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Ring-Opening Polymerization of Epoxidized Soybean Oil

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Abstract Ring-opening polymerization of epoxidized soybean oil (ESO) catalyzed by boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$) in methylene chloride was conducted in an effort to develop useful biodegradable polymers. The resulting polymerized ESO (PESO) were characterized using infrared (IR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), ^{1}H NMR, ^{13}C NMR, solid state ^{13}C NMR and gel permeation chromatography (GPC). The results indicated that PESO materials were highly crosslinked polymers. They had glass transition temperatures ranging from −16 to −48 °C. TGA results showed the PESO polymers were thermally stable at temperatures up to 220 °C. Decomposition of the polymers was found to occur at temperature greater than 340 °C. GPC results indicated the extracted soluble substances from PESO polymers were ESO dimers, trimers and polymers with low molecular weights. The resulting crosslinked polymers can be converted into hydrogels by chemical modification, such as hydrolysis. These soy based hydrogels will find applications in personal care and health care areas.

Keywords Epoxidized soybean oil · Boron trifluoride diethyl etherate · Methylene chloride · Ring-opening polymerization

Introduction

In recent years, natural oils have attracted renewed attention as raw materials for the preparation of polymeric materials to replace or augment traditional petro-chemical based polymers. Oils such as linseed and tung oil have long found various uses in the paint and varnish industries. Soybean oil, safflower oil, sunflower oil, and canola oil have also been used in industrial applications including: plastics, lubricants, adhesives, inks, paints and coatings, fuels/biodiesel, solvents, and surfactants [1–7].

Soybean is the second largest crop plant in the US [8]. About 3 billion bushels of soybean are grown annually in the US, of which current market demand is about 2.9 billion bushels (1 US bushel = 35.24 liters). Developing new uses for the surplus soybean oil is important to prevent price depression due to the oversupply. Typically soybean oil's fatty acid composition is about 10% palmitic, 5% stearic, 25% oleic (18:1), 51% linoleic (18:2), and 7% linolenic (18:3). The unsaturated sites in soybean oil may be used to introduce functional groups like epoxides. The epoxidized fatty acid derivatives from vegetable oils can be used in various applications as stabilizers and plasticizers in polymers, as additives in lubricants, or as components in plastics [9–12]. ESO is also an important intermediate that can be converted into polyols that are used in polyurethane materials [13–15]. ESO used as a raw material for the synthesis of new polymers has been previously reported [16–19]. We have reported the preparation of ionic polymeric surfactants from ESO and investigated their surface properties [20]. These materials may have potential uses in paints, coatings, food, medicine, and many other areas. Wu et al. [21] prepared anionic polymers from ESO and used them as a carrier for the water soluble anticancer drug doxorubicin hydrochloride (Dox) to enhance dox toxicity

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against multidrug-resistant (MDR) cancer cells. New applications utilizing ESO polymers are also desirable because of their availability from renewable resources and biodegradability. In this study, we report the ring-opening polymerization of ESO catalyzed by the Lewis acid, $BF_3 \cdot OEt_2$, in methylene chloride to give polymerized ESO (PESO) as described in the Fig. 1. The influence of temperature and catalyst concentration on the polymerization process and the resulting thermal properties of PESO polymers were investigated. The structures of the PESO polymers were characterized and confirmed using FT-IR, ^{1}H NMR, ^{13}C NMR, and solid state ^{13}C NMR. The thermal properties of the PESO polymers were studied by DSC and TGA.

Experimental

Materials

ESO was obtained from Elf Atochem Inc. (Philadelphia, PA) and used as received. The oxirane oxygen content was 7%, and molecular weight was 1,000 g/mol. Purified and redistilled $BF_3 \cdot OEt_2$ was obtained from Aldrich Chemical Inc. (Milwaukee, WI). Methylene chloride was purchased from Fisher Scientific (Fair Lawn, NJ) and used after drying with molecular sieves. Hexane was obtained from Aldrich Chemical Inc. (Milwaukee, WI) and used as received.

Ring-Opening Polymerization of ESO (PESO)

A typical procedure for the ring-opening polymerization of ESO is as follows: 30 g ESO and 300 mL methylene chloride were added to a 500-mL round-bottomed flask fitted with a mechanical stirrer, condenser, thermometer, nitrogen line and dropping funnel. The solution was cooled to 0 °C with an ice bath and $BF_3 \cdot OEt_2$, 0.396 g (2.79 mmol) was added drop-wise over 2 min. The solution was stirred at 0 °C for 3 h and ethanol (2 mL) was added to the mixture to deactivate the catalyst. The methylene chloride was removed using a rotary evaporator and the remaining residue was dried under vacuum at 70 °C to a constant weight to give a 99.3% yield of (29.8 g) a white colored polymer. The PESO polymers were insoluble in most solvents due to crosslinking through the multiple epoxy groups present in the ESO molecules. Here, experimental data reported are the average of three repeated trials.

