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Bio-Based Epoxy Resin from Epoxidized Soybean Oil

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Abstract

Epoxidized soybean oil (ESO) is the oxidation product of soybean oil with hydrogen peroxide and either acetic or formic acid obtained by converting the double bonds into epoxy groups, which is non-toxic and of higher chemical reactivity. ESO is mainly used as a green plasticizer for polyvinyl chloride, while the reactive epoxy groups imply its great potential in both the monomer synthesis and the polymer preparation fields. Functional polymers are obtained by different kinds of reactions of the ESO with co-monomers and/or initiators shown in this chapter. The emphasis is on ESO based epoxy cross-linked polymers which recently gained strong interest and allowed new developments especially from both an academic point of view and an industrial point of view. It is believed that new ring-opening reagents may facilitate the synthesis of good structural ESO based materials.

Keywords: epoxidized soybean oil, cross-linking reaction, acrylated epoxidized soybean oil, polyols, polyurethanes, bio-based polymer

1. Introduction

The utilization of renewable resources in the field of polymer synthesis has gained a great deal of attention due to the growing public concerns for the environmental concerns and the sustainable development [1, 2]. Epoxidized soybean oil (ESO) is the bio-based product from the epoxidation of soybean oil with hydrogen peroxide and either acetic or formic acid obtained by converting the double bonds into epoxy groups, which is non-toxic and of higher chemical reactivity [3]. It is mainly used as a green plasticizer for many plastics currently [4]. Meanwhile it has also attracted an increasing attention as a green epoxy resin utilizing the reactive epoxy groups into both the monomer synthesis and the polymer preparation due to its low cost, little toxicity, and large production, which imply its great potential in industrial process [5].

ESO can be converted by different kinds of reactions with co-monomers and/or initiators [6]. Permanent network that comes from the directing cross-linking of ESO and hardeners endows ESO with great stability, superior mechanical properties and satisfying chemical resistance, which make the products competitive among a variety of materials. In addition, the chemical modification of ESO has gained more and more attention in recent years. Introducing hydroxyl groups to make polyols for polyurethanes synthesis is one of the most important chemical modification methods [7]. Acrylated epoxidized soybean oil (AESO) obtained by ring opening

esterification between acrylic acid and ESO is of high reactivity for thermal and UV initiated polymerization [8, 9]. This chapter reviews the applications of ESO and its derivatives for the preparation of a series of bio-based polymeric materials.

2. Direct cross-linking

2.1 Amine hardeners

Functional amines are widely used as curing agents for generating epoxy resin. For ESO, a series of amines used as curing agents are listed in **Table 1** and the reaction scheme between ESO and amine is shown in **Figure 1**. Most of the researchers focused on the investigation of the cross-linking process of partially bio-based polymers because of the unsatisfying properties of fully bio-based ones. Three main methods can be applied to improve the properties of ESO-based thermosets, which are using commercial curing agents, adding commercial epoxy resins to ESO, and adding other materials to make composites [10–12].

The curing processes of ESO or the mixture of ESO and commercial epoxy resin have been investigated, and some of these systems have been made into composites through adding fibers [10–12, 14], clay [16, 18] and other reinforcement [19]. Viscoelastic properties, mechanical properties and many other analyses have been studied to evaluate their applicability to be used in industry. The partially bio-based polymers show great potential to replace fully petroleum-based polymers in many areas according to the testing results. Glass-transition (Tg) and viscoelastic properties of amine-cured ESO can be enhanced by increasing the amount of triethylene-tetramine (TETA) or triethylene glycol diamine (TGD). TETA endows the polymer with similar viscoelastic properties to a commercial rubber and a higher Tg than TGD does [13]. In this respect, the biopolymers made from ESO and amines have

No.	Epoxy resin	Hardener
1	ESO	Triethylene glycol diamine (TGD) [13, 14]
2	ESO	Triethylenetetramine (TETA) [10, 13, 15–18]
3	ESO	Diethylenetriamine (DETA) [10, 15]
4	ESO	Jeffamine D-230 [10]
5	ESO	Jeffamine T-403 [10]
6	ESO	Jeffamine EDR-148 [10]
7	ESO + diglycidyl ether of bisphenol A (DGEBA)	TETA [11, 12, 19]
8	ESO + DGEBA	DETA [11, 12]
9	ESO + DGEBA	Jeffamine D-230 [11]
10	ESO + DGEBA	Jeffamine T-403 [11]
11	ESO + DGEBA	Jeffamine EDR-148 [11]
12	ESO + DGEBA	Linear polyethylenimine [12]
13	ESO, ESO + DGEBA	Dicyandiamide (DICY) [20]
14	ESO [21]	Decamethylene diamine, succinic anhydride
15	ESO + DGEBA	Isophorone diamine(IPDA) [22]

Table 1.
Amines for curing ESO and ESO composites.

