

STRUCTURE AND PROPERTIES OF PARTIALLY EPOXIDIZED SOYBEAN OIL

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In the present study, the characteric-structure relationship of epoxidized soybean oils (ESO) with various degrees of epoxidation has been investigated. FTIR analysis was used to identify the relative extent of epoxidation of the samples during the epoxidation reaction. The viscosities of ESO were much higher than that of the raw oil, viscosity increased with degree of epoxidation. The viscous-flow activation energy of ESO was determined to be higher than that of the raw oil (20.72 to 77.93% higher). Thermogravimetry analysis (TG) of ESO was used to investigate the thermodynamic behavior of the samples. With increasing degree of epoxidation, the thermal stability of the samples initially decreased, then increased at the final reacting stage. Differential scanning calorimeter (DSC) indicated that the melting point of ESO was higher than that of soybean oil. Gel permeation chromatography (GPC) indicated the molecular mass of the samples increased initially, then decreased, with an increase in the extent of epoxidation.

Keywords: DSC, epoxidized soybean oil, GPC, thermogravimetry, viscosity

Introduction

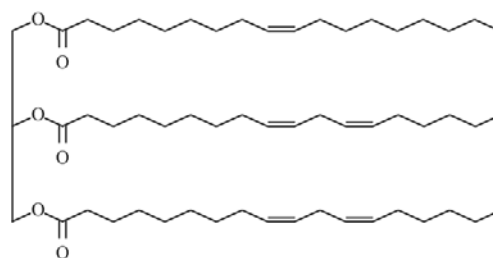
The preparation of polymers from renewable resources is of significant economic and scientific importance. Vegetable oils have a number of excellent properties that can be utilized in producing valuable polymeric materials. The oils are characterized for their hydroxyl value and fatty acid composition. The modified oils have higher hydroxyl values and lower levels of unsaturated acids than regular unmodified oils. The modified, soy-based, vegetable oil polyols can be incorporated as a replacement for conventional polyols, reacting with isocyanates to produce flexible slabstock polyurethane (PU) foams, elastomers and coatings. Soybean oil (SBO) is highly hydrophobic, thus a soy-based PU with excellent weather stability can be expected. The thermal and oxidative stabilities of the soybean oil-based PUs are comparable with those of the polypropyleneoxide-based PUs [1–10].

The preparation of polyols from oils has been the subject in many studies [11, 12], but limited attention has been paid to the characterics-structure relationship in ESO and the resulting polyurethanes. Studies on the decomposition of commercial vegetable oils have been done [13, 14], but studies on the decomposition behavior of partially epoxidized SBO are absent. SBO is a triglyceride with two dominant fatty acids, linoleic acid (ca. 50%, two double bonds) and oleic acid (ca. 25%, one double bond), fielding an average number of 4.6 double bonds per molecule, as depicted in Scheme 1 [15]. The average molecular mass (M_w) of SBO of American origin is 874 and despite varia-

tions in composition from molecule to molecule, it is virtually monodisperse.

ESO can be prepared by the epoxidation of SBO using peroxyacetic acid generated in situ in the presence of sulphuric acid as the catalyst. In the present work, according to the kinetic relationship for the epoxidation of SBO, a series of ESOs were prepared at 75°C by reaction for 1, 2, 3 and 4 h, respectively, for which the extent of epoxidation was different. It was clear that all of these epoxidation reactions gave a range of oxirane structures that could have different properties and, when converted to polyols and polyurethanes, could impart different properties to the final products. In this study, the characterics-structure relationship of ESO has been investigated.

Average functionality=4.6, (I.V.=120–140)
 –OOC(CH₂)₇CH=CHCH₂CH=CH(CH₂)₄CH₃ linoleic–51%
 –OOC(CH₂)₇CH=CH(CH₂)₇CH₃ oleic–25%
 –OOC(CH₂)₁₄CH₃ palmitic–11%
 –OOC(CH₂)₇CH=CHCH₂CH=CHCH₂CH₃
 linolenic–9%
 –OOC(CH₂)₁₆CH₃ stearic–4%



Scheme 1 Schematic representation of the soybean oil molecule

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Experimental

Materials

The refined soybean oil (I.V. 127 mg I₂/g) was kindly provided by Nanhai Oil Co. Ltd. Glacial acetic acid (99.5%), sodium carbonate, sodium hydroxide, hydrogen peroxide (30%), sulphuric acid (Analar) used were all AR grade and tetrahydrofuran was HPLC grade. All were purchased from Guangzhou Chemical Reagent Co. and used as supplied.