Soxhlet Extraction

Soluble materials were extracted using a Soxhlet extractor in refluxing hexane. Typically, a 10-g sample of the polymer powder was extracted with 150 mL of refluxing hexane using a Soxhlet extractor for 16 h. After extraction, the resulting solution was concentrated by rotary evaporation and vacuum drying. The soluble substances were isolated for GPC, FT-IR and NMR characterizations. The insoluble substances were dried before weighing and were characterized by FT-IR and solid state ^{13}C NMR.

Characterization

Infrared

FT-IR spectra were recorded on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) coupled with a Smart

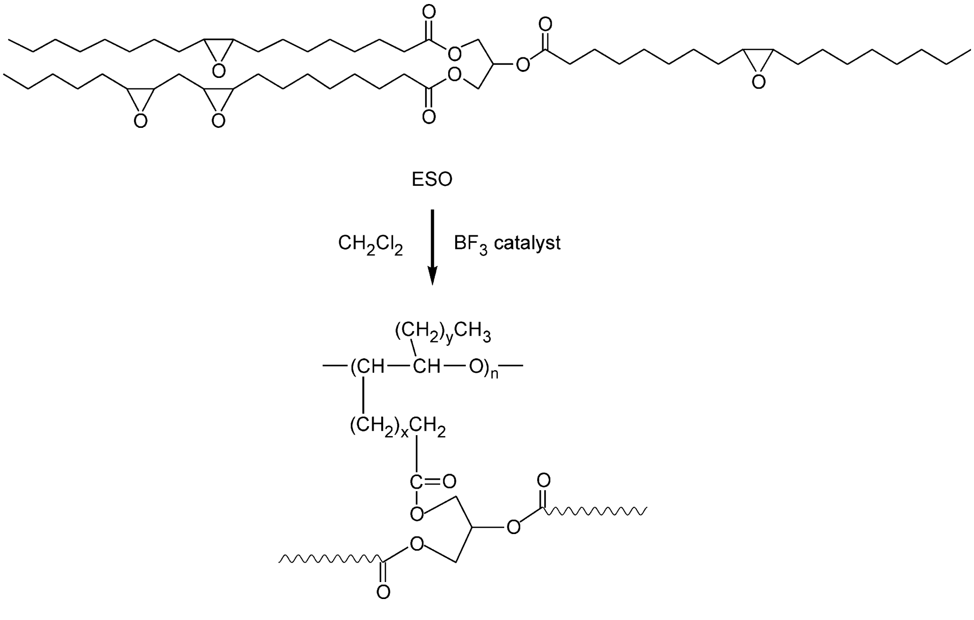


Fig. 1 Scheme outlining the synthesis of PESO polymers

ARK accessory for liquid samples over a scanning range of 650–4,000 cm^{-1} for 32 scans at a spectral resolution of 4 cm^{-1}. Solid samples were recorded on this FT-IR system coupled with a Smart Orbit accessory.

NMR

^{1}H-NMR and ^{13}C-NMR spectra for extracted soluble substances from PESO samples were recorded using a Bruker ARX-300 spectrometer (Bruker, Rheinstetten, Germany) operating at a frequency of 500.13 and 125.77 MHz, respectively, using a 5-mm inverse Z-gradient probe in $CDCl_3$ (Cambridge Isotope Laboratories, Andover, MA). Solid state ^{13}C-NMR spectra for extracted insoluble substances were recorded using a Bruker ARX-300.

