Reaction of epoxidized soya bean oil (ESBO) with hydrogen chloride formed in PVC: investigation on model systems

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Introduction

Epoxidized Soya Bean oil (ESBO) is widely used as an additive in poly(vinyl chloride) (PVC) and poly(vinylidene)chloride type materials. It serves as a plasticizer and as a scavenger for hydrochloric acid liberated from PVC during heat treatment applied for manufacturing.

ESBO became an issue in 1998 (1), when it was discovered that ESBO may migrate into baby foods sold in glass jars with metal lids in amounts exceeding the tolerable daily intake (TDI). ESBO is added to the PVC gasket sealing the lid against the glass jars; typical concentrations are 30–50 g/100 g. This seal must be rather soft to provide safe tightness at reasonable pressure (ease of opening). Subsequent surveys (3, 4) showed that the situation did not improve up to 2001.

The TDI of ESBO defined by the EU is 1 mg/kg body weight per day (5), based on a toxicological assessment performed in 1988 (6). This TDI results in a maximum tolerated migration (for adults of 60 kg) corresponding to the overall migration. On the basis of this, the use of ESBO as additive was authorized in Europe without a specific migration limit (SML) in foods (EU directive 72/2002 EC).

There is a second worrying issue concerning ESBO, the first time addressed some 25 years ago: the reaction products of ESBO with HCl formed during the manufacture of the lids, i.e. heat treatment for curing at about 200°C. These products formed by the intended activity as HCl scavenger have neither been fully identified, nor toxicologically tested – although chlorohydrins are commonly considered as toxicological alerts. *Gilbert et al.* (7–10) studied them using epoxidized methyl oleate and trioleate as model compounds. They identified the

expected chlorohydrins, but more than half of the removed epoxy fatty acids did not show up in the chromatograms. Dimers and trimers formed by reaction between the epoxidized trioleate and chlorohydrins were shown not to be the sink for the converted material and, hence, much of the transformation material was left unexplained.

The problem was tackled again in 2001 (11). ESBO or its fatty acid methyl esters (FAME) were reacted with HCl and the resulting products analyzed by GC-MS. Epoxy oleic acid was found to be largely converted to the chlorohydrins, but epoxidized linoleic acid formed a complex mixture and many of the compounds did not seem to be chlorohydrins. The vicinity of an epoxy group to the chlorohydrin in the partially reacted diepoxy linoleic acid was expected to be the cause: the hydroxyl group of the chlorohydrin attacks the neighboring epoxide. Cyclic reaction products incorporating a chloro atom are to be expected. However, these compounds have not been confirmed, nor did they seem to explain all the signals observed in GC-MS. The sum of the identified and unidentified reaction products observed in the gas chromatogram corresponded to less than half of the removed epoxy linoleic acid, i.e. the problem observed by *Gilbert et al.* was not resolved. The reaction products of epoxidized linolenic acid are even more complex and were not investigated.

The quantity of the ESBO reaction products migrating into the food could only be estimated. The ESBO in the gasket contained roughly 1 % chlorohydrin of the epoxy oleic acid (10). From model experiments it was extrapolated that this ESBO must have also contained several percents of derivatives of the epoxy linoleic and linolenic acid, reaching up to 5–10 % reacted ESBO. Since there is no reason to assume that partially reacted ESBO migrates into food to another extent than ESBO itself (derivatized epoxy fatty acids are on the same glycerol moiety as the underivatized), a migrate of 50 mg/kg ESBO in the food (the maximum found was 140 mg/kg (3)) is expected to be accompanied by up to 2.5–5 mg/kg reacted ESBO.

As it seemed little promising to invest into further work into the derivatives of epoxidized fatty acids, experiments were performed with more simple model substances, i.e. 1-epoxy-octane and epoxidized 1,4-pentadiene. The latter served as a model for linoleic acid, since the two double bonds are separated by a methylene group. GC separation of their derivatives of low molecular weight is more efficient, the risks of thermal degradation is reduced, the dimers are chromatographed more easily (visible in GC), and the mass spectra are more simple.

Experimental

1,2-epoxy-octane, 1,4-pentadiene, 4-chloro-perbenzoic acid, N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) and low molecular weight (Mr ~48000) poly(vinyl chloride) (product 81388) were purchased from Fluka (Buchs, Switzerland).

