Synthesis and characterization of a novel bio-based resin from maleated soybean oil polyols

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Abstract. In this paper, a novel bio-based resin was prepared by the radical copolymerization of maleated soybean oil polyols (MSBOP) and styrene (ST). Structure of the product was studied by Fourier transformation infrared spectrometer (FT-IR), and the result was found to be consistent with that of theoretical structure. Swelling experiments indicated that the crosslinking degree increased with the increase of hydroxyl value. Thermal analysis by differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TG) revealed that glass transition temperature (T_g) of the polymer increased with increasing hydroxyl values, and that its thermal stability showed a good correlation with the hydroxyl value. The tensile strength and impact strength were significantly affected by the hydroxyl value of soybean oil polyols. With increasing hydroxyl value, the tensile strength presented an increasing trend, while the impact strength showed a decreasing one. Moreover, the property of the polymer from elastomer to plastic character also depended on the functionality of the hydroxyl value of soybean oil polyols.

1. Introduction

In recent years, environmentally friendly substitutes of raw materials for preparing polymers have become crying needs with the development of materials science. Many scientific investigations were focused on polymer materials based on renewable resources. The main achievement is devoted to the preparation of polyols from plant oil due to its widely available, economical and eco-friendly characteristics [1]. Currently, polymer materials derived from renewable plant resources are becoming more and more important as the replacement of petroleum based polymers owing to various advantages, and have been widely used in many engineering and commodity applications [2-4]. Plant oil is one of the most interesting environmental resources for the synthesis of monomers or polymers, because its aliphatic chains and functional groups contribute a lot to the backbone of polymer as the primary element [5]. Consequently, plant oil has attracted much attention as a renewable resource for preparing chemicals and polymers [6].

Soybean oil (SBO) is an unsaturated triglyceride, which mainly consists of linolenic acid, linoleic acid, oleic acid, palmitic acid, and stearic acid. Double bonds in SBO molecules must be functionalized to form polymers, since it is difficult for them to participate in radical-initiated polymerization reaction [7, 8]. Many groups such as amines, hydroxyls, epoxies, thiols and halides have been introduced to plant oil triglycerides. Specially, by introducing reactive groups to soybean oil

[9], epoxidized soybean oil (ESO) and acrylated epoxidized soybean oil (AESO) can be prepared, and they have been widely used as monomers based on plant oil.

In previous work, we have successfully functionalized SBO, corn oil (CO) and other plant oils to introduce polymerizable functional groups, such as conjugation [10], epoxidation [11], hydroxylation [12], acrylation [13], and esterification [14]. Hydroxyl groups, ester groups and double bonds in these plant oil molecules make it available for performance modification and polymerization reaction [15]. The functional plant oils can be used to prepare poly urethane (PU), epoxy acrylate, alkyd resin and epoxy resin, and the applications of the product involve casting plastic, foamed plastic, coating, adhesive, paint and many other fields. It is noticed that SBOP is mainly used to prepare PU, whereas few studies use SBOP to prepare polymer materials through reaction with maleic anhydride. Moreover, SBOP with different hydroxyl values has seldom been used to prepare polymers and study the relationship between hydroxyl value and material properties.

In this work, a new monomer based on radically polymerizable triglyceride was synthesized by the reaction of SBOP and maleic anhydride (MA). Firstly, SBOP with different hydroxyl values has been synthetized. Then the prepared polyols were used to prepare MSBOP through the mono-esterification reaction with MA. Finally, MSBOP was polymerized with vinyl monomers to form the polymer. On this basis, the structure of the network, and the relationship between hydroxyl value and the properties of final materials were studied by several suitable test methods.

2. Experimental

2.1. Materials
Soybean oil was obtained from Nanhai Oil Co. Ltd., Guangzhou, China. Glacial acetic acid (99.5%), sulfuric acid (98%), sodium carbonate, hydrogen peroxide (30%), aqueous ammonia (30% in water), fluoroboric acid (48% in water), maleic anhydride, methanol, methylbenzene, styrene, and benzoyl peroxide (BPO) were purchased from Damao Chemical Reagent Co., Tianjin, China. All the reagents were analytically pure (AR).