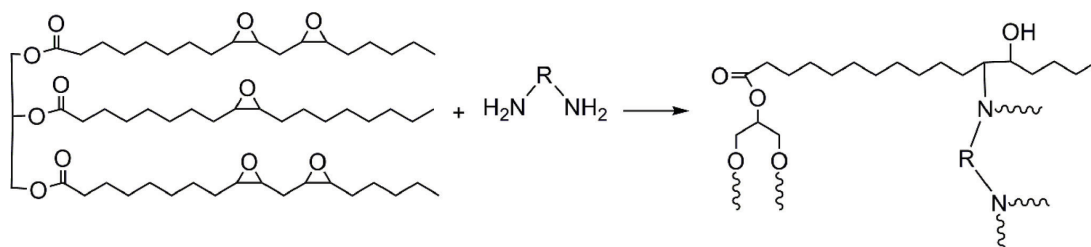


Figure 1.
 The curing process between ESO and amine curing agent [17].

great potential to replace some synthetic rubbers or plastics [13, 14]. Besides, the quasi-static and dynamic compressive properties of the cured products based on ESO and amines and the corresponding composites reinforced by clay have also been investigated to develop compressive one-dimensional stress-strain material models [15, 16]. Solid freeform fabrication method has been applied to the preparation of ESO-based composites and proved to be a suitable method for this kind of curing system [10–12]. ESO/TETA/clay composites show controllable biodegradability, low cost, good thermal and mechanical properties, and these properties indicates that the composites may work as alternative to petroleum-based polymers in the field of insulation materials and coating materials [18]. For clay-reinforced composites based on commercial epoxy resin the addition of ESO can enhance the impact strengths [22]. More interestingly, the product from ESO and TETA can be made into an ion-exchange resin through hydrolysis [17]. Usually, epoxy groups in the internal of the long aliphatic chain exhibits much poorer reactivity than those terminal epoxy groups. Due to this fact, the reported curing processes of ESO usually needs higher temperature and longer time than commercial petroleum-based epoxy resin, such as bisphenol A epoxy resin. However, the combination of the hardener, dicyandiamide (DICY), and the accelerator, carbonyldiimidazole (CDI), can make the gelation of ESO occur within 13 min at 190°C [20]. Moreover, the gelation of the mixture of ESO and DGEBA is achieved with the aid of DICY and CDI within 3 min at 160°C [20].

Fully or high bio-based polymers are also attractive to researchers owing to people's strong attention to environment concerns. A series of fully bio-based elastomers have been synthesized through the ring-opening reaction between ESO and a bio-based amine hardener, decamethylene diamine, and they can be cross-linked by further reaction with another bio-based anhydride hardener, succinic anhydride [21]. These fully bio-based elastomers have great potential to replace some petroleum-based rubbers in engineering because of their good damping property, low water absorption and weak degradability in phosphate buffer solution [21].

2.2 Anhydride and acid hardeners

Anhydrides, which are less toxic than amines, are another kind of mainly-used hardeners (**Table 2**). The structure of anhydride-cured ESO is shown in **Figure 2**.

The investigation of green anhydride curing agents is one of the research priorities. Maleopimaric acid (MPA), which comes from rosin acid, has been used for ESO curing to obtain new polymeric thermosets with a high bio-based content [24, 25]. The total heat release is only 31.7 kJ/mol epoxy group. Compared with its petroleum-based analogues, MPA endows the polymer with larger breaking elongation, higher storage modulus and better thermal stability. Sebacic acid is another bio-based curing agent for ESO in lab. A fully bio-based composite with highly improved thermal and mechanical properties can be produced through interaction between sebacic-cured ESO and PLA [26, 27]. What's more, sebacic acid-cured ESO

No.	Epoxy resin	Hardener
1	ESO	Maleopimaric acid (MPA) [24, 25]
2	ESO	Methyltetrahydrophthalic anhydride (MTHPA) [34, 35]
3	ESO + DGEBA	MTHPA [22, 36]
4	ESO [37–40], ESO + DGEBA [41, 42]	Methylhexahydrophthalic anhydride (MHHPA)
6	ESO	Maleic anhydride (MAL) [43, 44]
7	ESO	Phthalic anhydride [45]
8	ESO	Nadic methyl anhydride [46]
9	ESO	maleinized polybutadiene (MMPBD) [47]
10	ESO [30]	terpene-based acid anhydride (TPAn), maleinated linseed oil, hexahydrophthalic anhydride
11	ESO [44]	hexahydrophthalic anhydride (CH), MAL, succinic anhydride (SUC), dodecenylsuccinic anhydride (DDS)
12	ESO [26–28, 33], ESO + DGEBA [48]	Sebacic acid
13	ESO [33]	Adipic acid, 1,12-dodecanedicarboxylic acid, sebacic acid
14	ESO [32]	Citric acid, carboxylic acid functionalized MWCNTs
15	ESO [49], ESO + epoxidized linseed oil (ELO) [50]	Carboxyl-terminated polyester
16	ESO	Dicarboxyl terminated oligomeric poly(butylene succinate) [51]
17	ESO	Dicarboxyl-terminated polyimide1010 oligomers [23]
18	ESO + ELO	Phosphorylated castor oil [31]

Table 2.
Anhydride and acid for curing ESO and ESO composites.