Partial conversion of 1,2-epoxy-octane to chlorohydrins. 750 mg each of 1,2-epoxy-octane and 1,3,4-trimethylbenzene (pseudocumene, internal standard) were

mixed with 370 µl of concentrated hydrochloric acid (stoichiometrically ²/₃ of the epoxy-octane) and allowed to stand at ambient temperature during 1 h. 10 µl of the reaction mixture was silylated by addition of 30 µl BSTFA and 10 µl pyridine, heating to 60 °C for 30 min. For GC analysis, this mixture was completed to 10 ml with methyl tert. butyl ether (MTBE), then further diluted 1:10 with MTBE.

The partial chlorohydrins were heated in a Pasteur pipette with flame-sealed ends. Mostly 20 µl of the reaction mixture were brought to 200 °C for 15 min in an oven. The tip of the pipette containing the sample was crushed in an autosampler vial, then the reaction product silylated and diluted as described above.

For GC-MS analysis, the following mass spectrometers were used: Finnigan SSQ7000 quadrupole (Finnigan, San Jose, USA), QMD 1000 quadrupole, or PolarisQ ion trap (ThermoFinnigan, Milano, Italy), applying electron impact (EI) or chemical ionization (CI) with ammonia or methane as reagent gas. GC involved instruments from ThermoFinnigan. With the exception of figure 2, a 30 m×0.32 mm i.d. column coated in the laboratory with a 0.15 µm film of PS-255 (dimethyl polysiloxane; Fluka) was used with a 15 cm×0.53 mm i.d. deactivated uncoated precolumn; inlet pressure, 85 kPa (helium). 1 µl was injected on-column at 40 °C, followed by a temperature program of 5 °/min to 160 °C (5 min) and 20 °/min to 250 °C (10 min).

Synthesis of 1,2-4,5-diepoxy-pentane. 300 mg 1,4-pentadiene was epoxidized by addition of 2.4 g 4-chloro-perbenzoic acid in 24 ml chloroform (10). The mixture was allowed to stand overnight at ambient temperature, then washed three times with 5 ml sodium sulfite (5 g/100 ml), three times with 5 ml sodium bicarbonate (5 g/100 ml) and twice with 5 ml water. 50 mg 1-ethylnaphthalene was added as non-reacting internal standard.

Experiments with 1,2-4,5-diepoxy-pentane. Partial chlorohydrins were formed adding to 100 µl of the diepoxy-pentane solution in chloroform between 1.5 and 60 µl of a mixture of 10 % concentrated hydrochloric acid in tetrahydrofurane (THF) and allowing the mixture to stand at ambient temperature for 1 h. Before silylation, 50 µl of pyridine was added and the solvent reduced to about 40 µl in a stream of nitrogen (avoiding serious loss of volatiles during solvent evaporation). Then 100 µl BSFTA was added and the mixture heated to 60 °C for 15 min. For GC analysis, this mixture was filled up to 10 ml with MTBE.

For heating experiments, 100 µl of the partial chlorohydrins was transferred into a Pasteur pipette with a flame-sealed tip, the solvent removed by a fine stream of nitrogen and the pipette closed in a flame. After heating, the pipette was extracted with 50 µl pyridine and this extract silylated and diluted.

Experiments with PVC. A low molecular weight PVC was dissolved in THF at 50 mg/ml. 100 µl of diepoxy-pentane and 160 µl of PVC solution (12 g/100 g diepoxy-pentane referring to the PVC) were introduced into a pipette, the solvent gently removed and the pipette flame-sealed. After heating, the residue was extracted with pyridine (leaving behind some insoluble residue).

