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THE DETERMINATION OF THE TRANSFORMATION PRODUCTS OF EPOXIDES USED IN THE HEAT STABILIZATION OF POLY(VINYL CHLORIDE)

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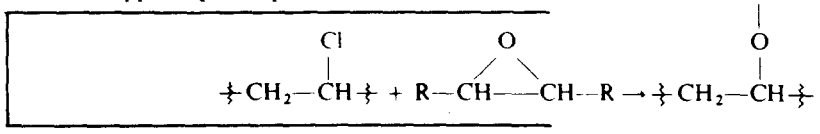
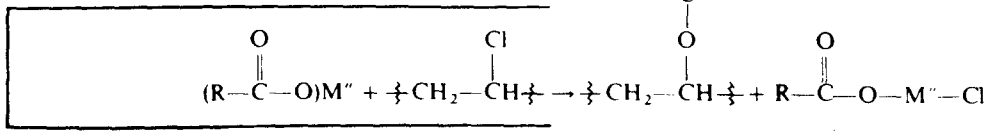
Abstract—Methyl 9, 10-epoxyoctadecanoate has been used as a model compound to study the mode of action of epoxides when employed in the stabilization of poly(vinyl chloride) (PVC). Sheets of PVC containing 2% radioactively labelled methyl (1-[^{14}C]) 9,10-epoxyoctadecanoate (both with and without calcium/zinc stearate) were prepared on a hydraulic press and subsequently heated in an oven for various times to simulate heat processing. The polymer was separated from the low molecular weight components by steric exclusion chromatography, the extent of bonding of epoxide to the polymer being monitored by the [^{14}C] activity of the high molecular weight fraction, and the level of residual methyl 9,10-epoxyoctadecanoate being determined colorimetrically on the basis of the epoxide concentration. The main transformation product was identified by combined gas chromatography–mass spectrometry as the methyl 9,10-chlorohydroxyoctadecanoate which was subsequently quantified after suitable derivatization by electron capture gas chromatography. A direct correlation was shown between the loss of epoxide and the extent of heat processing but this loss could not be fully accounted for on the basis of the estimated levels of chlorohydrins.

INTRODUCTION

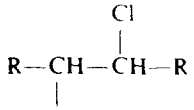
Aliphatic epoxy compounds, particularly epoxidized soya bean oil, are widely used as both stabilizers and plastizers in PVC compositions [1, 2]. In the role of stabilizer, epoxides are generally regarded as 'secondary', useful only to enhance the effectiveness of metal soaps (e.g. calcium/zinc stearate) [3, 4] but they may also function as emulsifiers for the metal soap [5] and lubricants during mixing [6]. Although it has been generally assumed that the mechanism of synergistic stabilization by epoxides in PVC involves reaction with hydrogen chloride (the elimination of which is the principal mode of PVC degradation) leading to the formation of chlorohydrins, there is little factual evidence supporting this speculation.



Data on residual epoxide and chlorine levels after treatment of epoxy compounds with hydrogen chloride, and changes in specific viscosity on heat processing have been interpreted as indicating only initial formation of the chlorohydrin as an intermediate, which then undergoes further reactions [7]. Subsequent intermolecular dehydrochlorination of the chlorohydrin to form a product with simple ester



bonds, or alternatively dehydrochlorination of the initially formed chlorohydrin proceeding intramolecularly to reform the epoxy compound which is then polymerized by the action of hydrogen chloride, has been proposed [7]. The latter suggestion of a reversible reaction has also been postulated elsewhere [8], where epoxy compounds are envisaged as transporting hydrogen chloride from the source of formation (polymer degradation) to the site of the acceptor (metal soap primary stabiliser). Somewhat in contrast it has been proposed [9] that the epoxide functions by bonding to the polymer molecule substituting a stable ether group for an unstable chlorine atom on the polymer chain.



This reaction is said to be catalyzed by metal ions and in particular by cadmium.

More substantial evidence from radioactivity studies [10] has led to a similar proposal of polymer bonding, this time via an ester linkage for the stabilization of PVC with metal soaps.