2.2. Methods
Epoxy value was determined by the ASTM D1652 testing standard. Hydroxyl value was determined by the ASTM D1957 testing standard. Degree of crosslinking of the polymer was determined by the swelling equilibrium method.

FTIR spectra of the samples were recorded using a Prestige-21 spectrometer (Shimadzu, Japan). DSC curves were recorded on a 200PC instrument (Netzsch, Germany). In each measurement, 8-10 mg of sample was used, and the sample was heated from -50 to 200℃ at a heating rate of 20℃/min with nitrogen as the purge gas. Thermo-gravimetric analysis was carried out on an STA 409PC instrument (Netzsch, Germany). The sample was heated from 30 to 600℃ at a heating rate of 10℃/min, with air as the purge gas. Tensile strength was determined on a WSM-100 tensile testing machine (Changchun, China) with an extension rate of 10 mm/min. Impact strength was determined on a JJ-20 impact testing machine (Changchun, China).

2.3. Preparation of ESO and SBOP
ESO with varying epoxy values was prepared through the reaction of SBO and peroxyacetic acid at 65℃ for different reaction times. Peroxyacetic acid was prepared in situ by the reaction of various mixtures of glacial acetic acid and H_2O_2, with sulphuric acid as the catalyst. The extents of epoxidation were 0.197 mol/100g, 0.220 mol/100g, 0.264 mol/100g, 0.331 mol/100g and 0.375 mol/100g, respectively.

SBOP with different hydroxyl values was synthesized from the reaction of methanol with ESO. The molar ratio of epoxy group to hydroxyl group is 1:11. Fluoroboric acid was used as the catalyst at a concentration of 0.2% in weight. The reaction mixtures were kept in water bath at 70℃ for 3 h. After complete reaction, the mixture was cooled to room temperature, and then washed by ammonia sodium. Finally, after removing the water and solvent, the samples were obtained. The hydroxyl values of the polyols were 86 mgKOH/g, 117 mgKOH/g, 126 mgKOH/g, 141 mgKOH/g and 156 mgKOH/g, respectively.

2.4. Preparation of MSBOP

MSBOP with different saturation degrees was obtained by the reaction of MA with the prepared SBOP. The molar ratio of hydroxy group to maleic anhydride is 1: 2, in order to ensure the complete reaction of hydroxy groups. SBOP and methylbenzene were placed into a 500 mL round bottom flask and kept at 110℃ for 1 h to ensure that there was no water in the mixture. After the reaction, the mixture was cooled down, and then washed by deionized water. After removing the water and solvent, the samples were obtained. The reaction extent was over 90% and the yield of the prepared MSBOP was over 95%.
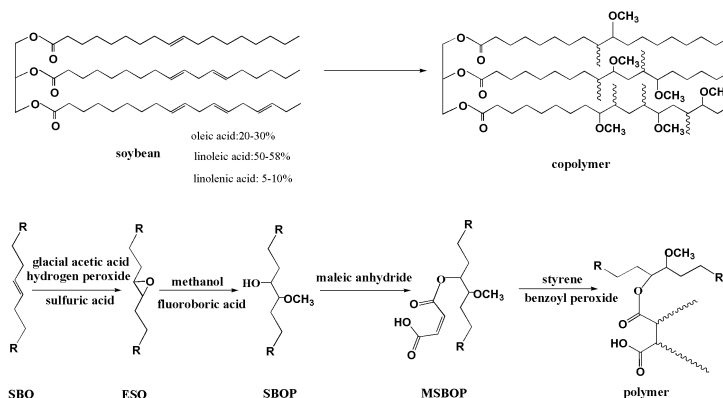
2.5. Synthesis of the cast resin

The polymer was prepared by mixing the prepared MSBOP with styrene (ST), with BPO at a concentration of 3% in weight as the initiator. The mass fractions of ST and MSBOP were 40% and 60% in weight, respectively. BPO was dissolved in ST by moderate stirring, and then blended with MSBOP. The mixture was put into vacuum oven to eliminate air bubbles, and then poured into a mould. Afterwards, the mixture in the mould was heated to 60 ℃ for one-hour heat preservation, and then to 100℃ for another three-hour heat preservation to complete the polymerization reaction.

