting part of hydroxyl groups with formic acid [50].

Photochemical oxidation to introduce hydroxyl groups has been reported (Fig. 3d) [51]. In this route, high oleic sunflower oil was photochemically oxidized in situ with singlet oxygen that was generated with a high pressure sodium-vapor lamp and tetraphenyl-

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