Synthesis and properties of a novel bio-based polymer from modified soybean oil

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Abstract. Maleated acrylated epoxidized soybean oil (MAESO) was prepared by acrylated epoxidized soybean oil (AESO) and maleic anhydride. AESO were obtained by the reaction of epoxidized soybean oil (ESO) with acrylic acid as the ring-opening reagent. The polymer was prepared by MAESO react with styrene. The structures of the products were studied by Fourier transformation infrared spectrometer (FT-IR), and were consistent with the theoretical structures. Swelling experiment indicated that the crosslinking degree increased with increasing epoxy value of ESO. Thermal properties was tested by thermo-gravimetric analysis (TG) and differential scanning calorimetry analysis (DSC), indicating that glass transition temperature (Tg) of the polymer increased with increasing epoxy value of ESO, and thermal stability of polymer have a good correlation with the crosslinking degree. Mechanical properties analysis presented that tensile strength and impact strength affected by epoxy value of ESO. With the increase of epoxy value, the tensile strength increase, while the impact strength decrease. The property of the polymer ranged from elastomer to plastic character depended on the functionality of the ESO.

1. Introduction
Problems of environmental pollution caused by polymer materials have recently attracted increasing attention. Research into environmentally friendly raw materials substitute for preparing polymeric materials has become crying needs in the development of materials science. Many raw materials available in nature can be used to prepare polymer. Such as bio-based polymers were gaining interest, they were applied to many life and industry fields. Triglycerides from plant oil can be utilized [1-4]. Polymer materials obtained from the plant are becoming extensively and important used to take place of petroleum based polymer, because of their environmental advantages and economic. These have been widely used in various engineering and commodity applications [5-7].
Plant oil is one of the most interesting environmental resources for the synthesis of monomers or polymers, because of the aliphatic chain and functional groups contribute as a primary element to the backbone of polymer [8]. Plant oil has received much attention as a renewable resource for preparing chemicals and polymers [9]. Soybean oil is one of the plant oil and widely used for bio-based polymers production. Double bonds in soybean oil molecule are difficult to take radical-initiated polymerization reaction to form the polymer. Thus the soybean oil must be functionalized; the usual method is to transform the soybean oil into epoxidized soybean oil [10]. In order to be use as a monomer for more polymerization, epoxidized soybean oil has to be further functionalized [11]. Many chemical methods have been applied to modify soybean oil, such as hydroxylolation reaction [12],...
acrylated reaction [13], epoxidation reaction [14], maleic anhydride esterification reaction [15], and so on.

The properties of polymer were controlled by the crosslinking density, functional group and flexibility of the macromolecule chain. Hydroxyl groups, ester groups and double bonds in the plant oil molecule make it available for modifications and reactions [16]. For AESO, hydroxyl groups on the triglyceride chain make it enable to be further modified, such as take mono-esterification reaction with maleic anhydride to form the maleated acrylated epoxidized soybean oil (MAESO). Afterwards, MAESO was free-radically copolymerized with vinyl monomers or polyfunctional monomers to form the polymers. The introduction of maleic anhydride increasing the degree of crosslinking of the final materials and introducing functional groups into the network of the polymers, providing more favorable performance for the materials.

For many publications, AESO was usually used in paints or inks. As its functionality not high enough, AESO was limited in the use of thermosetting resin to some extent. Nevertheless, AESO was modified by maleic anhydride greatly improved the degree of unsaturation of the functional monomer. Meanwhile, the carboxyl groups were introduced in the final products. Many attentions have been focused on the research of polyols based on soybean oil, and seldom studied the soybean oil based epoxy acrylate or maleate. Most of the reported materials based on soybean oil were made by ESO with high epoxy value. Few discussions about the relationship between epoxy value of ESO and properties of the polymer.

In this work, ESO with different epoxy values has been synthetized. AESO with different saturation was obtained by the reaction of ESO and acrylic acid. Then the synthetic AESO took mono-esterification reaction with maleic anhydride to form the MAESO. Finally, MAESO took free-radically copolymerized with vinyl monomers to produce the polymer.