GPC

GPC profiles were obtained on a Waters HPLC system including a 1515 isocratic HPLC pump, a 717plus automated injector, and a column heater, controlled with Breeze software, obtained from Waters Corporation (Milford, MA). Columns used for separation were a pair of PL gel 3 μm MIXED-E, 300 × 7.5 mm and a PLgel 5 μm Guard, 50 × 7.5 mm (part number PL1110-6300, PL1110-1520, respectively) from Polymer Laboratories (Varian Inc., Amherst, MA 01002). Signals generated from a miniDAWN TREOS triple-angle light scattering detector and Optilab rEX refractive index detector, obtained from Wyatt Technology Corporation (Santa Barbara, CA) were processed using ASTRA V macromolecular characterization software, also from Wyatt Technology Corporation. THF was used as the mobile phase at a flow rate of 1 mL min^{-1}, and columns were maintained at 40 °C. The liquid phase samples were brought into solution with tetrahydrofuran stabilized with butylated hydroxytoluene from Fisher Scientific (Suwanee, GA) at a known concentration near 4.00E−3 g/mL. The Waters Autosampler was used to make 100-μL injections from a 1-mL sample vial. Astra V software was used to calculate the molecular weight.

DSC

DSC thermograms of the test samples were recorded using a TA Instrument (New Castle, DE) Q2000 model with an autosampling apparatus. Typically about 10 mg of the PESO sample was accurately weighed in an aluminum pan and sealed with pin perforated lids. The DSC oven was ramped at 10 °C min^{-1} to 110 °C to eliminate thermal history and possible moisture. A DSC-refrigerated cooling system was used to equilibrate the sample at −90 °C, from 110 °C at a rate of 5 °C min^{-1}. Data were recorded while the oven temperature was raised from −90 to 200 °C at a rate of 5 °C min^{-1}. The DSC method applied an inert atmosphere by purging the oven with nitrogen at 50 mL min^{-1}. Thermal Advantage and Universal Analysis software provided by TA instruments were used for data analysis.

TGA

A TA Q500 thermogravimeter with an autosampling apparatus from TA Instruments (New Castle, DE) was used to measure the weight loss of the PESO samples under a flowing nitrogen atmosphere. Generally, 20 mg of PESO sample was used in the thermogravimetric analysis. The samples were heated from 30 to 600 °C at a heating rate of 10 °C min^{-1} and the weight loss was recorded as a function of temperature.

Results and Discussion

Effect of Ring-Opening Polymerization Temperature

The ring-opening polymerization was conducted at different temperatures ranging from 0 to 50 °C. The glass transition temperature (T_g) of insoluble PESO polymers after extraction was measured by DSC. It is well known that the crosslinking density influences T_g and as the crosslinking density decrease, the free volume of a material will increase, thereby, decreasing T_g correspondingly. Figure 2 showed a typical DSC curve of PESO-VIII. The temperature at inflection point was taken as the glass transition and Table 1 summarizes the results for each PESO polymer prepared at various temperatures. GPC analysis showed that PESO-I contained molecules with molecular weights ranging from 1.1×10^3 to 1.7×10^4 g mol^1. As can be seen from Table 1 there is no significant difference in the

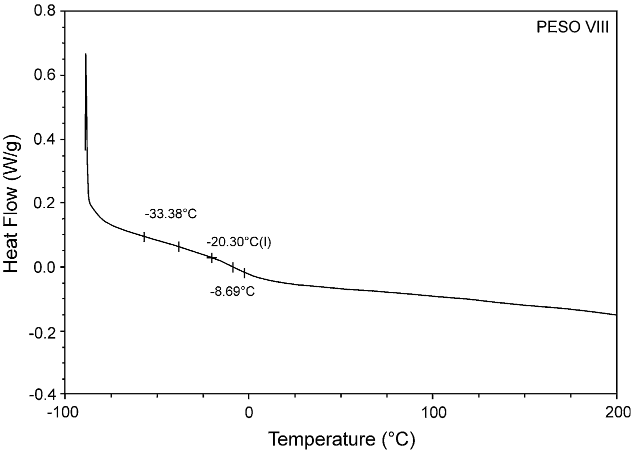


Fig. 2 DSC measurement of PESO-VIII

Table 1 The glass transition temperatures of PESO polymers and data related to the extracted soluble substances from their polymers

Sample	Polym. reac. temp. (°C)	$BF_3{\cdot}OEt_2$ catalyst. (mmol)	Mw(soluble)[a] (g mol^{1})	T_g (°C)	Soxhlet extraction (wt%)	
					Soluble	Insoluble
PESO-I	0	1.34		N/A[b]		
PESO-II	20	1.34	3.4×10^3	−23.6	22	78
PESO-III	30	1.34	3.2×10^3	−24.6	21	79
PESO-IV	40	1.34	3.8×10^3	−23.5	27	73
PESO-V	50	1.34	2.5×10^3	−23.9	14	86
PESO-VI	0	1.38	2.4×10^3	−16.6	16	84
PESO-VII	0	1.87	1.6×10^3	−16.8	1	99
PESO-VII	0	2.79	2.9×10^3	−23.3	7	93
PESO-IX	0	6.19	2.0×10^3	−24.2	9	91
PESO-X	0	7.72	2.5×10^3	−47.9	6	94