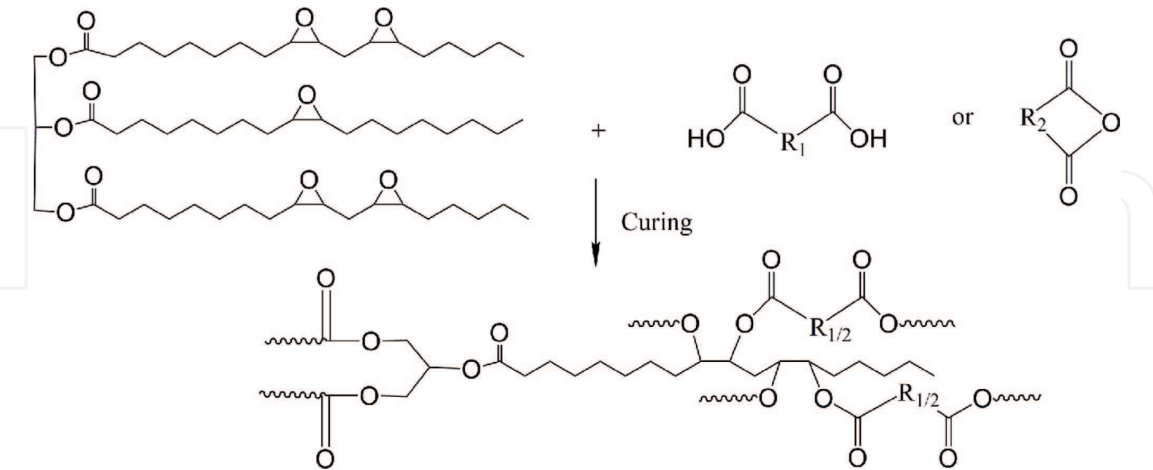


Figure 2.
The curing process between ESO and dicarboxylic acids or anhydrides [23].

can be applied in the field of superhydrophobic materials to make a sustainable and biodegradable superhydrophobic material [28, 29]. Other bio-based chemicals, such as terpene [30], vegetable oils [30, 31] and citric acid [32], are all the optional raw material for green curing agents. A terpene-based acid anhydride has been found to endow ESO with higher T_g, higher tensile strength and greater modulus than maleinated linseed oil and hexahydrophthalic anhydride do [30]. But maleinated

linseed oil makes the thermoset easier to biodegrade [30]. Biodegradable and biocompatible elastomers, which may be competitive in the field of implantable materials, can be obtained by curing ESO and Epoxidized linseed oil (ELO) with phosphorylated castor oil [31]. Carboxylic acid functionalized MWCNTs are always used as the filler for fully bio-based ESO/citric acid system [32]. The produced composites with good mechanical properties and high bio-based content may be applied in the field of industry [32]. Physical tests of fully sustainable polymers obtained from curing ESO with different dicarboxylic acids show the decreases of Tg and elongation at break, and the increases of tensile strength and Young's modulus with the increasing of chain-length of the curing agents [33]. In this respect, besides bio-based micromolecular chemicals, bio-based dicarboxyl-terminated polymers are also able to work as green curing agents for ESO to make fully bio-based polymers [23]. Polymer curing agents with long chain length can avoid the short, brittle and amorphous cross-link structures which may be the reason for the poor performance of ESO-based thermosets [23].

Like the situation occurring in amine-cured systems, anhydride-cured ESO with a high bio-based content usually cannot exhibit excellent properties as petroleum-based polymers do. In order to overcome this deficiency, ESO usually works together with some petroleum-based chemicals. For this kind of complicated reaction systems, many factors are worth investigations. We are going to discuss this kind of reaction systems in terms of the properties of epoxides, the addition of commercial curing agents, the influence of the catalysts and the incorporation of fillers.

The internal epoxy rings in ESO exhibits lower reactivity than terminal ones do and the epoxy equivalent weight of ESO is usually higher than commercial epoxy resins. The addition of ESO in the mixture of DGEBA and ESO results in the increase of peak exothermic temperature, and activation energy and the decrease of enthalpy of reaction [36, 48]. Tensile strength, modulus, fracture toughness, impact strength, storage modulus (E') in the glassy state and Tg of the cured products decrease because of the addition of ESO [36, 41]. Besides, the thermal and mechanical properties of the cured products has a positive correlation with the epoxide content of ESO [35].

Aside from the alteration of epoxides, the properties of the cured products can be enhanced with the aid of commercial curing agents. Bio-based foams based on methyl-tetrahydrophthalic anhydride (MTHPA)-cured ESO show similar mechanical properties to synthetic epoxy foams and the contents of ESO can be larger than 55 wt%, which indicates that this kind of green foams can be valuable alternative for commercial epoxy foams [34]. Polymers with anhydride groups [47] and dicarboxylic acids [49–51] are also able to work as curing agents for ESO. The carboxylic acid-terminated polyesters can work with ESO to produce green pressure-sensitive adhesives, which are environmentally friendly [50], thermal stable and with flame retardance [49]. In this kind of curing systems, the molecular weight of the polymer curing agents obviously have a great influence on the curing process and the physical properties of the cured bio-based products [51]. One of the remarkable advantages of bio-based polymers is their potential biodegradability. Lower crosslink density usually means higher biodegradability for ESO-based thermosets [40]. The cross-link density of the cured product reaches maximum at stoichiometric ratio between ESO and hardener [45].

