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THERMAL DEGRADATION OF EPOXIDIZED SOYBEAN OIL IN THE PRESENCE OF CHLORINE-CONTAINING POLYMERS *

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ABSTRACT

The thermal degradation of epoxidized soybean oil has been examined using thermal and spectroscopic methods. In both the presence and absence of chlorine-containing polymers, epoxidized soybean oil undergoes thermal degradation to form ring-opened products. In the absence of other reactants, the primary degradation reaction is apparently intermolecular ether formation. The degradation in a highly-chlorinated polymer matrix appears to be facilitated by reaction with hydrogen chloride generated by polymer degradation. Fully epoxidized soybean oil (7.0 wt.% oxirane oxygen) appears to contain two types of oxirane groups: type I which begins to undergo thermal ring-opening at about 175 °C and type II which opens at > 325 °C. Both ring openings are exothermic and irreversible. Type I oxirane groups account for approximately one-third of the total oxirane content of fully epoxidized soybean oil. Partially epoxidized soybean oil (3.28 wt.% oxirane oxygen) contains only type II oxirane functionality.

INTRODUCTION

Epoxidized fatty acid esters are often used as lubricants/plasticizers and secondary stabilizers for halogen-containing polymers [1–9]. Most commonly these are used in conjunction with primary stabilizers (metal soaps, acid acceptors, etc.), antioxidants or other additives, and function as lubricants during processing. The stabilizing influence of these materials often arises from a synergistic interaction with the primary stabilizer [6,7,10–12]. Some of the most prominent of these materials are based upon naturally-occurring oils. Perhaps the most common of these are epoxidized soybean oil (ESO) and epoxidized linseed oil (ELO). Both soybean oil and linseed oil are triglycerides of a distribution of fatty acids. Soybean oil is the glyceryl ester

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of approximately 14% stearic (octadecanoic) acid, 23% oleic (9-octadecenoic acid), 55% linoleic (9,12-octadecadienoic acid), and 8% linolenic acid (9,12,15-octadecatrienoic acid) [13]. Three of these, oleic, linoleic and linolenic, are unsaturated C_{18} acids containing one, two and three double bonds per molecule, respectively. Linseed oil is a similar triglyceride, but contains a much larger amount of esterified linolenic acid. Therefore, the level of unsaturation for this triglyceride is somewhat greater than that for soybean oil. Linseed oil is the glyceryl ester of approximately 9% stearic acid, 24% oleic acid, 17% linoleic acid and 50% linolenic acid. Either soybean oil or linseed oil may be partially or totally epoxidized to generate materials useful in polymer plasticization/stabilization [8]. For several reasons, including cost, ESO is the epoxidized oil used in greatest volume for this purpose [14].

While the mode of stabilization of PVC by epoxidized fatty acid derivatives has been studied using both the polymer [2,7] and model compounds [6] as substrate, much less is known about the interaction of epoxidized oils with vinylidene chloride polymers [11]. To better assess this interaction, the thermal degradation of ESO in both the presence and absence of heavily-chlorinated vinyl polymers has been examined using differential scanning calorimetry (DSC), thermogravimetry (TG), and nuclear magnetic resonance spectroscopy (NMR) to monitor changes which arise as a consequence of thermal treatment.

EXPERIMENTAL

Materials

Vinylidene chloride copolymers

Two sets of vinylidene chloride (VDC) copolymers containing at least 85% VDC were provided by the Dow Chemical Company. The first (VDC/MA copolymer) contained methyl acrylate as comonomer and the other (VDC/VC copolymer) contained vinyl chloride as comonomer. Both were prepared by suspension polymerization and were of approximately 100 000 weight-average molecular weight.

Vinyl chloride polymer

Poly(vinyl chloride), PVC, was obtained from the B.F. Goodrich Company, Chemical Group, Cleveland, OH (GEON 103 EP-F76, lot no. 0-774515).

Epoxidized soybean oil

Both fully epoxidized (Vikoflex 7170S; specified oxirane oxygen content 7.0% by weight) and partially epoxidized (code no. 61-14400C, lot no. 63-226; specified oxirane oxygen content 3.28% by weight) soybean oil were obtained from the Viking Chemical Company. Unepoxidized soybean oil was obtained from the same source.