[a] Molecular weight data were from GPC analysis of hexane-extracted substances

[b] T_g data is not available because the sample was a viscous liquid which probably contained ESO dimers, trimers and polymers with low molecular weight and all other samples were solid

glass transition temperature of PESO polymers prepared at higher temperatures. It is well known that the most important factor that determines whether a cyclic monomer can be converted into polymer is the relative stabilities of the cyclic monomer and the resulting polymeric structure [22, 23]. Ring-opening polymerization of 3-membered rings is thermodynamically favored (ΔG, free-energy change is negative) [24]. Considering the thermodynamic relation $\Delta G = \Delta H - T\Delta S$, where ΔH is the enthalpy change, ΔS is entropy change, T is temperature (K). ΔH is the major factor for determining ΔG for ring opening in 3-membered rings, while ΔS is very important for 5- and 6-membered rings. ΔH was reported negative (−113.0 kJ mol^{1}) for the 3-membered ring-opening [22, 23]. With this in mind, temperature, T, is not evenly important and this was confirmed in our results. On the other hand, since multiple epoxy groups are present in the ESO molecules, the polymers are easily formed by ring-opening polymerization leading to the formation of PESO with a high crosslink density.

Effect of Catalyst ($BF_3{\cdot}OEt_2$) Concentration

The effect of catalyst ($BF_3{\cdot}OEt_2$) concentration ranging from 1.38 mmol to 7.72 mmol on the thermal properties of PESO polymers was studied the results of which are shown in Table 1, it can be seen that the T_g decreases with increasing catalyst concentration. This result was expected since the molecular weight of a linear polymer usually decreases with increasing catalyst concentration. As discussed above, since the crosslink density of polymer decreases when its molecular weight decreases, the T_g decreases correspondingly. By comparison, with regard to physical properties of PESO-VI to PESO-I, it could be seen that as the catalyst concentration changed from 0.19 g (1.34 mmol) to 0.20 g. (1.38 mmol), the resulting polymer changed from a very viscous liquid (PESO-I) to a rubber-like solid (PESO-VI). At this point, it is clear that catalyst concentration critically affected the molecular weight of the polymers formed, by which the thermal properties of the polymers were influenced.

Soxhlet Extraction and Identification of Structure of PESO

After Soxhlet extraction in refluxing hexane for 16 h, the extracted soluble substances from PESO samples ranged from 1 to 27 wt%, as shown in Table 1. The insoluble substances remaining after Soxhlet extraction ranged from 73 wt% to 99 wt%. The extracted soluble substances and insoluble substances were characterized by methods discussed above. The results are described in the following.

Figure 3 shows the infrared spectra of ESO, extracted soluble substances, and insoluble substances after extraction from the PESO samples. Comparison showed that the characteristic oxirane absorption at 834 cm^{-1} in ESO (Fig. 3a) was not present in the hexane soluble substances (Fig. 3b), suggesting that the hexane-extracted soluble substances were low molecular weight ring-opening products (possibly some were the products formed by ESO intramolecular ring-opening). The IR spectrum of PESO extract soluble sample had a double peak around 1,700 cm^{-1} region, one peak at 1,745 cm^{-1} and another at 1,700 cm^{-1}. The peak at 1,745 cm^{-1} was assigned to an ester of oil structure. The peak at 1,700 cm^{-1} was assigned to the fatty acid carboxylic group produced from hydrolysis products of soybean oil polymers or from polymers of fatty acids (epoxidized fatty acids in ESO). The presence of acid