Results

Reaction of 1,2-epoxy-octane with HCl

Figure 1 shows GC-MS (EI) total ion chromatograms of 1,2-epoxy-octane partially reacted with HCl. The upper chromatogram is from the mixture obtained at ambient temperature. Apart from the internal standard and the non-reacted epoxy-octane, two peaks are observed, presumably representing the "normal" and the abnormal reaction products (1-chloro-2-hydroxy-octane and 1-hydroxy-2-chloro-octane, respectively). The EI mass spectra confirmed the molecular mass (236 Dalton for the silylated compounds) and the presence of one chloro atom. For the normal addition product, a 25% signal confirmed the loss of 49 (CH_2Cl), while there was no such signal for the abnormal product.
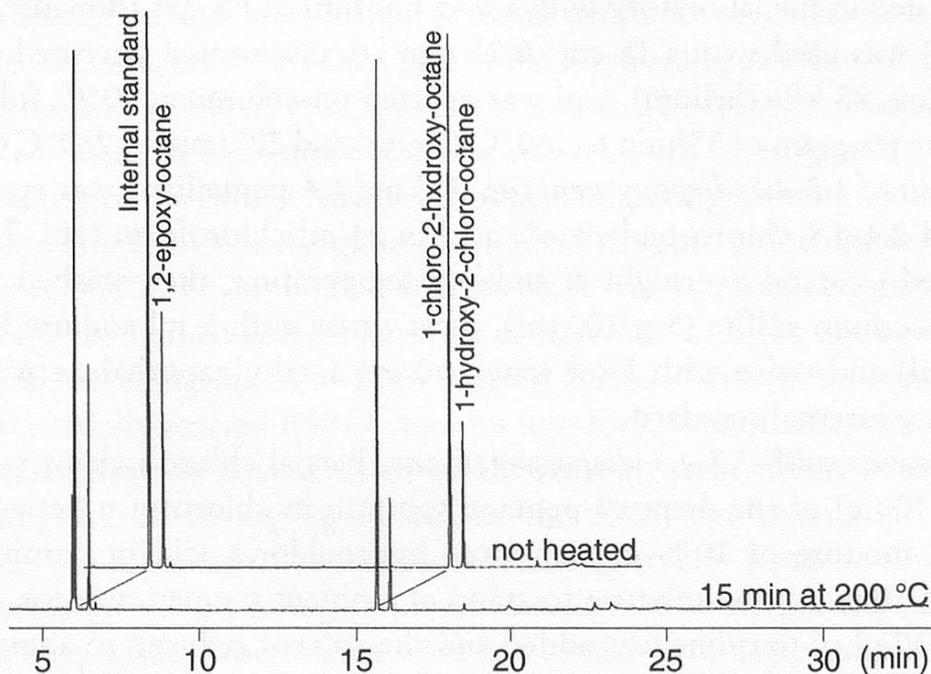
Figure 1 **GC-MS (EI) total ion chromatograms of the chlorohydrins of 1,2-epoxy-octane before and after heating. Internal standard, 1,3,4-trimethylbenzene**

Heating this partially reacted epoxy-octane to 200 °C for 15 min (shown in the lower chromatogram of figure 1) or to 250 °C for 30 min had no relevant effect on the chromatograms: there was no additional peak representing a new product formed by reaction within the molecule or between molecules, such as a dimer (the hydroxy group of a chlorohydrin reacting with the epoxy function of non-reacted epoxy octane). The peak areas of the chlorohydrins hardly decreased compared to the internal standard (from 50.4 to 48.7%). GC-MS analysis with CI did not show traces of dimers, with a detection limit of about 0.3% related to the original epoxy-

octane. It was concluded that the reaction of HCl with a mono-epoxy compound (such as epoxy-oleic acid) forms chlorohydrins which are stable during the heat treatment typically applied during the use of ESBO.

Reaction of diepoxy-pentane with HCl at ambient temperature

Epoxidation of 1,4-pentadiene formed a pair of peaks of equal size. The two mass spectra were virtually identical and confirmed that the two diastereomers of 1,2-4,5-diepoxy pentane were obtained (chiral carbon atoms in positions 2 and 4). This means that each peak represents a pair of enantiomers.