Not only the properties of the main reactants, but the loading and type of the catalyst have a great influence on the curing process [38] final polymers [39]. The curing kinetics of ESO/methyl hexahydrophthalic anhydride (MHHPA) system show a significantly autocatalytic characteristic and ESO with 1.5 phr (parts per hundreds of resin) of 2-ethyl-4-methylimidazole (EMI) catalyst is a recommended composition for ESO/MHHPA system to be cured effectively at relative low temperature and short time [38].

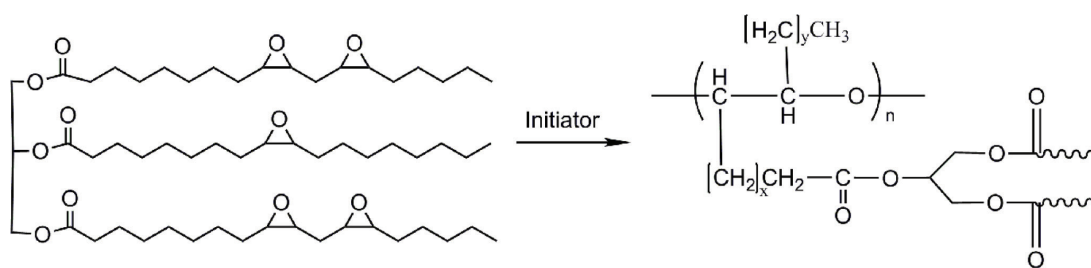


Figure 3.
Chain-growth polymerization of ESO under initiators [52].

ESO-based thermosets can also be used as good matrixes for organoclays [22, 35], organo-montmorillonite clay [37], proteins [46], regenerated cellulose [30] and other fillers. These works show that the thermal and mechanical properties of the composites can be improved significantly with the addition of different fillers.

2.3 Initiators for chain-growth polymerization

Besides adding curing agents, ESO can also be cross-linked only by initiators, as shown in **Figure 3**. Fluoroantimonic acid hexahydrate ($\text{HSbF}_6 \cdot 6\text{H}_2\text{O}$) [6] and boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$) [52–54] are commonly employed to initiate the ring-opening polymerization of ESO. As the special macromolecular structure and mechanical properties, the products have the potential to be made into hydrogels and applied in the areas of personal and health care [6, 53]. Besides, the cross-linked ESO initiated by $\text{BF}_3 \cdot \text{OEt}_2$ can be used to synthesize bio-based surfactants, which can help produce microbubbles effectively [54] and may take the place of petroleum-based detergents and surfactants [55].

3. Introducing hydroxyl groups

Besides the curing, introducing hydroxyl groups is one of the most important chemical modification of ESO. Hydroxyl groups are functional groups that can be compatible with matrixes through hydrogen bonding or can be able to covalently bond with matrixes using some active chemicals [56].

3.1 ESO-based polyols

Bio-based polyols with two or more hydroxyl groups can be synthesized from ESO by epoxy ring opening applying different approaches (see **Figure 4**). Ring opening reagents mainly include in mono-functional amines, alcohols (such as methanol, ethylene glycol, propylene glycol or butanol), acids (such as acrylic acid, acetic acid, phosphoric acid, fatty acids, carboxylic acid, hexanoic acids, or octanoic acids), thioethers or ketones [57–64]. Lewis acid is known as a kind of useful initiator for the hydroxyl reaction with epoxides. ESO-based polyether polyols are capable to be prepared by Lewis acids catalyzing ring opening with propylene glycol [60]. After that, the ESO-based polyether polyols with higher molecular weight can be cured with phenolic, melamine and other conventional crosslinkers to give reasonable film properties [65]. Besides, ESO phosphate ester polyols have been synthesized by using super phosphoric acid phosphorylated ESO, which is able to be incorporated in bake coatings with excellent performance [62]. A series of methoxylated soybean oil polyols (MSOLs) have been prepared with different hydroxyl functionalities by the ring opening of ESO with methanol [66]. These polyols have been applied to synthesize the environmentally friendly vegetable-oil-based