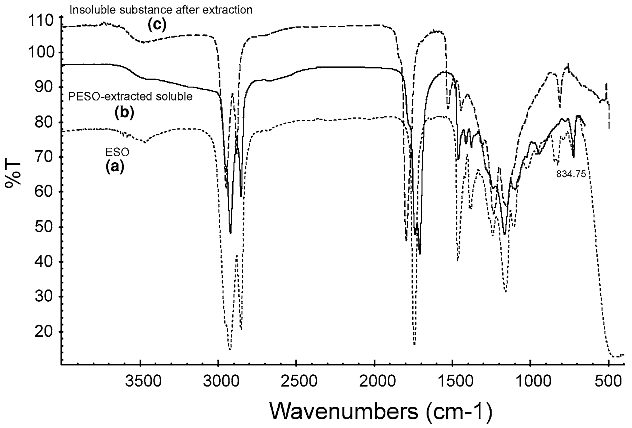


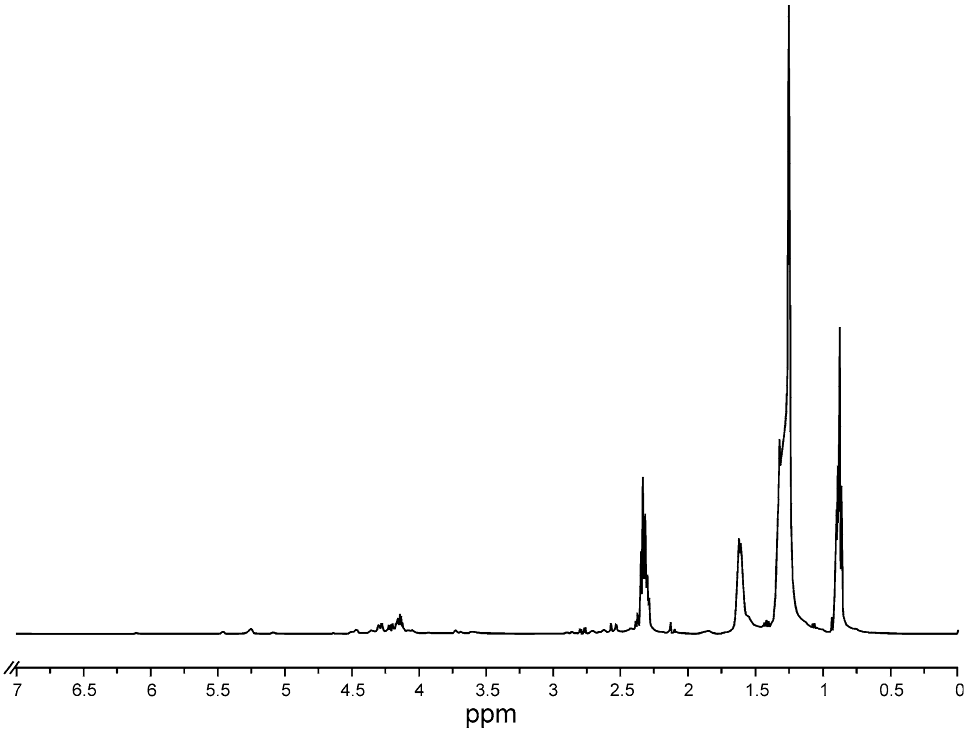
Fig. 3 IR spectra of ESO (**a**), extracted soluble substances (**b**), and insoluble substances (**c**) after extraction from PESO sample

in the starting ESO (Elf Atochem reported ESO acid value at around 0.5) combined with the possible existence of moisture may contribute to the hydrolysis reaction. Figure 3c showed insoluble substances remaining after extraction. That can be clearly seen by the absorption at 834 cm^{-1} for the oxrine group has disappeared, showing no epoxy group was present, there were also no hydrolysis products and indicated the PESO polymers were formed by the ring-opening polymerization of ESO.

The ^{1}H-NMR spectrum of the extracted soluble substances showed that the epoxy protons in the 3.0–3.2 ppm region had disappeared (Fig. 4). The methine proton of $-CH_2(O)-\mathbf{CH}(O)-CH_2(O)-$ glycerol structure at 5.1–5.3 ppm, and methylene proton of $-\mathbf{CH_2}(O)-CH(O)-\mathbf{CH_2}(O)-$ glycerol structure at 4.0–4.4 ppm were observed showing that the glycerin structure was present in the material. A very small peak at 5.4 ppm is attributed to the olefinic hydrogens and weak multiple peaks at 2.7 ppm assigned to the methylene protons between two carbon–carbon double bonds and these were observed possibly due to small amounts of the double bond left during epoxidation of soybean oil. A strong signal at 2.3 ppm assigned to the methylene protons adjacent to the carbonyl groups was observed and supports the supposition that an oil ester structure remains. The ^{13}C-NMR spectrum of the extracted, hexane-soluble substance is shown in Fig. 5 and it can be seen that the peaks at 54–57 ppm assigned to epoxy carbons have disappeared. Signals at 69 and 63 ppm assigned to the methine and methylene carbons of the glycerin structure were observed. Based on the ^{1}H-NMR and ^{13}C-NMR spectra data, it can be concluded that the extracted soluble substances were low molecular weight ring-opening products.