Figure 2 shows the relevant sections of GC-FID chromatograms from diepoxy-pentane partially reacted with HCl at ambient temperature as well as after heating to 200°C for 15 min. A 60×0.25 mm i.d. column coated with a 0.2 μm film of PS-255 was used. There are two principal groups of peaks representing HCl-reaction products, with the internal standard, 1-ethyl naphthalene, between them.
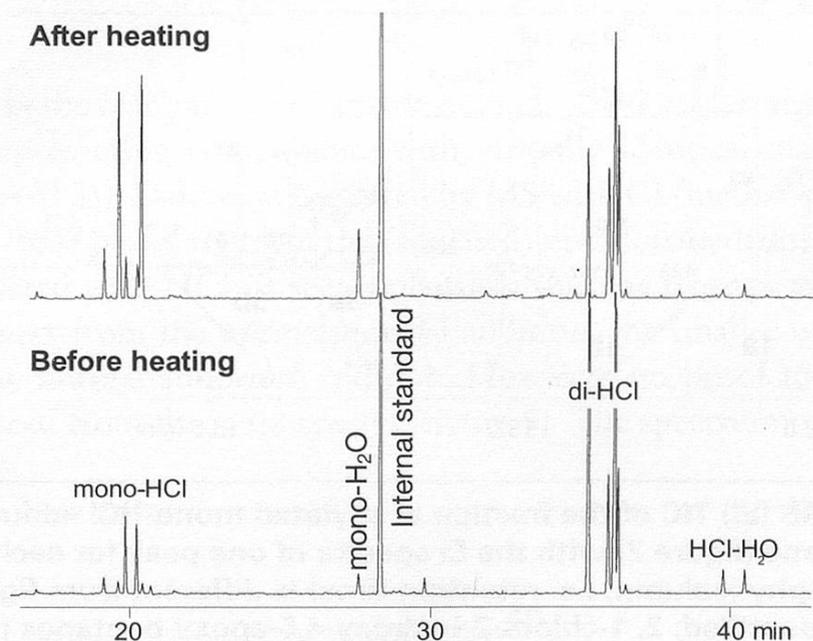
Figure 2 The mono- and di-HCl reaction products from diepoxy-pentane as obtained at ambient temperature and with heating to 200°C for 15 min. Internal standard, 1-ethyl naphthalene

In the chromatogram of the reaction products obtained at ambient temperature ("before heating"), three pairs of peaks were observed in the range of retention times of the products reacted with a single HCl (region called "mono-HCl"). Chemical ionization (CI) with ammonia and methane confirmed that all these silylated components have a molecular mass of 208 Dalton, corresponding to diepoxy pentane with one HCl added. Also the presence of one chlorine is confirmed for all

components. The EI mass spectra of the peaks forming a pair were not significantly different, suggesting that they represent diastereomers. One spectrum of each pair is shown in figure 3. From the MS fragmentation, no clear conclusions could be drawn on the structures. It is expected that the pair of large peaks 2a and 2b represents the normal HCl adduct, i.e. 1-chloro-2-hydroxy-4,5-epoxy-pentane (figure 4), the following pair of smaller peaks (3a and 3b) the abnormal adducts, 1-hydroxy-2-chloro-4,5-epoxy-pentane. Each of these compounds exists as four isomers resulting from the two chiral carbons in positions 2 and 4, i.e. two diastereomers composed of two non-separated enantiomers. The first eluted pair of small peaks (1a and 1b) could not be identified.
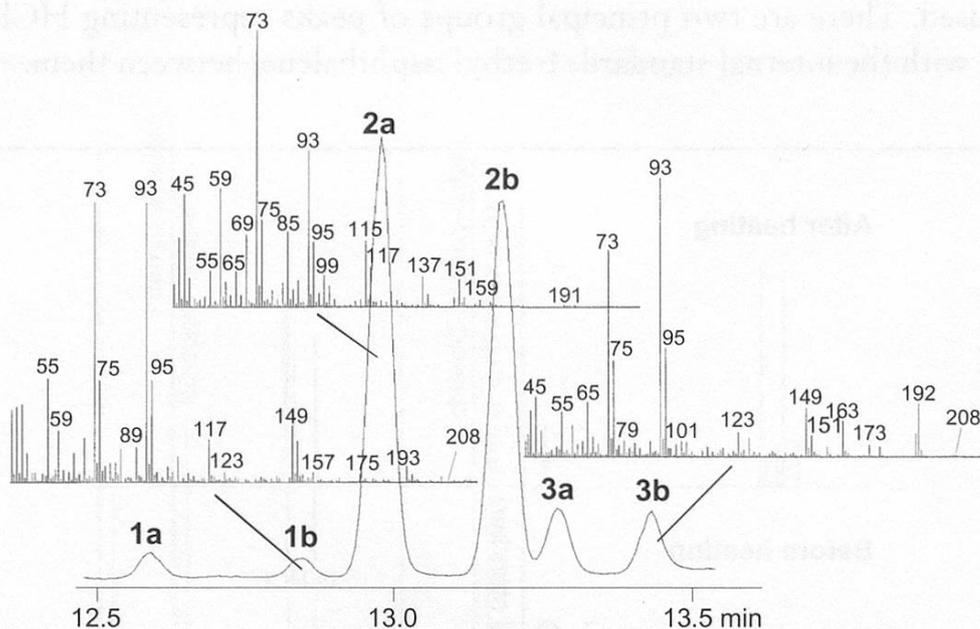