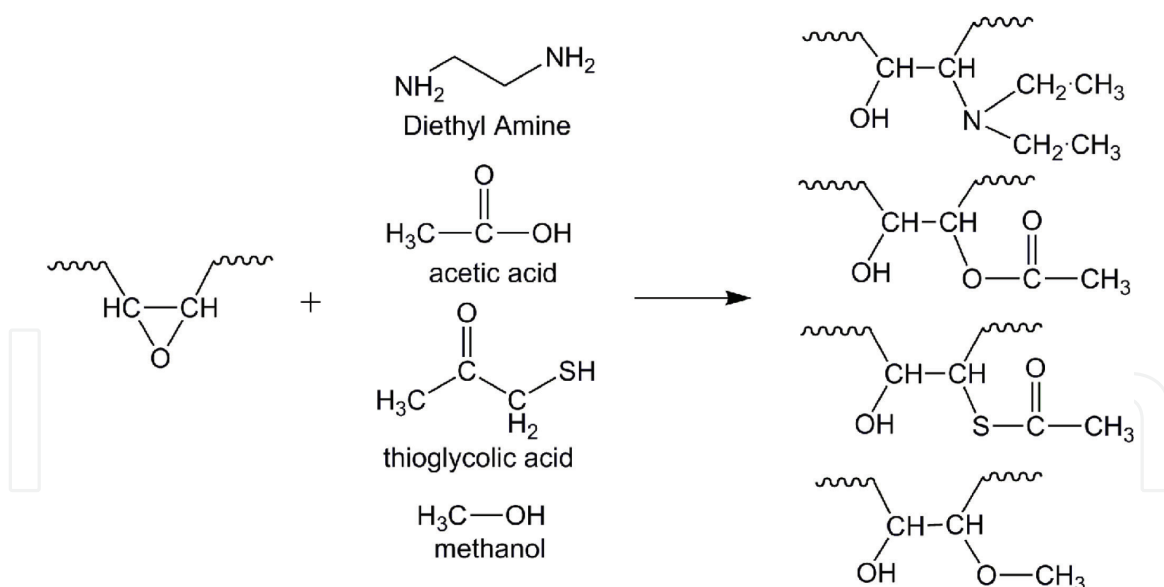


Figure 4.
 Epoxy ring opening reactions with various ring opening reagents [57].

polyurethane dispersions (PUDs) with very promising properties. Thioglycolic acid (TGA) bearing thiol and carboxylic acid as two different functional groups, glycolic acid (GA) containing hydroxyl and carboxyl functionality and methyl ester of thioglycolic acid (TGAME) have been also used as ring opening agents of ESO to synthesize novel bio-based polyols [57, 67]. Using TGA and GA, the epoxy rings are opened by the carboxylic acid group, while the epoxy rings are opened by the thiol group primarily when using TGAME. In addition, polyols obtained by ring opening with TGA have higher molecular weight comparing to GA and TGAME. That is because some of the thiol groups of TGA initially remain intact and then are involved in ring opening of other epoxy groups resulting in chain coupling [57, 67].

There are some side reactions occurring during the ring-opening of ESO epoxide groups, and these side reactions often depend on reaction parameters [68, 69]. A substantial degree of oligomerization due to oxirane-oxirane, and oxirane-hydroxyl reaction will take place in the presence of phosphoric acid. It is possible to synthesize ESO-based polyols having varying hydroxyl content and phosphate-ester functionality by controlling the type and amount of polar solvent and phosphoric acid content [70]. Inter-esterification or intermolecular ether formation are also observed as side reactions, depending on the molar proportion of the hydrogen donor [68]. Different catalysts for the ring opening of the epoxide groups in ESO have been evaluated in many works. The most common catalysts are sulfuric acid, p-toluenesulfonic acid, perchloric acid, tetrafluoroboric acid (HBF_4) and activated clays. HBF_4 have been found to produce polyols with a higher OH content, and lower viscosity than other catalysts in the ring opening reaction of ESO with methanol [69]. And, triflic acid is a very effective catalyst for preparing ESO polyether polyols [60]. As alcohol concentration relative to ESO is reduced, higher molecular weight polyether polyols can be produced in a controlled way [60].

3.2 ESO-based polyurethanes

Currently, vegetable oils-based polyols are gradually replacing petroleum-based hydroxyl for preparing PUs, which are considered as sustainable and environmentally friendly polymers from biomass industry [5]. ESO based polyols can be co-polymerized with some commercial isocyanates, such as toluene di-isocyanate (TDI), methylene-4,4'-diphenyldiisocyanate (MDI) or others, to obtain

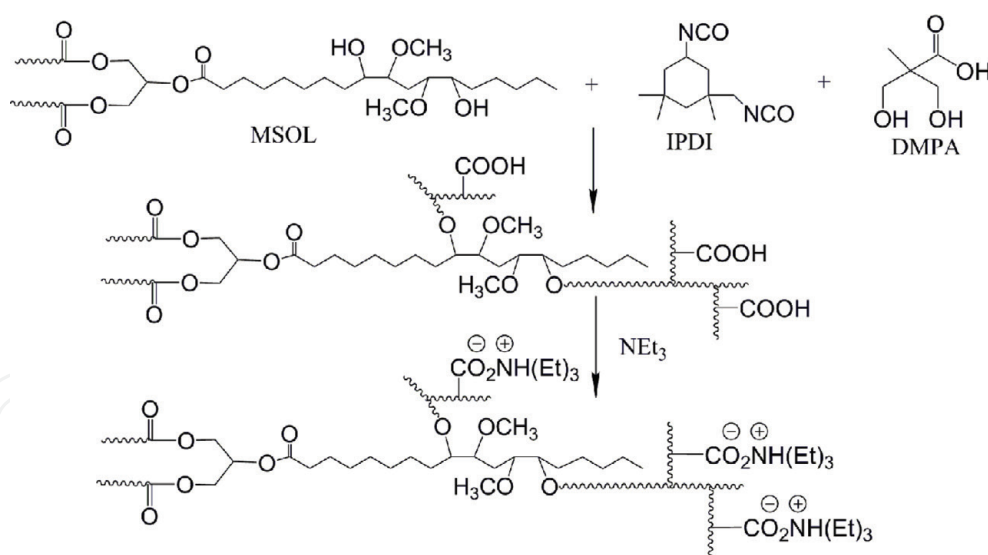


Figure 5.
Synthesis of soybean-oil-based PUs [66].