2. Experimental

2.1. Materials

Soybean oil was obtained from Nanhai Oil Co. Ltd (Guangzhou, China). Glacial acetic acid, acrylic acid, sulfuric acid, hydrogen peroxide (30%), hydroquinone, ethyl ether, sodium carbonate, sodium bicarbonate, sodium chloride, maleic anhydride, methylbenzene, styrene, benzoyl peroxide (BPO), all the reagents were AR grade and purchased from Damao Chemical Reagent Co. (Tianjin, China). Triphenyl phosphine was GR grade and purchased from Aladdin Chemistry Co. Ltd (Shanghai, China).

2.2. Methods

Epox value was determined by the ASTM D1652 testing standard. Hydroxyl value was determined by the ASTM D1957 testing standard. Degrees of crosslinking of the polymer was determined by swelling equilibrium method. FTIR spectra of the samples were recorded using a Prestige-21 spectrometer (Shimadzu, Japan). DSC analysis was recorded on a 200PC instrument (Netzsch, Germany). Sample (8-10 mg) was used each measurement with nitrogen was use as purge gas. The sample was heated from -50 to 200℃ at a heating rate of 20℃/min. Thermo-gravimetric analysis was recorded on a STA 409PC instrument (Netzsch, Germany). The sample was heated from 30 to 800℃ at a heating rate of 10℃/min with air as the purge gas. Tensile strength of the sample was determined on a WSM-100 tensile testing machine (Changchun, China). The rate of extension was 10 mm/min. Impact strength of the sample was determined on a JJ-20 impact testing machine (Changchun, China).

2.3. Preparation of modified soybean oil

ESO with different epoxy value have been prepared from the epoxidation reaction of SBO. Peroxyacetic acid was used as oxidizing agent and sulphuric acid was used as catalyst. The reaction
took place at 65°C and different reaction time. The extent of epoxidation was 0.25 mol/100g, 0.33 mol/100g, 0.35 mol/100g, 0.38 mol/100g, respectively.

AESO was obtained from the reaction of ESO and acrylic acid. The molar ratio of epoxy group to carboxyl was 1 to 1.2. Triphenyl phosphine was used as catalyst at concentration of 1.5% in weight. Hydroquinone was used as inhibitor at concentrations 0.1% in weight. The reaction took place in a round bottomed flask and kept in 110 °C for 8 hours. After finishing reaction, the mixture was cooled to room temperature. And then it was dissolved in ethyl ether. Saturated NaHCO 3 sodium and NaCl sodium were used to wash the mixture. After removing the water and solvent, the samples were obtained. The hydroxyl values of the AESO were 119 mgKOH/g, 151 mgKOH/g, 164 mgKOH/g, 178 mgKOH/g, respectively. The samples were used for preparing MAESO.

MAESO was obtained by reaction of AESO and maleic anhydride. The molar ratio of maleic anhydride to hydroxy group is 2:1, ensuring that the hydroxy group completely reacted. AESO and methylbenzene were placed into a 500 mL round bottom flask and kept in 110 °C for 1 hour to ensure that there was no water in the mixture. Then the maleic anhydride was added into the mixture. The reaction kept in 110°C for 5 hours. After the reaction, the mixture was cooled down. Deionized water was used to wash the mixture. After removing the water and solvent, the samples were obtained.

2.4. Synthesis of polymer

The polymer was prepared by mixing the MAESO with styrene. BPO was used as initiator at a concentration of 3% in weight. The mass fractions of styrene and MAESO were 40% and 60%, respectively. BPO was stirred to dissolve in styrene, and blended with MAESO. The mixture was put into vacuum oven to eliminate air bubbles, and poured into a mold. Then it was heated to 60 °C for 1 hour, and 100°C for 3 hours. The degrees of crosslinking of the polymers were characterized by the swelling experiments.