Figure 3 **GC-MS (EI) TIC of the fraction of silylated mono-HCl adducts of diepoxy-pentane (figure 2) with the EI spectra of one peak for each pair. Chromatography (column, i.e. retention time) is different from figure 2. Peaks 1, not identified; 2, 1-chloro-2-hydroxy-4,5-epoxy-pentanes (two diastereomers); 3, 1-hydroxy-2-chloro-4,5-epoxy-pentanes**

A sample of the partially reacted diepoxy-pentane was treated with an excess of HCl at ambient temperature in order to confirm the presence of an epoxy group. The peak pairs 2 and 3 were totally removed (converted to the di-chlorohydrins), but the first eluted pair of small peaks was not affected. This suggests that the first pair differs from the two others in a modified epoxy group, whereby this modification has no effect on the molecular weight. The conversion of the epoxide to a carbonyl group would fit, but presupposes that equal amounts of the aldehyde and ketone (carbonyl in 1 and 2) were formed in order to explain the double peak (there are no diastereomers of the ketone). The mass spectra were not conclusive on this hypothesis.
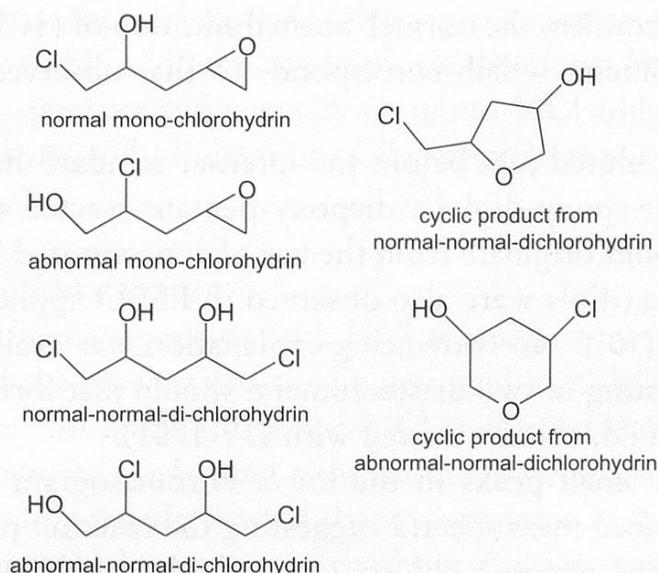
Figure 4 **Chemical structures of some of monomeric derivatives formed by reaction of diepoxy-pentane with HCl**

The peaks in the rear part of the chromatogram ("di-HCl" in figure 2) form two pairs, again representing components with virtually identical mass spectra. The molecular mass of 316 Dalton, as observed by MS with CI (methane and ammonia), confirms that these peaks are from the (silylated) di-chlorohydrins, i.e. both epoxy groups are reacted with HCl. It seems plausible that the large peaks 4a and 4b are the diastereomers from the normal-normal addition, the smaller ones (5a and 5b) those from the normal-abnormal addition. However, no proof for this structure could be deduced from the mass spectra (figure 5). The spectrum of component 4a

Figure 5 **GC-MS (EI-TIC) of the silylated di-HCl adducts with the mass spectra for one peak of each pair**