Preparation of ESO

The epoxidized soybean oils with varying epoxidation values were synthesized with peroxyacetic acid generated in situ in the presence of sulphuric acid as the catalyst at 75°C by reacting for 1, 2, 3 and 4 h, respectively. The extent of epoxidation was 0.243, 0.317, 0.356 and 0.383 mol 100 g⁻¹ and the iodine value of which was 60.03, 42.15, 21.89 and 15.54, respectively. The extent of epoxidation of ESO increased linearly, while the iodine value decreased linearly as the epoxidation reaction time increased. It was clear that all of these reactions gave a range of ESO structures that could have different properties and, when converted to polyols and polyurethanes, could impart different properties to the final products.

Methods

Iodine value, as the measure of concentration of double bonds, was determined using the AOCS method. Epoxy oxygen content determination was carried out according to the standard procedure for oils and fats [16]. The IR spectra were recorded on a Fourier transformation infrared (FTIR) spectrometer (IR Prestige-20, Shimadzu, Japan). The samples were prepared as thin films on KBr salt plates. The GPC chromatograms were acquired on a Waters model 1515 pump system equipped with a model 2414 differential refractometer using THF as the eluent operating at 1.00 mL min⁻¹ at 40°C. Three Styragel HR columns from Japan covering a molecular mass range of 2·10³–10⁶ Da were used and calibrated using five polystyrene narrow standards from BF Goodrich (Richfield, Ohio).

The viscosities of the samples were measured at different temperature on a rheometer (MPJ-5S, Shanghai Dixue Apparatus Institute, Shanghai, China). In the process, the test conditions were carefully controlled to maintain constant temperature during the viscosity measurements. Thermal characteristics were measured on a differential scanning calorimeter (DSC 200PC Netzsch) with a heating rate of 20°C min⁻¹ from -60 to 100°C. In the test process, 20 mg of sample were used in aluminium pans in each analysis and nitrogen

was used as the purge gas at a 50 mL min⁻¹ flow rate. The analyses of the thermogravimetric behavior of the 10 mg samples were performed on a model STA 409PC (Netzsch) TG, with a heating rate of 10°C min⁻¹ from 50 to 650°C. Air was used as the purge gas at a flow rate of 100 mL min⁻¹.

Result and discussion

FTIR spectra of SBO and ESO

SBO and the purified samples spread on a KBr plate were analyzed using FTIR to check whether SBO was converted to ESO. The FTIR spectra of SBO and ESO are shown in Figs 1 and 2. The characteristic peak at 3009 cm⁻¹ was attributed to the C–H stretching of SBO C=C–H. The peak at 3009 cm⁻¹ decreased gradually as the reaction time increased. As can be seen from the partial FTIR spectrum of the SBO and ESO (Fig. 2), the presence of new peak in the FTIR spectra of ESO at 823 and 833 cm⁻¹ was attributed to epoxy group, indicating that the C=C double bonds have been converted into epoxy groups partially or completely

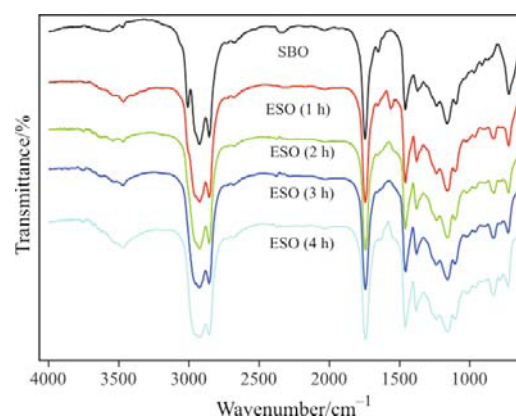


Fig. 1 FTIR of soybean oil and epoxidized soybean oils

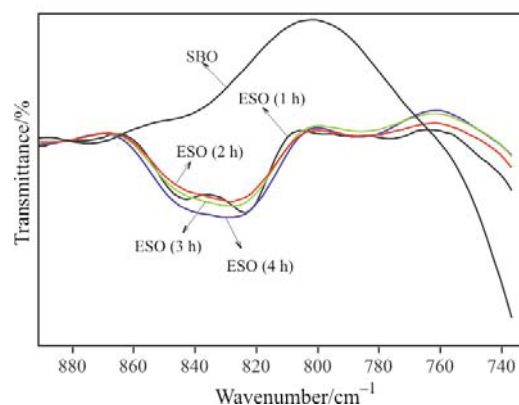


Fig. 2 The part of the FTIR spectra of soybean oil and epoxidized soybean oils: (ESO (1 h), ESO (2 h), ESO (3 h) and ESO (4 h) representing the product of reaction for 1, 2, 3 and 4 h, respectively)

after epoxidation. The intensity of the peak indicates the extent of epoxidation of the samples. It was very clear that with an increase in the reaction time, the extent of epoxidation of the samples increased.