The insoluble substances remaining after Soxhlet extraction, which ranged from 73 to 99 wt%, were the highly crosslinked polymers. These materials were not soluble in solvents such as THF, $CHCl_3$ or CH_2Cl_2. Solid state ^{13}C-NMR spectroscopy provided valuable information on these insoluble materials after the extraction of the PESO sample (Fig. 6). The spectrum clearly showed the presence of ester carbonyls (167 ppm). The carbon–carbon epoxy bond at 52 ppm disappeared and indicated that ESO had been polymerized through ring-opening polymerization, whereby highly crosslinked polymer networks were formed.

Fig. 4 ^{1}H-NMR spectrum of the extracted soluble substances from a PESO sample



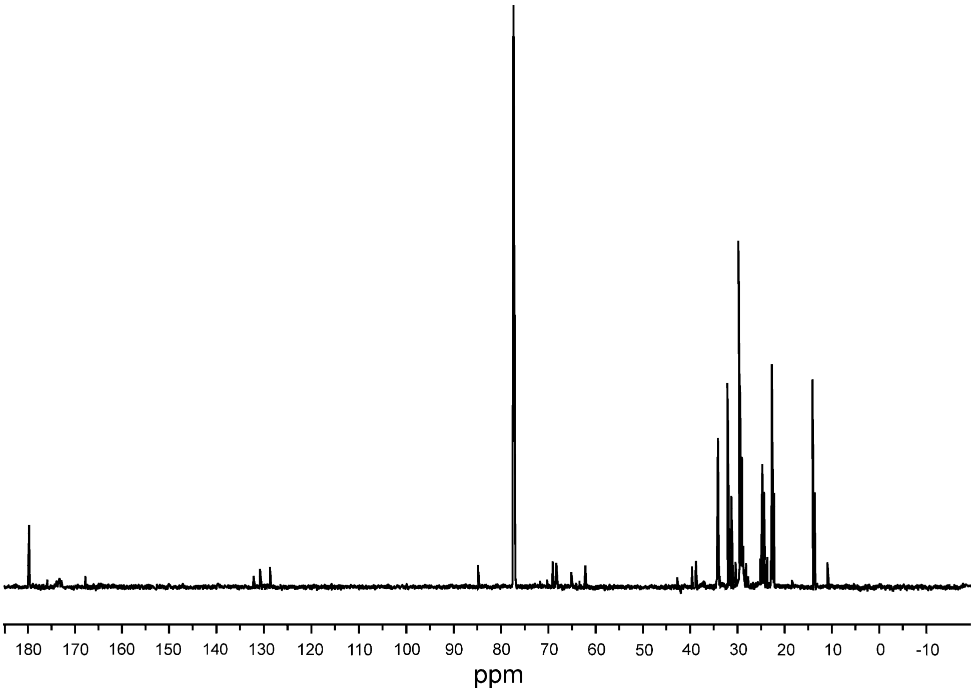


Fig. 5 ^{13}C-NMR spectrum of the extracted soluble substances from a PESO sample

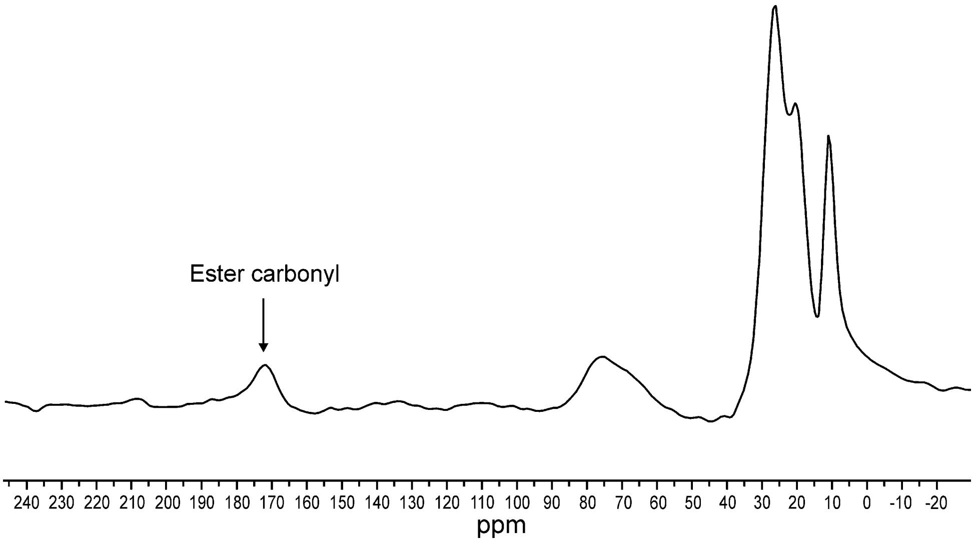


Fig. 6 Solid state ^{13}C-NMR spectrum of the insoluble substances remaining after extraction