contains a strong signal at m/z 117 which is virtually absent in the spectrum of component 5a. It might confirm the normal-normal addition of HCl by a ring formation in the mass spectrometer which corresponds to that observed upon heating (see figure 7).
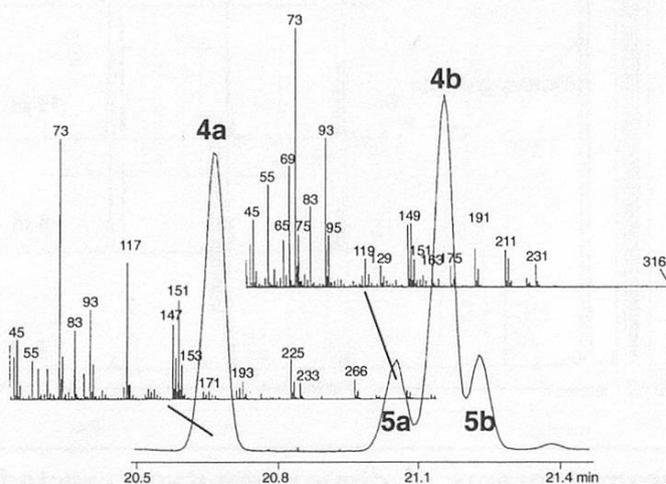
The single peak eluted just before the internal standard has a molecular mass corresponding to the epoxy-diol, i.e. diepoxy-pentane reacted with one molecule of water. The water could originate from the use of concentrated hydrochloric acid in the reaction mixture (diols were also observed in ESBO applications in gaskets or organosol coatings (10)). No convincing explanation was available, however, why this compound (existing in two diastereomers) should just form a single peak (also on a 30 m×0.25 mm i.d. column coated with OV-1701).

The last pair of small peaks in the lower chromatogram of figure 2 (labeled "HCl-H$_2$O") produced mass spectra suggesting the reaction products of diepoxy-pentane with HCl and water (1-chloro-2,4,5-trihydroxy pentane). In this case, the two diastereomers are widely separated.

Independent reaction of the two epoxy groups of diepoxy-pentane or diepoxy-linoleic acid would suggest that with the rather small amount of HCl released from PVC virtually only mono-chlorohydrins are formed. However, the model experiment showed a different behavior. As shown in figure 6, an amount of HCl stoichiometrically corresponding to merely 3 % of the epoxy groups resulted in
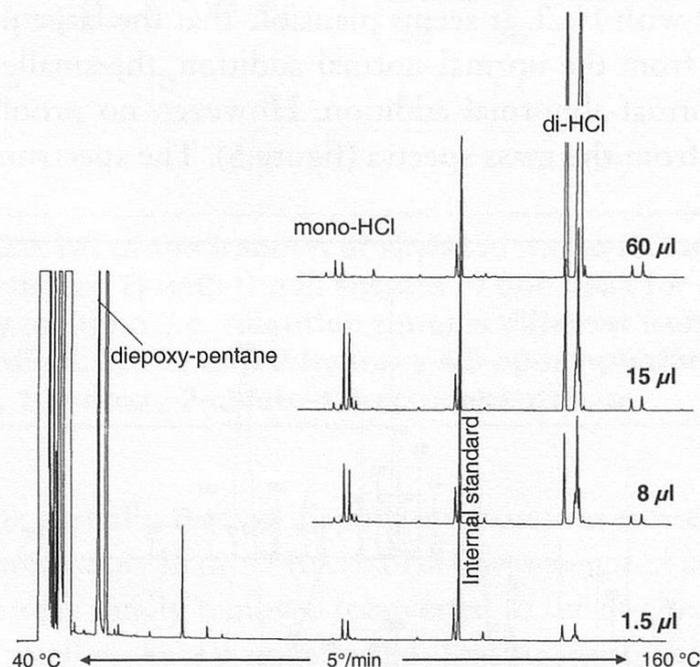

Figure 6 **GC-FID chromatograms of diepoxy-pentane reacted with 1.5–60 µl of HCl solution (stoichiometrically corresponding to 3–120 % of the epoxy groups). The internal standard, 1-ethyl naphthalene, corresponded to 20 g/100 g of the 1,4-pentadiene used to form the diepoxy-pentane**

approximately equal formation of the mono- and di-HCl adducts. In the early part of the chromatogram, the non-reacted diepoxy-pentane is visible. With larger amounts of HCl, the di-HCl adducts predominate the mono-HCl. With 60 µl HCl-solution, no diepoxy-pentane and virtually no mono-HCl adducts were left – with the exception of peaks 1a and 1 b mentioned above which do not seem to contain an epoxy group.

Heating of the reaction mixture

The reaction of diepoxy-pentane with HCl at ambient temperature only simulates the first step of the conversions the linoleic acid in ESBO undergoes in PVC materials, because in real applications the HCl is formed during heat treatment. These additional reactions at elevated temperature were simulated by heating the solvent-free mixture of partially reacted diepoxy-pentane to 200 °C for 15 min. It should be expected that the heat treatment without dilution (compared to a concentration of 10–50 g/100 g in a PVC matrix) favors the intermolecular reaction (dimer formation) compared to the intramolecular reaction. The small molecular weight of our model compound should further accentuate this.