bio-based PUs with useful properties, including enhanced hydrolytic and thermal stability, as shown in **Figure 5**.

The structure-property relationships between ESO based polyols and PUs have been extensively investigated. Several factors have important influences on the properties of the PUs, such as chemical structure of the segment, chemical composition, hydroxyl group position, hydroxyl values of polyols and cross-linking densities of the PUs networks [71]. The structure and properties of PUs prepared from halogenated as well as non-halogenated soybean polyols with commercial isocyanates have been studied which shows that brominated polyols and their corresponding PUs have the highest densities and Tg while their thermal stabilities are lowest. Chlorinated polyols have comparable glass transition and strength to brominated polyols, somewhat higher than the methoxy-containing and hydrogenated polyols [69]. Besides, the NCO/OH mole ratios also show effects on the properties of the PUs networks that the cross-linking densities, Tg, and tensile strengths deteriorate as the NCO/OH ratios decrease and glassy polymers can be produced when the NCO/OH ratio is between 0.8 and 1.05 [72]. The studies on polyurethane resins from a blend of glycerol and polyol show that the increasing of Tg caused by the incorporation of glycerol into soy polyols obviously enhances the rigidity of PUs [73]. The polyurethanes elastomers synthesized from ESO based polyols obtained by ring opening with Ricinoleic acid (RA) and sebacic acid with citric acid as the cross-linker display biocompatibility and biodegradability and are very suitable for bone tissue engineering [74].

Furthermore, ESO is able to be effectively converted to carbonated soybean oil (CSBO) containing five-membered cyclic carbonates by reacting with carbon dioxide in the presence of tetra-butylammonium bromide at 110°C in high yield [75]. Then, CSBO can easily react with diamines to give the corresponding non-isocyanate polyurethane networks (NIPUs), and the thermal and mechanical properties of NIPUs can be well adjusted and controlled by changing the CSBO/amine ratio [76].

4. Acrylated epoxidized soybean oil (AESO)

4.1 Synthesis of AESO

AESO is commercially-manufactured derivative of ESO and has been extensively used in coatings, resins and composites. The acid-catalyzed synthesis process

of AESO is shown in **Figure 6**. The acid catalyst promotes the formation of an oxonium ion, which can be stabilized by local epoxide group. And the ring-opening reaction happened between acrylic acid and the oxonium ion. Inhibitor is needed in this reaction to prevent polymerization of vinyl groups. The acrylation reaction has a first-order dependence on the concentration of epoxy groups, but the rate constant increases with the decreasing of epoxides per fatty acid due to steric hindrance and the stabilization effect of local epoxide group on oxonium groups [77].

4.2 Thermal initiation of AESO

Through reversible addition-fragmentation chain transfer (RAFT) polymerization, AESO can be made into a hyper-branched bio-based polymer without macrogelation [8, 79]. The conversion of vinyl is usually over 50%, which indicates that it is possible for multifunctional renewable feed stocks to be made into bio-based thermoplastics polymers at a high conversion without gelation [8].

Most of the researches focused on the cross-linking reaction of AESO through free radical polymerization. Like the ESO, the cross-linked homopolymers from AESO also have the shortage that the polymers exhibit poor mechanical properties [80]. One of the common methods used to enhance its mechanical properties is adding reinforcements to make polymer composites. There are many polar groups in the structure of AESO, including C=O, —OH and epoxy groups. These polar groups provide the possibility for the formation of hydrogen bonds between AESO and fillers [80]. Thermoplastic polyurethane [81], microcrystalline cellulose (MCC) [80] and cellulose fiber [82] are the common reinforcements worth investigation for poly(acrylated epoxidized soybean oil) (PAESO). The interaction between PAESO and polyurethane can be enhanced by the formation of hydrogen bonds between hydrophilic functional groups from both of the two components which give rise to the result of improving the toughness and increasing the elongation of PAESO [81]. As a green filler, microcrystalline cellulose will increase the density, hardness, flexural strength and modulus of the material without decreasing the bio-based content [80]. Cellulose-reinforced PAESO can also be successfully made into bio-based foams with enhanced mechanical properties, which shows the great potential to replace petroleum-based foams [82].