3. Results and discussion

3.1. Characterization of MSBOP

Scheme 1 presents the reactions for preparing MSBOP and polymer, through which a series of ESO with different epoxy values and SBOP with different hydroxyl values can be synthesized. Table 1 indicates that the hydroxyl value increases with the epoxy value. The crosslinking degree of the polymer was characterized by the swelling experiments. It is found that the gel fraction increases with the hydroxyl value obviously. The polymer mainly consists of linear polymer or low polymer at low hydroxyl values, while cross-linked polymer is dominated at high hydroxyl values. The polymer with low gel fraction behaves as an elastomer, whereas that with higher gel fraction displays rigid plastic properties.

Scheme 1. Synthesis routes of MSBOP and polymer

Table 1. Gel fraction of polymer derived from MSBOP

Sample	a	b	c	d	e
Epoxy value of the epoxidized soybean oil/(mol/100g)	0.197	0.220	0.264	0.331	0.370
Hydroxyl value of the polyols / (mgKOH/g)	86	117	126	141	156
Properties of the polyols	liquid	liquid	grease	grease	grease
gel fraction of the cast resin/%	34.84	62.59	71.12	85.49	93.41
Properties of the cast resins	elastomer	elastomer	elastomer	elastomer	plastic

3.2. FTIR spectra analysis

Figure 1 presents the FTIR spectra. The peak at 3009 cm^{-1} in the spectrum of SBO is attributed to the carbon-hydrogen stretching vibration in the carbon-carbon double bond, and it disappears in the

spectrum of ESO. The peak at 825 cm^{-1} in the spectrum of ESO corresponds to the epoxy groups, and its appearance indicates the occurrence of epoxidation reaction. Compared with the spectrum of ESO, the peak at 3464 cm^{-1} is attributed to the hydroxy group stretching vibration of SBOP, while that at 825 cm^{-1} corresponding to the epoxy groups disappears. For MSBOP, the peak at 1645 cm^{-1} corresponding to the stretching vibration of carbon-carbon double bond and that at 3464 cm^{-1} corresponding to the hydroxy groups both widen and present dispersive characteristics, indicating that single-esterification reaction occurs for SBOP and MA. This means that alcoholic hydroxyl groups have transformed into carboxyl groups. In the spectrum of the polymer, the peaks at 3064 cm^{-1} and 3034 cm^{-1} correspond to the carbon-hydrogen stretching vibration of the benzene ring, and those at 1584 cm^{-1}, 1494 cm^{-1}, 1453 cm^{-1} and 1402 cm^{-1} are attributed to the bending vibration of carbon-carbon double bond in the benzene ring. However, the stretching vibration peak of the carbon-carbon double bond at 1653 cm^{-1} almost disappears, implying that the polymerization reaction has occurred.
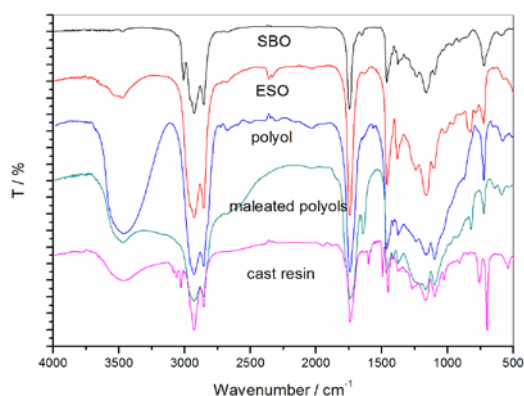