However, the synergistic involvement of epoxides has not been studied in relation to this system.

In this paper we have employed methyl 9,10-epoxyoctadecanoate as a model compound to study the action of epoxides as stabilizers for PVC in the presence and absence of calcium/zinc stearate. Our interest has been primarily in the identity and amount of transformation products formed in the PVC, as a source of constituents for migration from plastic packaging materials into foodstuffs rather than an interest in a detailed understanding of the mechanism. However, the identification and quantification of transformation products, together with radiochemical balance studies of the additive present after processing, inevitably lead to some speculation about the stabilization mechanism.

In order to assess losses of additive through bonding to the polymer and to quantitate recoveries of otherwise "unknown" components, [^{14}C] radiochemical labelling of methyl 9,10-epoxyoctadecanoate was employed. Steric exclusion chromatography, previously shown to be a valuable technique for isolating polymer additives [11], was used for the initial separation of the low molecular weight components from the polymer fraction. The chlorohydrin transformation product was previously shown to be unstable to gas chromatographic analysis [12] although it can be analysed as the trimethylsilyl derivative [12].

However, to enhance sensitivity and increase selectivity, the electron capturing flophemesyl derivative [13] was formed and quantification was carried out with ethyl 9,10-chlorohydroxyoctadecanoate as an internal standard introduced prior to steric exclusion chromatography.

EXPERIMENTAL

(i) *Materials*

PVC resin of a type commonly used for bottle manufacture was supplied by ICI Plastics Ltd (Welwyn Garden City, U.K.) and the calcium zinc stearate stabiliser (mark LN 28) was obtained from Lankro Chemicals.

(ii) *Preparations*

(a) *Methyl (1-[^{14}C]) 9,10-epoxyoctadecanoate.* Methanol (20 ml) and conc H_2SO_4 (5 ml) were added to (1-[^{14}C]) 9,10-octadecenoic acid (5 g) (250 μCi obtained from Radiochemical Centre, Amersham) and heated under reflux for 30 min. The product was added to 6% NaCl solution (50 ml) and extracted with hexane (3 × 20 ml). The combined extracts were washed with $NaHCO_3$ solution (2%) dried over $MgSO_4$ and the solvent removed on a rotary evaporator.

Epoxidation of the methyl ester was carried out in chloroform solution with 3-chloroperbenzoic acid (BDH, Poole, U.K.) using 5% molar excess of reagent and allowing the reaction mixture to stand overnight at room temperature. After washing successively with equal volumes of sodium metabisulphite solution (5%), $NaHCO_3$ solution (5%), and water the solution was dried over Na_2SO_4 and the solvent removed on a rotary evaporator to give an overall yield of 86%. The purity of the product was checked by gas chromatography.

In order to obtain a desired specific activity for incorporation in pressed PVC sheets, the [^{14}C] product was diluted with an appropriate amount of inactive material.

(b) *Ethyl 9,10-epoxyoctadecanoate.* Ethyl 9,10-epoxyoctadecanoate was prepared in an analogous manner to the above from 9,10-octadecenoic acid and ethanol, at an overall yield of 90%.

(iii) *Manufacture of PVC sheets*

PVC base resin (100 g) was coated with methyl (1-[^{14}C]) 9,10-epoxyoctadecanoate (2 g) by slurrying in diethyl ether; after solvent removal, the resin was dried for 2 hr at 35° in a vacuum oven. For the sheets containing calcium/zinc stearate (1 g), mixing with the resin prior to coating was carried out initially in a pestle and mortar and then by tumbling the powder on a "Rolamix" for 2–3 hr. PVC resin was pressed into sheets at 15 tons pressure/170° for a minimum possible time (approx 45 sec) on a hand operated hydraulic press with heated platens (George E. Moore & Son, Birmingham, U.K.). Heat processing was then simulated in a fan circulating oven at 170° by taking a series of strips from the same pressed sheet, heating for various times, and at the end of the heat treatment rapidly cooling by immersion in cold water, wiping dry and storing at −20° in the dark prior to subsequent analysis.