Analysis of GPC

The GPC chromatograms of soybean oil and the prepared epoxidized soybean oils are shown in Fig. 3. The molecular mass of SBO, ESO (1 h), ESO (2 h), ESO (3 h), ESO (4 h) are 881, 922, 950, 937, 934 respectively. The GPC analysis of epoxidized products did not show the presence of oligomers. Compared with SBO, all the peaks of ESO shifted to lower retention times, indicating that the molecular mass of ESO was higher than that of SBO. During the initial 2 h reaction time, the molecular mass of the products (ESO (1 h) and ESO (2 h)) increased with reaction time. The molecular masses of the samples (ESO (3 h) and ESO (4 h)) were inferior to the initial (1 and 2 h) products, indicating that part of chains of the triglyceride may have been segmented, fielding an organic acid. This could be confirmed from the Fig. 1 which has a smaller peak at 3440 cm^{-1} , meaning that the products (ESO (1 h) and ESO (2 h)) maintained the integrity of the triglyceride structure. As a result, the molecular mass of the products could decrease with longer reaction time and in order to maintain the integrity of the triglyceride structure with epoxy groups, the reaction temperature must be controlled.

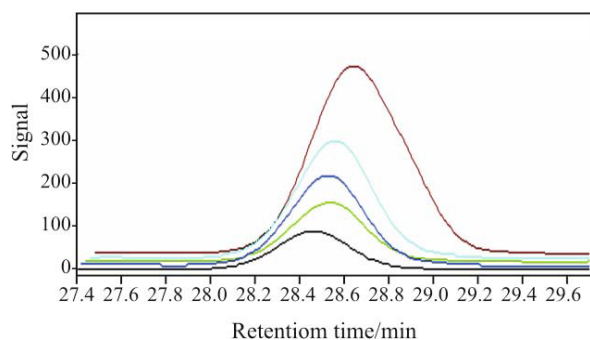


Fig. 3 Chromatograms of the soybean oil and epoxidized soybean oils. (From top: SBO, ESO (1 h), ESO (3 h), ESO (4 h), ESO (2 h))

Rheological behavior of SBO and ESO

The rheological behavior of SBO and these ESO as a function of temperature has been examined in the present work. The viscosities, plotted against the reciprocal temperature, as described in the Fig. 4, obeyed an Arrhenius dependence:

$$\eta = Ae^{E/RT}$$

where A is a reference viscosity, E is the viscous-flow activation energy, R is the gas constant and T the

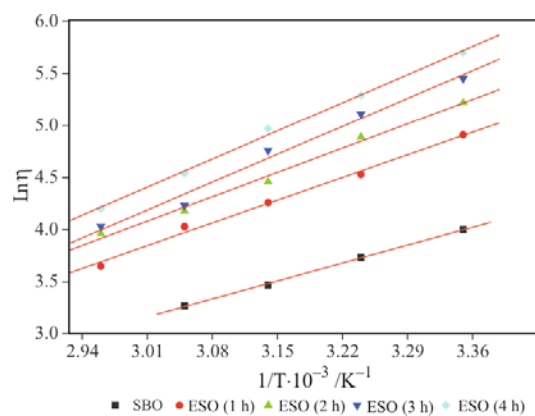


Fig. 4 Viscosity–temperature relationships of soybean oil and epoxidized soybean oils

absolute temperature (K). Activation energies were calculated from the slopes of these straight lines and are summarized in Table 1. It was very clear that the activation energies of the ESO were significantly higher than that of SBO (20.72%–77.93% higher) and that with an increase in the extent of epoxidation of ESO, the activation energy increased; the larger the extent of epoxidation of the samples, the higher the viscosity at the same temperature. This difference may result from the increase of the number of epoxy group and the decrease of the number of C=C double bonds, creating a defect in the packing of the triglycerides and allowing formation of hydrogen bonds in the products, which were not in the raw material. The viscosity at 45°C and activation energy of viscous flow (E_a) for SBO and ESO are presented in Table 1.

Table 1 Viscosity at 45°C and activation energy of viscous flow (E_a) for the SBO and ESBO