3. Results and discussion

3.1. Characterization of MAESO

Synthesis routes of MAESO and polymer were provided in Figure 1. A series of ESO and AESO were synthesized and shown in Table1, indicating that the hydroxyl value increases with the epoxy value. The degrees of crosslinking of the polymers were characterized by the swelling experiments; the results indicating that gel fraction of the polymers increase with the epoxy value. The polymer with an epoxy value of 0.25 mol/100g had low gel fraction, due to the low average functionality of the MAESO, presenting the elastomer character. While the polymer with higher gel fraction displayed rigid plastic properties.

| Table 1. properties of polymer derived from MAESO |
|--------------------------------------------------|
| Sample                                         |
| Epoxy value of ESO/(mol/100g)                   |
| 0.25                                           |
| 0.33                                           |
| 0.35                                           |
| 0.38                                           |
| Hydroxyl value of AESO /(mgKOH/g)               |
| 119                                            |
| 151                                            |
| 164                                            |
| 178                                            |
| Gel fraction of polymer/%                       |
| 75.2                                           |
| 89.9                                           |
| 93.4                                           |
| 97.0                                           |
| Character of the polymer                        |
| elastomer                                      |
| plastic                                        |
| plastic                                        |
| Glass transition temperature /°C                |
| 10.5                                           |
| 47.2                                           |
| 52.9                                           |
| 54.6                                           |
3.2. FTIR spectra analysis

FTIR spectra were showed in Figure 2. FTIR spectrum of SBO showed a peak at 3010 cm\(^{-1}\) due to the carbon-hydrogen stretching vibration in the carbon-carbon double bond. In the ESO spectrum, there was no peak in the same wave number, and the peak at 823 cm\(^{-1}\) due to the epoxy group, illustrating that the epoxidation reaction has took place. In the spectrum of AESO, the peak at 1653 cm\(^{-1}\) due to stretching vibrations of carbon-carbon double bond. The stretching vibrations of hydroxyl appeared at 3467 cm\(^{-1}\). The peak of epoxy group at 823 cm\(^{-1}\) not appeared, indicating that the reaction of ESO with acrylic acid has taken place extensively. The peak at 1743 cm\(^{-1}\) showed the stretching vibration carbonyl. In the spectrum of MAESO, The peak of hydroxy group at 3467 cm\(^{-1}\) widened, and presents dispersion characteristics, indicating that the AESO has taken mono-esterification reaction with maleic anhydride, and generated carboxyl group. In the spectrum of the polymer, the peaks at 3064 and 3034 cm\(^{-1}\) due to the carbon-hydrogen stretching vibrations of the benzene ring. The peaks at 1584, 1494, 1453 and 1402 cm\(^{-1}\) are attributed to the bending vibrations of carbon-carbon double bond of benzene ring. The stretching vibration peak of the carbon-carbon doubles at 1653 cm\(^{-1}\) almost disappeared, indicating that the reaction of MAESO and the styrene has occurred.
3.3. Thermal properties analysis

Properties of polymer affected by the crosslinking degree, which correlated with the degree of functionality of the monomer molecules, such as the hydroxyl group and the epoxy group. DSC thermograms were given in Figure 3. Glass transition temperatures of the polymers (T<sub>g</sub>) were showed in Table 1. The result indicating that T<sub>g</sub> of the polymers increased with the increasing hydroxyl value and epoxy value. Due to the crosslinking degree of the polymer increased with the degree of functionality, as the number of active carbon-carbon double bond increased. Also, carbon-carbon double bond in the triglyceride chain effect flexibility of the macromolecule chain. Glass transition temperature of the polymer with an epoxy value of 0.25 mol/100g was 10.5°C, which low and under the room temperature, because of low crosslinking degree and gel fraction. The polymer was conjectured an imperfect networks. While the epoxy value of the ESO was 0.38 mol/100g, the resulting material was glassy; the glass transition temperature was 54.6°C. This result was proved by the mechanical properties as provided in Table 2.