Solvents and reagents

Common solvents and reagents were obtained from Fisher Scientific Company and the Aldrich Chemical Company, respectively, and were used as received.

Instrumentation

Differential scanning calorimetry

Analysis by DSC was accomplished using a Du Pont 9900 thermal analyzer coupled to a model 912 DSC unit equipped with a dual cell and mechanical cooling accessory. The cell was calibrated using an indium sample (T_m onset = 156.61°C, $\Delta H_f = 28.42$ J g^{-1}). DSC plots (heat flow versus temperature) were generated using a model 7475A Hewlett-Packard plotter supplied by Du Pont Instruments. In general, 7–15 mg samples and sealed aluminum sample pans were used. For some analyses, the aluminum pans were replaced with sealed glass ampules. The cell was subject to a constant nitrogen purge. After equilibration at 35°C, the temperature was ramped at 10°C min^{-1} to 350°C. The onset temperature, peak temperature, and the heat of exothermic decomposition (ΔH_D) of ESO were recorded for all samples. The ΔH_D was calculated as follows

$$\Delta H_D(\text{J g}^{-1}\text{ ESO}) = (\text{measured exothermic heat}) \times (\text{total sample weight/weight ESO})$$

$$\Delta H_D(\text{kJ mol}^{-1}\text{ oxirane oxygen}) = \Delta H_D(\text{kJ g}^{-1}\text{ ESO}) \times (100\text{ g ESO}/7\text{ g oxirane oxygen}) \times (16\text{ g oxygen mol}^{-1})$$

Thermogravimetry

Thermogravimetric analysis was conducted using a Du Pont 9900 thermal analyzer coupled to a model 951 TG unit. The TG cell was swept with a nitrogen flow, 50 ml min^{-1}, during degradation runs and the sample, 7–9 mg, was contained in a platinum sample pan. In a typical run the temperature was ramped at a rate of 5°C min^{-1} from 35°C to 450°C. The output (Du Pont software was used for all data manipulations) was plotted as percent weight versus temperature. The temperature for the onset of weight loss was taken as the point at which the derivative of the weight loss curve deviated from the baseline (deviation from zero slope).

Nuclear magnetic resonance spectroscopy

NMR spectra were recorded using solutions in $CDCl_3$ and a Nicolet NT-300 spectrometer. Carbon spectra were observed at 75.5 MHz with a pulse width of 18 μs (90 °), a pulse delay of 10 s, an acquisition time of 0.41 s, gated decoupling without NOE, a sweep width of 20 KHz, and an acquisition size of 16 K. For the ESO samples the longest T_1 observed was that for the carbonyl carbon atoms, 1.90 ± 0.2 s. Thus a pulse delay of 10 s is adequate for 99% relaxation and assures the quantitative aspects of the experiment.

SAMPLE PREPARATION

Vinylidene chloride copolymer / ESO blends

The vinylidene chloride copolymers were dry-blended with 1.0, 2.0, 5.0 and 10 parts ESO per hundred parts dry resin (pph), respectively, in a Hobart mixer for 3 h. The samples containing ESO and a control (no ESO) were annealed overnight in an air oven at 60 ° C.

Vinyl chloride polymer / ESO blends

A stock solution of 1% ESO in methanol was prepared. Aliquots of this solution were diluted with methanol to provide 10 g solutions containing 0.1, 0.2, 0.5 and 1.0 percent ESO, respectively. A one gram sample of PVC was added to each of these solutions and to 10 g of pure methanol. The resulting mixtures were maintained at 60 ° C for 10 min. The solvent was removed by evaporation and the residual solids were dried at 80 ° C and reduced pressure for 1 h to afford samples containing 0, 1.0, 2.0, 5.0 and 10 pph ESO.

RESULTS AND DISCUSSION

The thermal degradation of fully-epoxidized soybean oil was examined initially by DSC. As can be seen in Fig. 1, the thermogram contains two exotherms, both presumably due to oxirane ring-opening reactions.