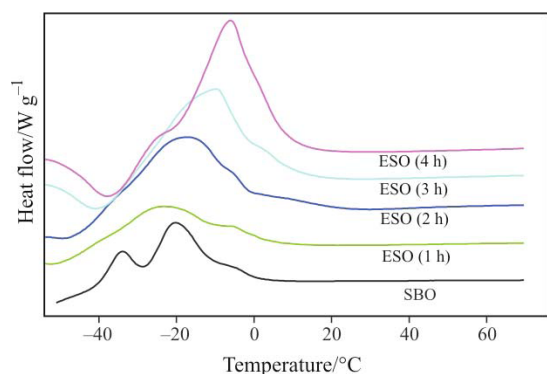
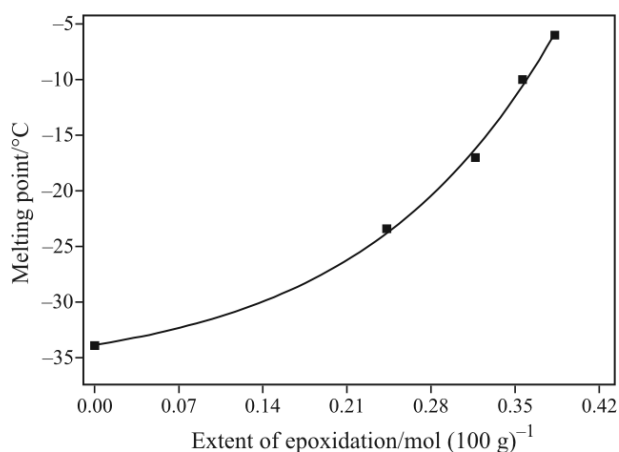
Sample	Viscosity at $45^\circ\text{C}/$ mPa s	$E_a/\text{kJ mol}^{-1}$
SBO	31.98	2.22
ESO (1 h)	70.86	3.45
ESO (2 h)	86.57	3.46
ESO (3 h)	116.4	3.64
ESO (4 h)	144.6	3.95

DSC analysis

The physical properties of SBO and ESO are related to the structural order and the physical state (above or below the melting point) of the samples. The DSC patterns of the prepared ESO significantly differed from the starting material, SBO, as described in Fig. 5. The double peaks of SBO were attributed to the two main components, linoleic acid (ca. 50%, two double bonds) and oleic acid (ca. 25%, one double bond), indicating that there were two melting points in SBO. It was clear that the peak at -33.9°C disappeared after the

Table 2 Thermal decomposition temperature of soybean oil and epoxidized soybean oils

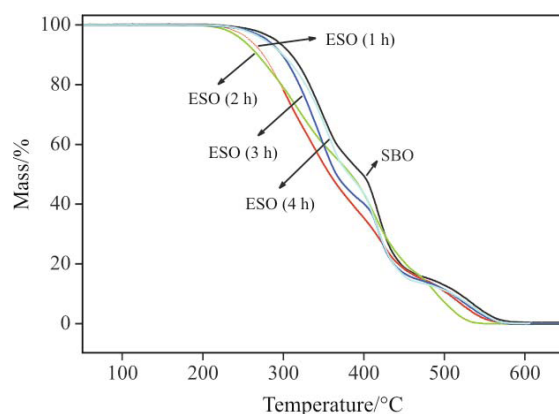
Sample	SBO	ESO (1 h)	ESO (2 h)	ESO (3 h)	ESO (4 h)
First step/ $^{\circ}\text{C}$	304.6	259.7	250.1	294.2	302.0
Second step/ $^{\circ}\text{C}$	405.9	409.1	395.4	410.1	402.2
Third step/ $^{\circ}\text{C}$	499.6	484.0	473.0	498.5	504.4

**Fig. 5** DSC patterns of soybean oil and epoxidized soybean oils**Fig. 6** Dependence of the melting point of epoxidized soybean oils on the extent of epoxidation

epoxidation reaction; with an increase in the extent of epoxidation, the peak shifted to a higher temperature, due to the increased polarity of the epoxy group compared to that of the C=C double bonds thereby increasing the intermolecular interaction force. Figure 6 shows the relationship between the melting point determined by DSC and the extent of epoxidation.

Thermogravimetric analysis

It can be seen from Figure 7 that the decomposition temperature of the raw material decreased after epoxidation. For the lower extents of epoxidation, the decomposition temperature decreased with an increase in the extent of epoxidation, decreased thermo-oxidative behavior and stability. With a further increase in the extent of epoxidation, the

**Fig. 7** TG curves of soybean oil and epoxidized soybean oils

decomposition temperature improved significantly, the thermal decomposition temperature of ESO (4 h) was slightly higher than that of ESO (3 h). Among the studied samples, SBO presented three thermal decomposition steps and the highest thermal decomposition temperature, due to the higher thermal stability unsaturated C=C double bonds relative to the epoxy group. The reason for the increase in the thermal stability of the products in the latter step of the epoxidation reaction is not clear. The thermal decomposition temperature (initial decomposition temperature of the three steps) of the samples is shown in Table 2.

Conclusions

Four products with different extents of epoxidation were synthesized by epoxidation of SBO with peroxyacetic acid generated in situ in the presence of sulphuric acid as catalyst for the reaction, for various times at 75°C . The raw material, soybean oil and the products were characterized by chemical and physical methods. The molecular mass and thermal decomposition temperature of the raw material increased and decreased, respectively, after the epoxidation reaction. As the extent of epoxidation increased, the viscosity and the viscous-flow activation energy at the same temperature were highest for the ESO (4 h), followed by ESO (3 h), ESO (2 h), ESO (1 h) and SBO. The analysis of DSC data indicated that the melting point of the studied samples increased with an increase in the extent of epoxidation.

Acknowledgements

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