(iv) *Isolation of low molecular weight fraction by steric exclusion chromatography*

A detailed evaluation of the procedure for the separation of low molecular weight components (M_W < 1000) by steric exclusion chromatography using Sephadex LH60 (Pharmacia, Uppsala, Sweden) has been reported elsewhere [11]. PVC (0.04–0.06 g) accurately weighed into a screw capped vial and dissolved in redistilled THF (2 ml) was chromatographed in the usual manner [11] at a flowrate of up to 6 ml/min. Two bulk fractions were collected, the first containing the polymer, the second the additive. The fractions were then immediately evaporated under vacuum at 35° to either a small volume and transferred for analysis, or evaporated to dryness, redissolved in a volatile solvent (normally diethylether) and transferred for subsequent analysis.

(v) *Liquid scintillation counting*

All counting was carried out using a Beckman liquid scintillation counter (Model LS-100C) with a preset energy window covering [^{14}C] and [^{3}H] (0–0.156 meV). Aliquots of polymer (up to 0.07 g PVC) or additive in THF (up to 3 ml) were transferred to polyethylene scintillation vials (Koch-Light Ltd) and scintillator (9 ml) consisting of 2,5-diphenyloxazole (4 g/l in toluene) was added. Counting efficiencies were determined from an external standard ratio, and counting was normally continued until 40,000 counts had been accumulated (2σ = 1%) or for 20 min.

(vi) *Estimation of epoxide concentration*

The epoxide concentration was estimated by a modification of the picrate method of Fioriti *et al.* [14, 15] Aliquots (1 ml) of the ethereal epoxide solution (after steric exclusion chromatographic separation) contained in a 25 ml volumetric flask were mixed with 0.2 ml of 0.25 M solution of picric acid in ethanol and allowed to stand for 24 hr. The solutions were made up to volume with NaOH (1%) in 20:80 water:ethanol and the absorption at 490 nm measured immediately. A linear calibration curve was obtained for amounts of methyl 9,10-epoxyoctadecanoate covering the range 0–0.001 g.

(vii) *Estimation of methyl 9,10-chlorohydroxyoctadecanoate by electron capture gas chromatography as its flophemesyl derivative*

Standard solutions (4 mg/ml) of each of the methyl and ethyl 9,10-chlorohydroxyoctadecanoate were prepared from the corresponding epoxide by dissolution in ethereal HCl, evaporation to dryness and making to volume with diethyl ether. For chlorohydrin estimations, ethyl 9,10-chlorohydroxyoctadecanote was employed as internal standard, a calculated level being added by syringe to the weighed PVC contained in a small vial. After allowing the ether to evaporate, the THF was added and the PVC allowed to dissolve prior to steric exclusion chromato-

graphic separation. For recovery experiments and for blanks, PVC processed sheet (heated for similar times) but with no additives present was employed. The low molecular weight fraction (90 ml THF solution) containing the chlorohydrins was evaporated to dryness under vacuum at 40°, and the residue transferred to a 2 ml screw capped vial with diethyl ether and then blown to dryness under a stream of N_2. Pyridine (10 μl) and flophemesylamine (2–10 μl) (Lancaster Synthesis Ltd, St Leonard Gate, Lancaster) were added and the mixture allowed to stand for a few minutes at room temperature to effect derivatisation. The reaction mixture was then diluted with diethyl ether (0.2–2.0 ml) and the solution analysed by electron capture gas chromatography.

The apparatus used consisted of a Pye 104 chromatograph equipped with a ^{63}Ni electron capture detector. The column 33 m × 0.5 mm i.d. glass SCOT coated with SE 30 (SGE Ltd, London) was pressure controlled at a H_2 carrier gas flow-rate of 5 ml/min, with a N_2 make-up gas employed to give a total flowrate of 65 ml/min through the detector. The column temperature was 260° and the detector operated at 300° in a pulsed mode with a spacing of 150 μsec.

Quantification was based on integrated peak areas of the ratio of the methyl to the ethyl flophemesyl chlorohydrin. From prior experience, levels of internal standard were chosen to give an approximate 1:1 ratio and the level of methyl chlorohydrin thereby estimated from a series of calibration runs carried out with differing absolute amounts of the standards.