The first of these begins at approximately 175 ° C and terminates at 320 ° C. The higher temperature exotherm starts at approximately 330 ° C and is complete well above 400 ° C. The magnitude of this higher temperature exotherm is diminished somewhat by the endothermic vaporization of ESO which occurs at this temperature. Further, and more interestingly, this exotherm is the only one present in the corresponding thermogram of the partially epoxidized soybean oil.

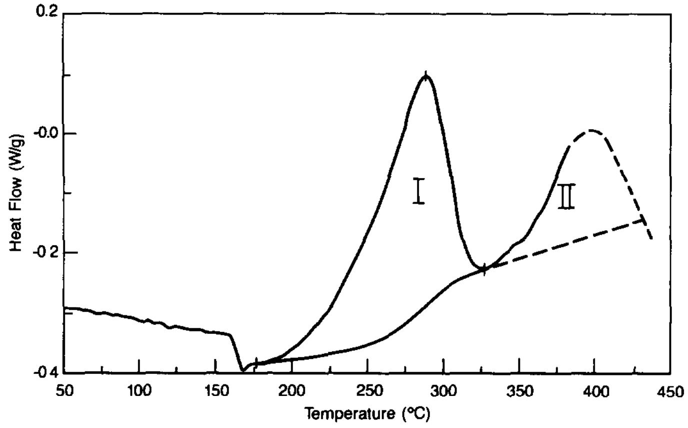


Fig. 1. DSC thermogram for the decomposition of epoxidized soybean oil (ESO).

Figure 2 reflects the thermogram obtained by heating an ESO sample to 325 °C, cooling to 35 °C and reheating to 325 °C, all at 5 °C min^{-1}. For the initial heating, the exotherm centered at 286 °C is readily evident. However, no corresponding endotherm is present in the cooling curve and, further, the exotherm is absent on reheat. This clearly demonstrates that the oxirane ring-opening is irreversible.

The observation that the thermogram for the fully-epoxidized oil contains two exotherms suggests that two kinds of oxirane groups may be present in this material. Only one of these is present in the partially-epoxidized oil. It is well established that oxirane functionality in different chemical environments ring-opens at different temperatures. For example, glycidol (2,3-epoxy-1-propanol) undergoes exothermic ring-opening in the range of 140–260 °C [15]. However, two model compounds examined in this study,

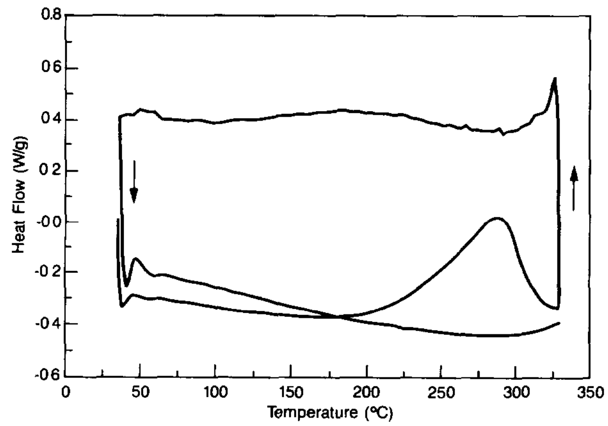
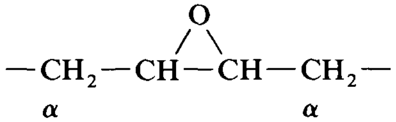


Fig. 2. DSC thermogram for the irreversible decomposition of ESO.

dicyclopentadiene dioxide and epichlorohydrin, ring-open above 300° C. For epichlorohydrin, the onset of exothermic decomposition occurs at approximately 392° C and reaches a maximum at 431° C. However, it is unclear how the oxirane groups in ESO might differ structurally. The primary structure in every case may be represented by



$$\underset{\alpha}{-CH_2}-\overbrace{CH-CH}^{O}-\underset{\alpha}{CH_2-}$$

Any structural variation must necessarily occur at the β position or further removed from the oxirane group. It hardly seems plausible that such remote structural differences might induce a difference in thermal stability for the oxirane units. Yet, such variations in structure rather dramatically influence the ease of hydrogenation of the various double bonds present in fatty esters [16]. A double bond in a fatty ester is increasingly difficult to hydrogenate as its proximity to the carboxylate group increases. Esterified unsaturated fatty acids present in soybean oil include

oleic:

$HOOC-(CH_2)_6-CH_2-CH=CH-CH_2-(CH_2)_6-CH_3$

linoleic:

$HOOC-(CH_2)_6-CH_2-CH=CH-CH_2-CH=CH-CH_2-(CH_2)_3-CH_3$

linolenic:

$HOOC-(CH_2)_6-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$

All of these contain an initial double bond at the 9-position with respect to the carboxyl group. It may reasonably be assumed that the reactivity of this double bond is comparable in all the structures. Further, it is the least reactive toward hydrogenation [16]. Unlike oleic acid, linoleic and linolenic acids contain additional remote double bonds at the 12-position and at the 12- and 15-positions, respectively. Should the ease of epoxidation [17] of the various double bonds reflect that of hydrogenation, it is conceivable that the partially epoxidized oil contains a preponderance of oxirane groups remote to the carboxylate function while the fully-epoxidized material contains oxirane units derived from both the remote double bonds and double bonds proximate (9-position) to the carboxylate. Should the two kinds of oxirane groups have different thermal stabilities, it would account for the appearance of two exotherms in the DSC thermogram for the fully epoxidized oil.

To explore this possibility, samples of ESO were degraded at 250° C and then examined by ^{13}C NMR spectroscopy. The spectrum of a typical fully-epoxidized soybean oil is shown in Fig. 3. In this spectrum resonances due to the presence of oxirane carbon atoms appear at 52.8, 55.3 and 56.6 ppm. This suggests that all three kinds of double bonds have undergone

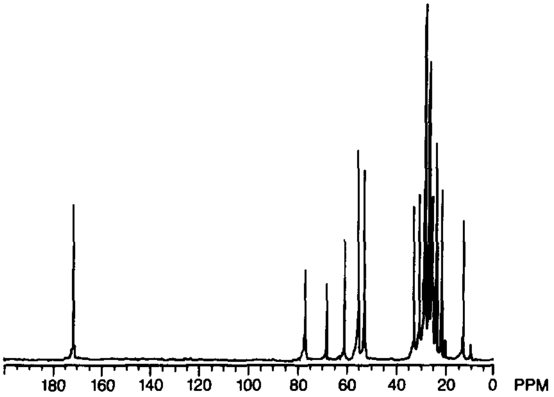


Fig. 3. The ^{13}C NMR spectrum of a typical fully-epoxidized soybean oil.

relatively complete epoxidation. Samples of this material were heated at 250 °C in an oven for varying lengths of time and then analyzed by ^{13}C NMR spectroscopy. The level of oxirane present in these samples could be readily determined from the ratio of the areas of the resonances due to the oxirane carbon atoms to those of the glyceryl OCH and OCH_2 resonances at 68.5 and 61.6 ppm, respectively. The results are displayed in Table 1.

Undoubtedly some degradation occurs even at short times at 250 °C. However, changes due to degradation are not apparent in the NMR spectra of the samples through 20 min of heating. Beyond that time the decrease in oxirane content as a function of time at 250 °C may be readily quantified. The appearance of broad resonances between 65 and 85 ppm accompany the decrease in oxirane absorption. Other changes are also apparent. The samples were observed to yellow after about 40 min and to become insoluble after 90 min at 250 °C. The sample heated for 90 min only swelled in deuterochloroform and the sample heated for 150 min did not swell significantly.

The spectrum of the sample held at 250 °C for 90 min is shown in Fig. 4.