GPC profile results of the extracted soluble substances from PESO polymers are summarized in Table 1. It can be noted that average weight molecular weights ranged from 1.6×10^3 to 3.8×10^3 g mol^1. The polydispersity index (PDI) by light scattering measurement was found to be 1.5. Based on the ESO molecular weight of 1.0×10^3 g mol^1, it is expected that the extracted soluble substances were the ESO dimers, trimers and low molecular weight polymers. Along with the above-mentioned FT-IR and NMR analysis, the GPC results provided further evidence that the extracted soluble substances were ESO dimers, trimers and polymers with low molecular weights.

Thermal Stability of PESO

The glass transition temperature of insoluble PESO polymers after extraction was measured by DSC. To better understand the thermal properties of PESO polymers, TGA was used to investigate their thermal decomposition behavior in a nitrogen atmosphere. Figure 7 showed the TGA curve of the PESO-VIII. It can be seen that the PESO-VIII appears to be thermally stable at temperatures below 220 °C. Two distinct temperature regions were observed where samples experienced weight loss (240–320 °C) and (340–437 °C). The material slowly loses

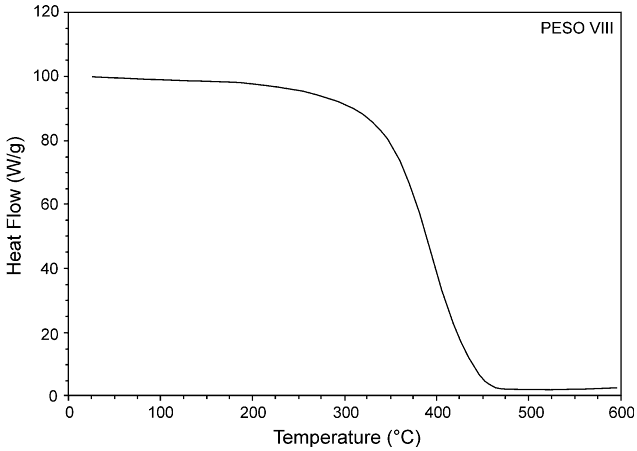


Fig. 7 TGA thermogram of the PESO-VIII weight loss versus temperature (under N_2 atmosphere)

Table 2 Thermal stability data of PESO polymers prepared by various temperatures and catalyst concentrations

Sample	≤220 (°C)	240–320 (°C)	340–450 (°C)
PESO-II	Stable	9 wt% loss	89 wt% loss
PESO-III	Stable	9 wt% loss	89 wt% loss
PESO-IV	Stable	9 wt% loss	87 wt% loss
PESO-V	Stable	8 wt% loss	90 wt% loss
PESO-VI	Stable	11 wt% loss	85 wt% loss
PESO-VII	Stable	9 wt% loss	89 wt% loss
PESO-VIII	Stable	10 wt% loss	87 wt% loss
PESO-IX	Stable	10 wt% loss	83 wt% loss
PESO-X	Stable	8 wt% loss	89 wt% loss

about 10% of its weight at temperatures between 240 and 320 °C, followed by an abrupt weight loss of 87% between 340 and 437 °C. TGA measurement revealed a total 97% weight loss observed at temperatures between 240 and 437 °C. For the other PESO samples obtained at various temperatures and catalyst concentrations, their TGA curves had the same trend as the PESO-VIII. Table 2 summarized the thermal stability results of PESO polymers studied by TGA. It can be seen that all PESO polymers showed two distinct weight loss temperature regions, first a 10% weight loss then again at a higher temperature an 83–90% weight loss. In summary, these materials appeared to be relatively thermally stable at temperatures lower than 220 °C.

Conclusion

Polymers were prepared by ring-opening polymerization of ESO using a $BF_3 \cdot OEt_2$ catalyst in a methylene chloride medium. The PESO polymers were found to be typically highly crosslinked networks. They had glass transition temperatures ranging from −16 to −48 °C. All PESO polymers were shown to be thermally stable at temperatures lower than 220 °C by thermogravimetric analysis and had a decomposition temperature above 340 °C. GPC results showed the extracted soluble substances were ESO dimers, trimers and low molecular weight polymers. The resulting crosslinked polymers can be converted into hydrogels by saponification, which makes them suitable for use in personal care and health care areas.