(viii) *Gas chromatography-mass spectrometry*

Confirmation of the identity of methyl 9,10-chlorohydroxyoctadecanoate isolated from processed PVC was carried out by combined GC-MS. Spectra were obtained on a Du Pont model 21-490B mass spectrometer interfaced with an all-glass jet separator to a Varian 2700 gas chromatograph. A 6′ × 2 mm i.d. glass column packed with 3% OV1 on Diatomite CLQ (100–120 mesh) was operated isothermally at 260° with a He carrier gas flow of 30 ml/min.

RESULTS

(a) *Development of methodology*

Initially a series of PVC sheets were pressed for between 0 and 30 min, the heating being wholly provided by the platens. As there was irreproducibility in the extent of degradation within an individual sheet, it was decided to press sheets for a minimum possible time (*ca.* 45 sec) and then heat strips cut from the same sheet for various times.

The steric exclusion chromatographic procedure had previously been evaluated in terms of showing quantitative recovery of low molecular weight polymer additives [11]. However, some additional evaluation was carried out using both active and inactive methyl 9,10-epoxyoctadecanoate. Recoveries on the basis of picrate measurements from solutions (containing between 0.1–1.0 mg epoxide) in THF with added PVC (50 mg) were 96.8% (standard deviation of 10 measurements = 3.5) and experiments using [^{14}C] labelled epoxide (1 mg = 0.008 μCi) showed recoveries of 100%. The possibility of degradation of THF causing interferences in the picrate determination was examined and solutions of epoxide in THF found to give consistent results over several days dark storage with either stabilised or re-distilled THF. A blank of THF, re-distilled and stored for several days, gave a negligible response; in practice PVC samples were analysed within 12 hr of addition of THF for dissolution.

(b) *Distribution of additive in coated polymer and pressed sheets and its loss through volatilization*

As facilities for milling of resin and additives prior to processing were not available, it was important to examine the polymer coating procedure for even distribution of epoxide. PVC resin coated as described was shown in a single batch to have a specific activity of 0.0901 μCi/g with a standard deviation of 1×10^{-3} μCi/g indicating an essentially uniform distribution.

During heat processing, both for the initial brief heating on the press and for subsequent oven heat treatment, a loss of overall activity was found and attributed to volatilization of the epoxide. Examination of a number of PVC samples taken from recorded positions on a single sheet showed mean levels of activity of 0.0896 μCi/g near the centre of a sheet dropping to 0.0858 μCi/g near the outside edge. Strips of PVC cut from single sheets were therefore carefully chosen to minimise local variation within a single strip. Table 1 shows the losses of activity through volatilization for portions of three such individual sheets, after having been subjected to heat treatment for various times in air-circulating oven at 170°. Losses of up to 8% of the initial activity in the pressed sheet occurred during processing times of up to 30 min. Hence all subsequent results have been corrected for this loss of activity and are therefore expressed on the basis of residual total active material present in the PVC sheet at the end of the heat treatment.

(c) *Identification and quantification of methyl 9,10-chlorohydroxyoctadecanoate*

Figure 1 shows the mass spectrum of the flophemesyl derivative of methyl 9,10-chlorohydroxyoctadecanoate isolated by steric exclusion chromatography from PVC heat treated for 15 min. This spectrum showed good agreement with the authentic compound. Characteristic fragment ions at m/e 367 and 411 demonstrated the presence of an unresolved mixture of positional chlorohydrin isomers as previously observed [12], the fragments produced by cleavage between the adjacent carbons bearing the chlorine and -*O*-flophemesyl groups. Details of the mass spectra of flophemesyl chlorohydrins will be published elsewhere [16] Figure 2 shows a typical chromatogram for a PVC sample illustrating the separation of the methyl derivative from the corresponding ethyl internal standard. The chromatogram was free of interferences although two additional electron captur-

Table 1. Effect of processing time on the loss of total [^{14}C] activity through volatilization