Another common way to adjust the properties of AESO-based materials is the incorporation of co-monomers. Styrene [83–86], N-vinyl-2-pyrrolidone (NVP) [64, 87], 3-isopropenyldimethylbenzyl isocyanate (TMI) [88], isocyanatoethyl methacrylate (IEM) [88], 1,6-hexanediol diacrylate [89], divinylbenzene [86, 89] and unsaturated polyester [90–94] are widely used as co-monomers for AESO. The diblock copolymers based on AESO and styrene are able to work as an additive for asphalt to modify the rheological performance so that the corresponding stiffness, elasticity and rutting resistance of the asphalt can be substantially improved [83]. The copolymer based on AESO and styrene can also be reinforced by natural fibers

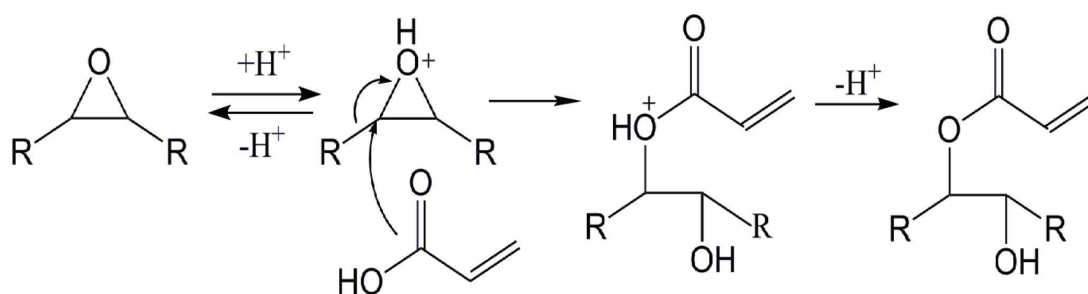


Figure 6.
 Mechanism of AESO synthesis [78].

[84] and denim [85] to obtain bio-based composites for structural applications, such as roof structure and safety helmets. Due to the toxicity of styrene, styrene-free polymers become more attractive recently. NVP is an alternative to styrene in the synthesis of copolymer based on AESO, and the corresponding hemp fibers (HFs) composites exhibit superior static and dynamic mechanical properties [64]. As both AESO and HFs contains —OH groups in their structures, the addition of isophorone diisocyanate, whose isocyanate groups can react with —OH groups, to the AESO/HFs/NVP system can improve the properties by working as both a cross-linker and a coupling agent [87]. Accordingly, TMI and IEM bringing both $\text{C}=\text{C}$ double bonds and isocyanate groups into the reaction systems may also be good co-monomers for AESO/HFs system. Besides the free radical polymerization of vinyl groups, the reactions between isocyanate groups and the —OH groups of AESO and HFs also occurred at the same time in this bio-based polymer composite systems [88]. Consequently, the crosslinking density and interfacial reaction between reinforcement and the matrix can be improved significantly, leading to the enhancement of storage modulus, T_g and water resistance. As a nonvolatile and nonhazardous chemical, AESO is a suitable replacement for styrene in unsaturated polyester (UPE) resin to obtain hybrid polymer networks [90–94]. The UPE with unsaturated sites works as the co-monomer for AESO, and the final products usually exhibit comparable properties to correspondingly styrene-based products. The combination of a variety of co-monomers may provide AESO based copolymers with more possibilities. The thermosets based on the combination of AESO, styrene and divinylbenzene can be the potential replacements for commercial electronic materials [86]. The combination of AESO, 1,6-hexanediol diacrylate and divinylbenzene is able to make into the matrix for bacterial cellulose nanocomposite foams and the properties of the composites can be tailored by adjusting the compositions [89].

Although petroleum-based co-monomers can bring excellent properties, the decrease of the bio-based content is still not expected. Functional bio-based co-monomers are desired in consequence. Isosorbide can be used to synthesize a bio-based co-monomer for AESO through the reaction with methacrylate anhydride [95]. The product, isosorbide-methacrylate (IM), which has stiff structure, endows the bio-based networks with ideal thermal and mechanical properties. Similarly, rosin is also a bio-based raw material with a rigid molecular structure. Its derivative, N-dehydroabietic acrylamide (DHA-AM), can enhance the storage modulus, T_g , thermal stability, tensile strength and hydrophobicity of AESO/DHA-AM thermosets [96]. Methacrylated lauric acid (MLAU) is another bio-based reactive diluent for AESO. The mixture exhibits a suitable viscosity for liquid molding techniques to get AESO based thermoset specimens with low densities and T_g around room temperature [97].

4.3 UV curing of AESO

AESO has been widely applied in the UV curing systems for their lower volatility and relatively higher reactivity of $\text{C}=\text{C}$ bonds which are able to conduct free-radical polymerization in the presence of functional initiator. In general, residual internal stress in the UV-curing coating film often leads to poor adhesion with substrate. AESO can be used to synthesize cured films with reduced internal stress and its flexible triglyceride structure can improve adhesion [9]. UV-curable materials based on AESO have been found many applications like coatings, adhesives and composite materials [98]. As petroleum-based fiber composites often swell after water absorption resulting in deterioration of mechanical properties, the dried distillers grains (DDGS)-flax mat coated with AESO polymerized by UV light with the initiation of irgacure 819 shows improved water resistance property [99].