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References

1. Cunningham A, Yapp A (1974) Liquid polyol compositions. US Patent 3,827,993
2. Bussell GW (1974) Maleinized fatty acid esters of 9-oxatetracyclo-4.4.1.^{2,5}O^{1,6}O^{8,10} undecan-4-ol. US Patent 3,855,163
3. Hodakowski LE, Osborn CL, Harris EB (1975) Polymerizable epoxide-modified compositions. US Patent 4,119,640
4. Trecker DJ, Borden GW, Smith OW (1976) Method for curing acrylated epoxidized soybean oil amine compositions. US Patent 3,979,270
5. Trecker DJ, Borden GW, Smith OW (1976) Acrylated epoxidized soybean oil amine compositions and method. US Patent 3,931,075
6. Salunkhe DK, Chavan JK, Adsule RN, Kadam SS (1972) World oilseeds: chemistry, technology and utilization. Van Nostrand Reinhold, New York
7. Force CG, Starr FS (1988) Vegetable oil adducts as emollients in skin and hair care products. US Patent, 4,740,367
8. Naeve SL, Orf JH (2006) Quality of the United States Soybean Crop. In: 2006 US Soybean Crop Quality Survey. The United Soybean Board. http://www.unitedsoybean.org/Library/RecentLibraryItems.aspx
9. Gruber, B (1993) Manufacture of oligomeric fatty acids as lubricating oil additives. DE Patent 4201343
10. Gan LH, Ooi KS, Goh SH, Gan LM, Leong YC (1995) Epoxidised esters of palm olein as plasticisers for poly (vinyl chloride). Eur Polym J 31:719–724
11. Sherringham JA, Clark AJ, Keene BRT (2000) New chemical feedstocks from unsaturated oils. Lipid Technol 12:129–132
12. Bunker SP, Wool RP (2002) Synthesis and characterisation of monomers and polymers for adhesives from methyl oleate. J Polym Sci A Polym Chem 40:451–458
13. Guo A, Cho Y, Petrovic ZS (2000) Structure and properties of halogenated and nonhalogenated soy-based polyols. J Polym Sci A Polym Chem 38:3900–3910
14. Petrovic ZS, Guo A, Zhang W (2000) Structure and properties of polyurethanes based on halogenated and nonhalogenated soy-polyols. J Polym Sci A Polym Chem 38:4062–4069
15. Kiatsimkul P, Suppes GJ, Hsieh F, Lozada Z, Yuan-Chan Tu YC (2008) Preparation of high hydroxyl equivalent weight polyols from vegetable oils. Ind Crops Prod 27:257–264
16. Liu ZS, Erhan SZ, Calvert PD (2004) Solid freeform fabrication of epoxidized soybean oil/epoxy composites with di-, tri- and polyethylene amine curing agents. J Am Oil Chem Soc 81:605–610
17. Rösh J, Mülhaupt R (1993) Polymers from renewable resources: polyester resins and blends based upon anhydride-cured epoxidized soybean oil. Polym Bulletin 31:679–685

18. Doğan E, Küsefoğglu S (2008) Synthesis and in situ foaming biodegradable malonic acid ESO polymers. J Appl Polym Sci 110:1129–1135
19. Wool RP (1999) Development of affordable soy-based plastics, resins, and adhesives. Chemtech 29:44–48
20. Biresaw G, Liu SZ, Erhan SZ (2008) Investigation of the surface properties of polymeric soaps obtained by ring-opening polymerization of epoxidized soybean oil. J Appl Poly Sci 108:1976–1985
21. Wong HL, Rauth AM, Bendayan R, Manias JL, Ramaswamy M, Liu ZS, Erhan SZ, Wu XY (2006) A new polymer-lipid hybrid nanoparticle system increase cytotoxicity of doxorubicin against multidrug-resistant human breast cancer cells. Pharm Res 23:1574–1585
22. Allcock HR (1970) Ring-chain equilibria. J Macromol Sci Rev Macromol Chem C4:149–151
23. Sawada H (1975) Thermodymanics of polymerization, Chap 6. Marcel Dekker, New York, pp 257–297
24. Chanda M (2000) Advanced polymer chemistry: a problem solving guide. Marcel Dekker, New York