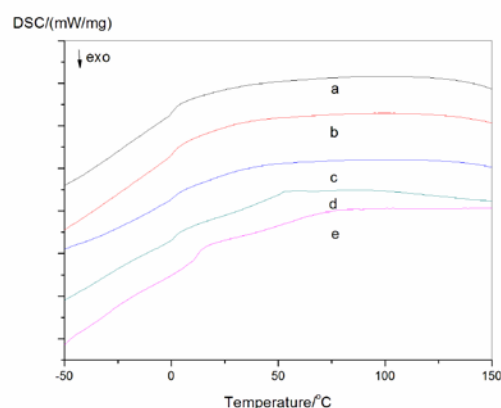**Figure 1.** Infrared spectra of the samples

Figure 2. DSC curves of polymers derived from MSBOP

3.3. Analysis of thermal properties

Properties of polymer are significantly affected by the cross linking degree, which depends on the functionality degree of monomer molecules, such as hydroxyl groups and epoxy groups. Figure 2 shows the DSC curves of the polymers, and the glass transition temperatures (T_g) of the polymers are provided in Table 2. As can be seen, T_g of the polymers increases with the hydroxyl value and the epoxy value. Since the number of active carbon-carbon double bonds increases with the reaction of MSBOP, the degree of functionality also increases accordingly. In addition, carbon-carbon double bonds in the triglyceride chain have an obvious effect on the flexibility of macromolecule chain. T_g of the polymers with hydroxyl values ranging from 86 to 126 mg KOH/g is lower than room temperature and displays only one glass transition temperature because of the variable crosslinking degree and the low gel fraction. Consequently, these samples have a large amount of linear polymer, low polymer or unreactive species. Thus, the resulting materials are soft, weak, and rubbery. In contrast, polymers made from polyols with hydroxyl values of 141 to 156 mg KOH/g have high T_g and display two glass transition temperatures. This can be attributed to the phase separation in the polymers caused by the high gel fraction. To be specific, the gel park with high crosslinking density has higher T_g, while the sol park shows lower T_g. Hence, the two samples present rigid plastic properties, which can be proved by the analysis of mechanical properties.

Table 2. Thermal properties of polymers derived from MSBOP

Sample	T_g	$T_{5\%}$/℃	$T_{10\%}$/℃	$T_{50\%}$/℃	T_{max}/℃
a	0.4	314.6	349.9	401.8	405.4
b	0.7	324.3	351.8	399.6	402.1
c	19.1	311.4	345.6	399.2	403.3
d	50.4	247.0	325.2	395.0	400.3

e	58.6	243.5	312.0	386.3	391.8

Figure 3 shows the TG and DTG thermograms of the polymers in air atmosphere. The temperatures corresponding to 5%, 10% and 50% mass loss, and the temperature at which mass loss occurs with the maximum rate (T_{max}) are listed in Table 2. Thermal stability of the polymers shows a good correlation with the hydroxyl value. With the increase of hydroxyl value of SBOP, the decomposition temperature of the polymers increases at lower hydroxyl values, while decreases at higher hydroxyl values. Meanwhile, as the hydroxyl value increases, the number of active carbon-carbon double bonds introduced from MA also increases, thus increasing the crosslinking degree of the polymers. Besides, the number of carboxyl groups in the resulting materials increases with increasing hydroxyl values. Because of the low thermal stability of the carboxyl groups, the thermal stability of the polymers shows a decreasing trend within limits.
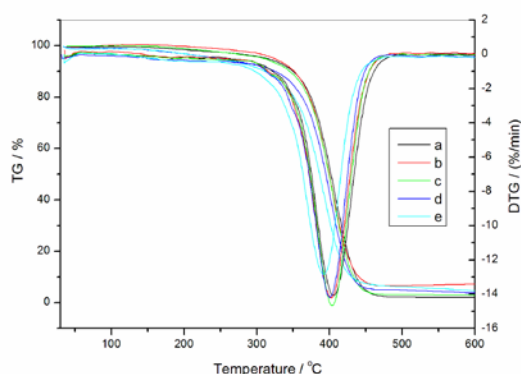