Besides, AESO-based UV-cured PUDs with higher functionality can be used in textiles printing. Different content of AESO based UV-curable PUDs pigment prints adhesive have been successfully synthesized with isophorone diisocyanate (IPDI), poly(caprolactone glycol) and 2-hydroxyethyl methacrylate, and all UV-curing films have excellent thermal stability [98]. With the increasing of AESO content, the color strength of printed fabrics can be enhanced correspondingly. Conversely, the increasing of UV radiation time shows positive impact on the color fastness [100]. UV-curable, AESO-based organic shape-stabilized phase change materials also can be obtained by UV technique with enhanced thermal performance, decreased melting and freezing temperature, which verify the promising application of UV-curable material for thermal energy storage [100].

However, the existing of soft long aliphatic chains usually results in low mechanical or thermal properties and some rigid compounds are often added as the co-monomers to improve the performances of AESO-based UV-curable materials. Acrylate acid is one of the most common-used petroleum-based rigid compounds. The performances of AESO-based UV curable coating materials by using petroleum-based hyper-branched acrylates (HBAs) as co-photo-polymerization monomer, using acrylated sucrose (AS) as tougheners and using tetra-hydrofurfural acrylate (THFA) as reactive diluents show the increased coating hardness, adhesion, modulus, solvent resistance and glass transition temperature [101]. Nowadays, many researchers are devoted to exploit bio-based co-monomers to develop high bio-based content UV-curable coatings. Monomer acrylated betulin (AB) synthesized from betulin [102], unsaturated monomer (named IG) synthesized from itaconic acid and glycidyl methacrylate [103], monomers (named EM2G and EM3G) synthesized from eugenol via a thiol-ene reaction and epoxide ring-opening reaction [104] have been all evaluated to be successfully used with AESO matrix polymer and have great potential to improve the properties of UV curable coating. Coating films containing AB from 5 to 10 wt% contents have better modulus of elasticity, tensile strength, abrasion resistance and hardness, higher T_g and lower strain at break value, while the transmittance of the cured films is reduced with increasing AB loading, especially for wavelengths below 650 nm. In comparison, the polycyclic structure of betulin imposes a more rigid structure on AESO matrix polymer to enhance the applied performance [102]. In the presence of irgacure 184 as initiator, a series of UV-cured coatings without any solvent can be successfully prepared with IG (EM2G or EM3G) and AESO, and EM2G and EM3G show higher reactivity when copolymerized with AESO. The introduction of IG, EM2G and EM3G in the UV-curing system results in significantly improved mechanical and thermal properties as well as coating performances such as hardness, flexibility, adhesion, solvent resistance [103, 104].

5. ESO-based polymer composites

ESO is initially used as a plasticizer in industry for poly(vinyl chloride) chlorinated (PVC) rubber, and poly(vinyl alcohol) (PVA) emulsions to improve stability and flexibility [105, 106], and ESO is also considered to be potential nontoxic biocompatible plasticizers for poly(3-hydroxybutyrate) (PHB) and polylactic acid (PLA) when combined with other plasticizers [107–109]. Moreover, it is an interesting trend to prepare composites of ESO or its homo-polymers with other materials because of their special properties. A double network composites with ESO and a di-hydrocoumarin derived network can be synthesized with toughening effect, which make the ESO-based polymer possible to be applied in the fields of coatings and films [110]. The composites of cross-linked ESO and acrylic monolith [111] or

poly(lactic acid) [112] apparently exhibit much larger Young's modulus and tensile strength than ESO homo-polymer and can work as shape memory materials, which makes ESO a potential component for manufacture of intelligent polymer materials.

Interestingly, the long chain alkane fatty acid residues in ESO can give the composites hydrophobicity, so cross-linked ESO can also work as a water-resistant film for paper that the obtained composites may be competitive in the field of packaging considering their good properties [113]. An efficient method has been reported for the formation of cellulose-based materials grafting with poly epoxidized soybean oil (PESO) with controllable hydrophobic properties [114] 1–2. A kind of PESO coated paper composites with good water-resistant property have been obtained via in situ polymerization of ESO on the surface of the paper cellulose fibers [113].

6. Conclusions

This chapter summarizes the most recent advances in the application of ESO and its derivatives for preparation of bio-based polymeric materials. The multiple reactive epoxy groups from triglycerides of unsaturated fatty acids imply its great potential in the bio-based polymer preparation fields with controllable biodegradability, thermal and mechanical properties. ESO can crosslink directly with variety curing agents to form permanent network, or to introducing reactive function groups by chemical modifications. Two most important modifications are introducing hydroxyl groups and esterification to produce acrylates. Based on these, varieties of new polymeric materials have been prepared recently from ESO and derivatives that exhibit industrially viable thermos-physical and mechanical properties and thus may find many possible applications. It is believed that ESO based compounds will gain continuously strong interest and allow new developments both in academic and industrial points of view.

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Conflict of interest

The authors have declared that no conflict of interest exists.

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