TABLE 1

Thermal degradation of ESO at 250 °C

Sample	Degradation time (min)	Mol oxirane/mol ESO
1	0	4.5
2	10	4.5
3	20	4.5
4	40	4.3
5	60	3.7
6	90	0.6
7	150	(Insoluble)

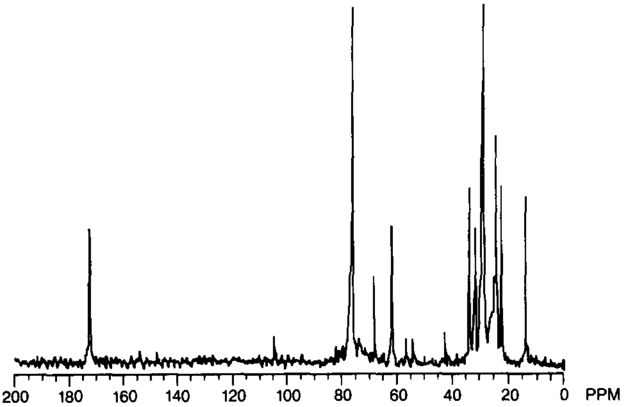


Fig. 4. The ^{13}C NMR spectrum of a typical fully-epoxidized soybean oil maintained at 250 ° C for 90 min.

The broad resonances due to the presence of degradation products are readily apparent in this spectrum. It is important to note that although 87% of the oxirane groups initially present have undergone conversion to some other species, the distribution of oxirane functionality remaining is identical to that in the starting material, i.e. there would seem to be no difference in the degradation characteristics of the various oxirane groups in ESO. The degradation chemistry cannot be defined from this spectrum or those of other degraded samples because the resonances are so broad but the breadth of the lines suggests that the molecular motion of the carbon atoms has been restricted as the result of chemical reaction. The chemical shifts (65 to 85 ppm) of product resonances are consistent with the presence of ether structures. In sum, the foregoing may be suggestive of intermolecular ether formation which arises as a consequence of thermally-induced oxirane ring-opening.

To probe the behavior of ESO in the presence of both thermal stress and a highly chlorinated resin, blends of ESO (fully epoxidized) with a VDC/VC copolymer, a VDC/MA copolymer and PVC were examined using thermal methods. The DSC thermograms of the VDC copolymer/ESO blends contain two exotherms, the first (T_p = 211° C) corresponding to the irreversible oxirane ring-opening for ESO and the second (T_p = 245 ° C) corresponding to the exothermic degradative dehydrochlorination of the polymer. The DSC thermograms for the PVC/ESO blends lack the second exotherm. The data from the DSC studies are presented in Tables 2 and 3.

These data indicate that ESO undergoes decomposition in the presence of these chlorine-containing polymers and that the exothermic heat of reaction is proportional to the amount of ESO present. This is even more apparent from Fig. 5.

The exothermic heat of ESO decomposition varies linearly with ESO content in the blend and is independent of the chlorine-containing polymer

TABLE 2

Decomposition of ESO in the presence of VDC polymers

Copolymer	ESO present (pph)	Onset temperature (°C)	ESO decomposition[a] peak temperature (°C)	ΔH_D ($J g^{-1}$ sample)
VDC/MA	1	172	194	−4.1
	2	172	202	−7.2
	5	172	210	−18.6
	10	172	215	−36.8
VDC/VC	1	174	201	−3.8
	2	176	204	−8.4
	5	176	214	−18.1
	10	176	218	−33.5

[a] All values are averages of duplicate runs; temperatures are reproducible to ±2°C and heats of decomposition to ±0.5 $J g^{-1}$.

matrix. The heat of decomposition of ESO is the same in a VDC/VC, a VDC/MA or a PVC polymer matrix. The average value for ΔH_D is −394 $J g^{-1}$ ESO (−90 $kJ mol^{-1}$ oxirane oxygen). The low temperature oxirane ring-opening (type I in Fig. 1) of ESO accounts for approximately one-third of the total ring-opening observed for ESO (−33 $kJ mol^{-1}$ oxirane oxygen versus a total of −90 $kJ mol^{-1}$ oxirane oxygen).