TG and DTG thermograms were provided in Figure 4. The 5% mass loss temperatures of all the polymers ranged from 183.1°C to 231.9°C. All the polymers have been found to start degradation below 250°C, due to the thermolabile groups of carboxyl and allyl ester. Thermal stability material showed a correlation with the epoxy value. The decomposition temperature decreases with epoxy value at lower epoxy value, and increases at higher epoxy value. Due to the crosslinking degree and stability of functional group. While at low epoxy values, the resulting materials were mainly affected by the increasing of carboxyl group. Whereas the active carbon-carbon double bond introduced from maleic anhydride and acrylic acid increases obviously at higher epoxy value, thus the crosslinking degree of the polymer was extremely high and controlling the thermal stability. The variation of the decomposition temperatures was obviously at low temperature, and verging to unconspicuous with the increases of the temperature, because of most of decompositions synchronized at high temperature.

**Figure 2.** Infrared spectra of expoxidized soybean oil and its products

**Figure 3.** DSC curves of polymer derived from MAESO
3.4. Mechanical properties analysis

Mechanical properties of the polymers presented in Figure 5 and Table 2. The result indicated that tensile strength increases with the increasing epoxy value and the crosslinking degree of the polymers, yet the elongation at break decreases. The active carbon-carbon double bond introduced from maleic anhydride and acrylic acid increases with the increasing epoxy value, thus the crosslinking degree increase and the flexibility of the polymer chain decrease. It was confirmed by the DSC analysis. The polymer obtained from the ESO with an epoxy value of 0.25 mol/100g has very low tensile strength of 3.17 MPa, which was characteristic of elastomer, because of the low crosslinking degree and imperfect networks of the polymer. The fact was related to the low glass transition temperature of the polymer, under the testing temperature of 25°C. While epoxy value of ESO was 0.33 mol/100g, the final material presents a moderate tensile strength of 23.62 MPa, and the tensile strength was higher (31.65 MPa) for the polymer from the ESO with an epoxy value of 0.38 mol/100g, revealing rigid plastic properties to the materials. The result was supported by the elongation at break. The elongation at break was shown in Table 2, which decreases with the increasing epoxy value of the ESO.

Table 2. Mechanical properties of polymer derived from MAESO

| Sample | Epoxy value/ (mol/100g) | Tensile strength/ MPa | Elongation at break/ % | Impact strength/ KJ/m² |
|--------|-------------------------|-----------------------|------------------------|------------------------|
| a      | 0.25                    | 3.17±0.21             | 27.86±3.22             | 39.32±1.46             |
| b      | 0.33                    | 23.62±2.49            | 19.04±2.54             | 21.19±2.93             |
| c      | 0.35                    | 26.47±1.11            | 10.84±1.67             | 16.75±3.01             |
| d      | 0.38                    | 31.65±2.30            | 5.74±0.89              | 12.16±1.39             |

Impact strength of the polymers was given in Figure 5 and Table 2. The result showed that impact strength decreases with the increasing epoxy value, due to decreasing of flexibility of the polymer chains. The variation trend of the impact strength was similar to trend of the elongation at break, whereas countering to the tensile strength. The flexibility of the polymer chain was low at high epoxy value of the ESO, whereas the crosslinking degree of the network was high. In this case, the effect of the flexibility of the polymer chain was not obvious, because of the strong cross-linked network mainly controlled the strengths, thus the material also have a certain degree of impact strength. Soybean oil molecular chain also makes a contribution to the flexibility of the final material.

4. Summary

A series of bio-based polymers were 1. Relationship of the structure and property on the polymer has been studied. Mechanical and thermal properties depended on the functionality of ESO.
distribution of the epoxy values of ESO was reflected in different crosslinking degree of polymer. Crosslinking degree of the polymer increased with the increasing epoxy value. The polymer with an epoxy value of 0.25 mol/100g had low gel fraction, due to the low average functionality of the MAESO, presenting the elastomer character. While the others with higher gel fraction displayed rigid plastic property. T_g of the polymers increased with the increasing hydroxyl value and epoxy value. Thermal stability displayed a well correlation with the epoxy value. Glassy polymer displayed excellent mechanical strength reached up to 31.65 MPa and glass transition temperature of 54.6°C. The bio-based polymer showed a range of attractive properties and a wide range of uses. Also, these polymers were prepared from renewable environmentally friendly resource.

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