Processing time at 170° (min)	Percentage of original activity Individual sheets			Mean
0	100	100	100	100
5	97	98	98	98
15	96	94	95	95
30	90	90	92	91

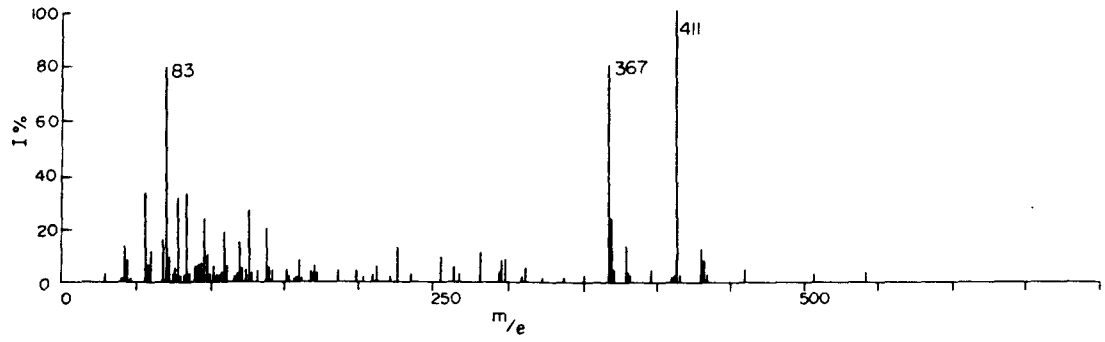


Fig. 1. Mass spectrum of flophemesyl derivative of methyl 9,10-chlorohydroxyoctadecanoate isolated from heat processed PVC sheet containing the corresponding epoxide.

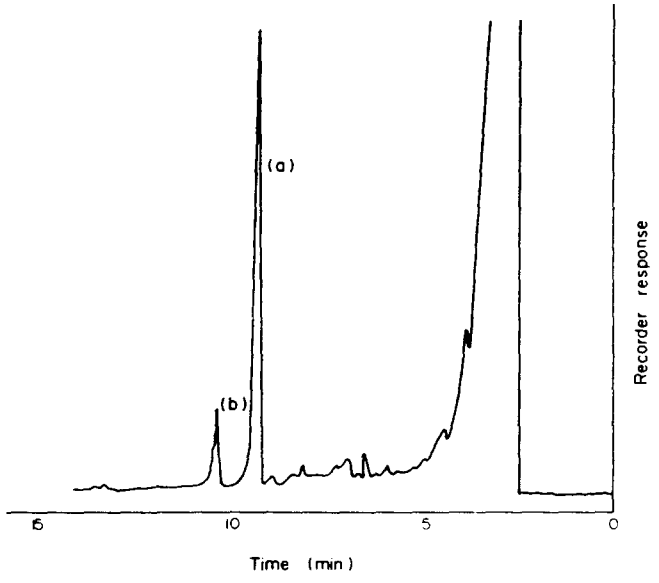


Fig. 2. Gas chromatogram with electron capture detection showing the flophemesyl derivatives of (a) methyl 9,10-chlorohydroxyoctadecanoate and (b) ethyl 9,10-chlorohydroxyoctadecanoate isolated from heat processed PVC containing methyl 9,10-epoxyoctadecanoate. Column: 33 m × 0.5 mm i.d. SCOT coated with SE 30; flowrate 5 ml/min H_2; temperature isothermal at 260° (attenuation 2 × 10^2).

Table 2. Effect of processing time on the residual level of methyl 9,10-epoxyoctadecanoate and on the extent of formation of the chlorohydrin transformation product