The exotherm corresponding to ring-opening of ESO in these blends begins at approximately 175°C and is complete between 210°C and 230°C. In this temperature range, the vinylidene chloride polymers undergo significant dehydrochlorination. The fate of the hydrogen chloride produced is impacted by the presence of ESO. As can be seen from the data in Table 4 the time required for complete oxirane ring-opening, as evidenced by the temperature at which ring-opening is complete, increases as the level of ESO in the blends increases, i.e. complete oxirane ring-opening is dependent upon sufficient hydrogen chloride being generated. For the blend containing two

TABLE 3

Decomposition of ESO in the presence of VC polymer

Polymer	ESO present (pph)	Onset temperature (°C)	ESO decomposition[a] peak temperature (°C)	ΔH_D ($J g^{-1}$ sample)
PVC	1	178	215	−4.1
	2	178	222	−7.4
	5	178	236	−20.0
	10	178	244	−34.2

[a] All values are averages from duplicate runs; temperatures are reproducible to ±3°C and heats of decomposition to ±1.0 $J g^{-1}$.

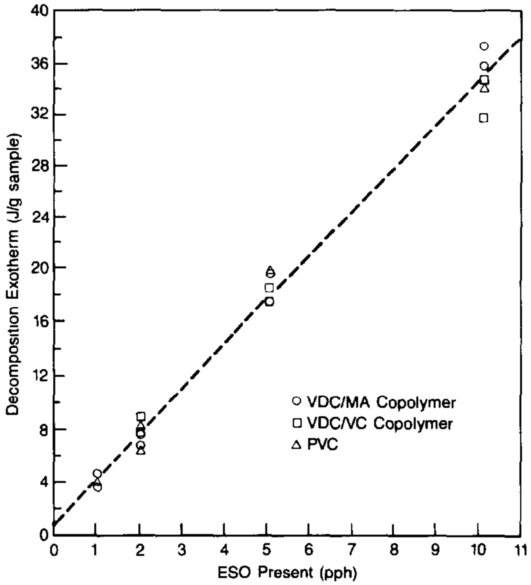


Fig. 5. Heat of ESO decomposition for ESO/polymer blends as a function of ESO loading.

parts ESO per hundred parts resin, ring-opening is complete at 208° C. In contrast, for the blend containing 10 pph ESO, ring-opening is not complete until a temperature of 220° C is reached.

Examination of the decomposition of blends of ESO with the VDC/MA copolymer by thermogravimetry provided little additional insight. The weight

TABLE 4

Decomposition of ESO as a function of temperature for blends of ESO with a VDC/MA copolymer

Temperature	ΔH_D (% reaction)		
	2 pph ESO	5 pph ESO	10 pph ESO
172	0.0	0.0	0.0
180	3.0	1.2	0.44
185	10.5		
190	24.2	7.5	3.4
195	46.1		
200	74.5	27.4	13.3
205	96.3		
208	100.0		
210		80.4	44.1
213		97.1	
214		100.0	77.6
218			98.7
220			100.0

loss versus temperature profiles for blends containing 0, 5, and 10 pph ESO are essentially identical. It is possible that at temperatures where weight loss is significant, particularly in the presence of basic stabilizers [11], that the reaction of hydrogen chloride with oxirane functionality is reversible. This is known to be the case for PVC stabilization. In this instance the ESO acts as a reactive transfer agent to deliver hydrogen chloride to the primary stabilizer [6,7].

CONCLUSIONS

Epoxidized soybean oil undergoes thermal degradation to form ring-opened products. In the absence of other reactants, the primary degradation reaction would appear to be intermolecular ether formation. Fully epoxidized soybean oil (7.0 wt.% oxirane oxygen) appears to contain two types of oxirane groups: type I which begins to undergo thermal ring-opening at about 175 °C and type II which opens at > 325 °C. Both ring openings are exothermic and irreversible. Type I oxirane groups account for approximately one-third of the total oxirane content of fully-epoxidized soybean oil. Partially epoxidized soybean oil (3.28 wt.% oxirane oxygen) contains only type II oxirane functionality.

The thermal degradation of ESO in a highly-chlorinated polymer matrix appears to be facilitated by reaction with hydrogen chloride generated by polymer degradation. The stability of the adduct produced, as well as the role of ESO as a polymer additive, remains unclear. It seems probable that its role as a plasticizer and as a processing lubricant far overshadow any part it may play in the stabilization of these materials.

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