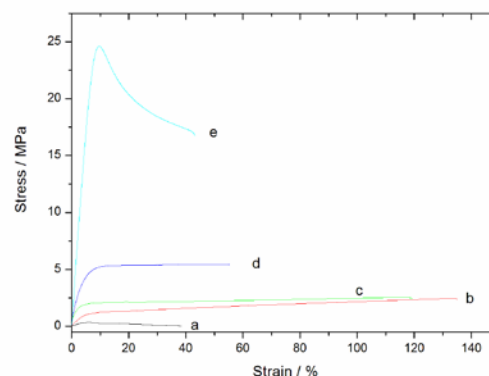**Figure 3.** TG and DTG curves of polymers derived from MSBOP

Figure 4. Stress-strain curves of polymers derived from MSBOP

3.4. Mechanical properties of the cast resin

Figure 4 presents the stress-strain curves of the polymers, and the tensile strengths are listed in Table 3. The polymer derived from SBOP with a hydroxyl value of 86 mgKOH/g has a very low tensile strength of 0.37 MPa and a low elongation of 40.47%, which displays soft and weak characteristics. In this case, due to the low average functionality degree of MSOP, the crosslinking degree is low and the network is imperfect. Higher hydroxyl values contribute to higher crosslinking degree and the formation of relatively complete network, and can improve the tensile strength of glassy polymers. With a hydroxyl value of 156 mgKOH/g, the polymer presents a high tensile strength of 23.63 MPa and a moderate elongation of 43.08%, which displays rigid plastic properties.

Table 3. Mechanical properties of polymers derived from MSBOP

Sample	Hydroxyl value of the polyols / (mgKOH/g)	Tensile strength /MPa	Elongation at break/%	Impact strength /KJ/m^2
a	86	0.37±0.02	40.47±4.24	5.28±0.63
b	117	2.11±0.32	136.63±2.19	25.28±5.99
c	126	2.37±0.15	119.78±0.16	15.29±3.56
d	141	5.50±0.06	55.15±1.20	4.38±0.62
e	156	23.63±1.39	43.08±2.38	4.11±0.35

The impact strengths of the polymers with different hydroxyl values are also given in Table 3. As it reveals, the impact strength of the polymers decreases with increasing hydroxyl values, due to the decrease of the flexibility of polymer chains. Especially, the polymer derived from SBOP with a hydroxyl value of 86 mgKOH/g is distinguished from others, and shows a lower impact strength of 5.28 KJ/m^2 due to its lower crosslinking degree and imperfect networks. At higher hydroxyl values, since the strengths of the polymer are mainly controlled by the strong cross-linked network, the effect of the flexibility of the polymer chain is not obvious, so that the strength decrease of the materials is

inconspicuous. Meanwhile, the soybean oil molecules also make certain contributions to the flexibility of the polymer chain.

4. Conclusions

In summary, polymers derived from SBOP with different hydroxyl values were obtained, and the effects of hydroxyl value on the properties of the polymers were studied. Mechanical and thermal properties of the polymers depended on the functionality degree of SBOP. The wide distribution of hydroxyl values determined different crosslinking degrees of the polymers. Thermal analysis revealed that T_g increased with increasing hydroxyl values. Mechanical analysis illustrated that the tensile strength increased while the impact strength decreased with increasing hydroxyl values. Polymers derived from SBOP with lower hydroxyl values behaved as elastomers, whereas those from SBOP with higher hydroxyl values displayed rigid plastic properties. The bio-based polymers could be prepared from renewable environmentally friendly resources, and showed attractive properties and wide application prospects in many fields.

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