Processing time at 170° (min)	Methyl 9,10-epoxyoctadecanoate level* (% w/w in PVC) Individual sheets			Mean	Methyl 9,10-chlorohydroxy octadecanoate level (% w/w in PVC) Individual sheets			Mean	Missing methyl 9,10 epoxy octadecanoate (converted to other unidentified products) (mean % w/w in PVC)
					(a) 2% *epoxide*				
0	1.67,	1.78,	1.71	1.72	0.012,	0.010,	0.013	0.012	0.09
5	1.33,	1.53,	1.59	1.48	0.050,	0.027,	0.025	0.034	0.35
15	0.96,	1.08,	1.05	1.03	0.17,	0.21,	0.16	0.18	0.59
30	0.18,	0.20,	0.15	0.18	0.39,	0.42,	0.46	0.42	1.15
					(b) 2% *epoxide* + 1% *calcium/zinc stearate*				
0	1.83,	1.86,	1.84	1.84	0.019,	0.004,	0.008	0.010	0.05
5	1.64,	1.75,	1.58	1.65	0.057,	0.023,	0.045	0.041	0.17
15	1.12,	1.17,	1.12	1.14	0.40,	0.29,	0.36	0.35	0.31
30	0.11,	0.05,	0.10	0.09	0.63,	0.37,	0.55	0.51	1.15

* Initially present at 1.97% w/w in the coated polymer.

Table 3. Effect of processing on the extent of association of [^{14}C] activity with the high molecular weight fraction after steric exclusion chromatography

Processing time at 170 (min)	[^{14}C] activity associated with high M_W material (% of total activity) Individual sheets			Mean	Mean overall recoveries [sum of activities of fraction (1) and fraction (2)]
			(a) 2% *epoxide*		
0	0.46,	0.82,	1.53	0.93	101
5	0.54,	0.61,	0.73	0.62	100
15	1.08,	1.26,	1.10	1.14	98
30	1.55,	1.57,	2.35	1.82	98
			(b) 2% *epoxide* + 1% *calcium zinc sterate*		
0	0.29,	1.02,	1.20	0.83	98
5	1.08,	0.56,	1.04	0.89	99
15	3.08,	1.99,	1.92	2.33	99
30	1.58,	3.54,	4.01	3.04	95

ing components of longer retention times (not shown) were found in the PVC samples and could be additional transformation products.

DISCUSSION

Table 2 presents data showing the loss of measurable epoxide and the extent of formation of the chlorohydrin transformation product as a function of processing time. When epoxide was present alone, 90% was lost after 30 min of heating whereas, for the system with the additional calcium/zinc stearate, 95% was lost after the same period. In contrast, for up to 15 min heating the rate of loss of epoxide was less for the calcium/zinc stearate than for the sheet without stabilizer. This fits well with the physical appearance of the two types of degraded sheets; less discolouration was evident for up to 15 min heating for the calcium/zinc stearate sheet showing the effect of the primary stabilizer, whereas at some time between 15 and 30 min the well known "catastrophic" blackening occurred with the calcium/zinc stearate system, resulting in an increased evolution of HCl, and therefore increased loss of epoxide.

Some similar trend is evidenced from the measured levels of chlorohydrin present in the degraded sheets, although our main interest has been in the overall balance and the fact that, for sheets heated for 30 min, up to 63% of the lost epoxide was still unaccountable in terms of identified transformation products. Further work is in progress on the identification and quantification of these additional products.

The results in Table 3 show that by steric exclusion chromatography quantitative recovery is possible on the basis of activity distributed between the two fractions. The extent of bonding to the polymer although somewhat variable is clearly low (from between 0.6 and 3.0%) and there is a trend towards increased bonding with increasing heat processing, and a greater degree of bonding in the system additionally stabilized with calcium/zinc stearate. Previous predictions [9] as to polymer bonding of epoxide via an ester linkage have been based on model systems employing chloroalkenes as degrading PVC and cyclohexene oxide as a model epoxy plasticizer, for which reactions were carried out in organic solvents. The attraction of model systems to facilitate isolations and identification of reaction products is easy to understand, but the results presented here make it evident that data so obtained cannot be correlated with the true situation in a stabilized polymer system. For this reason in future work we shall be extending our studies to the use of an epoxy triglyceride to replace methyl 9,10-epoxyoctadecanoate, and to examine the effect of additional additives e.g. phosphites on loss of epoxide and on the rate of chlorohydrin formation. In this way results can be more closely related to the true situation for formulations employed in commercial practice.

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