As shown in the upper chromatogram of figure 2 and the enlarged section of a similar chromatogram in figure 7, heat treatment produced two new, large peaks eluted amongst the mono-HCl adducts (peaks 6a and 6b). They are different from those observed after reaction at ambient temperature. The peaks of the mono-HCl adducts are still there, although smaller. Most of the material forming the new peaks must have its origin in the two large peaks of the normal-normal di-chlorohydrins
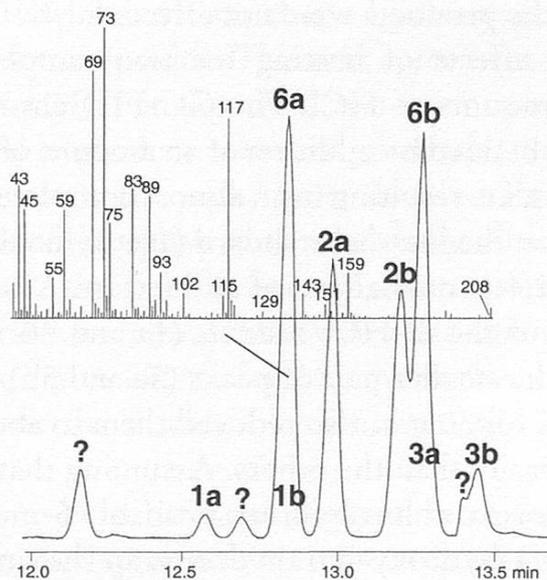

Figure 7 **GC-MS (EI-TIC) of the mono-HCl fraction after heating, i.e. with the thermal degradation products 6a and 6b; peaks 1–3 labeled in correspondence with figure 3; EI mass spectrum of peak 6a**

(peaks 4a and 4b), which are clearly reduced in size. Also a substantial part of the mono-chlorohydrins 2a and 2b was removed. The absence of new peaks of a size corresponding to the reduction of peaks 2a and 2b suggests that these mono-chloro-hydrins were converted to the same components as the di-chlorohydrins 6a and 6b.

The EI mass spectra of the two new peaks 6a and 6b were virtually identical, suggesting stereoisomers. Since peak 6a overlapped peak 1b, the virtually identical spectrum from peak 1a was subtracted. The CI spectra indicated a molecular mass of 208 Dalton, which corresponds to that of the silylated mono-HCl adducts; the presence of one chlorine is confirmed. Ring formation is assumed: starting from the normal-normal di-chlorohydrin, the hydroxy group in position 2 substitutes the chlorine in position 5, resulting in the tetrahydrofuranic structure shown in figure 4. Starting from the normal mono-chlorohydrin, the hydroxy group in position 2 reacts with the epoxy group in position 5 and results in the same substituted tetrahydrofuran. There is no firm proof for the assumed structure. The fragment m/z 159 without chlorine isotope results from the loss $Cl-CH_2$. The signal m/z 117 might seem to be from the loss of the silylated hydroxy function, but the absence of chlorine suggests cleavage of the ring (silylated ethanol).

Additional evidence for the cyclic structure was obtained from acetylation, a test on the presence of epoxy groups previously used for the confirmation of reaction products formed in epoxy coatings from bisphenol A diglycidyl ether (BADGE) (11). In a first step, the mixture was derivatized with acetanhydride/pyridine at 50°C for 30 min to acetylate the hydroxyl groups (instead of silylation). Under these conditions, epoxy groups remain unaffected. Then the mixture was trifluoro acetylated with trifluoro acetanhydride (TFAA) at 50°C, opening the epoxy groups. Indeed, the mono-chlorohydrins were removed from the region in the chro-matogram, while the cyclic products were not affected.

Figure 8 shows the effects of heating for two samples of diepoxy-pentane reacted with different amounts of HCl. The GC-FID chromatograms on the left side are from a mixture obtained by addition of an amount of HCl corresponding to 80% of the epoxy groups, i.e. resulting in an almost complete conversion. The chro-matograms were scaled on the internal standard (1-ethylnaphthalene), which corre-sponded to 20% of the 1,4-pentadiene used at the start. After heating to 200°C for 15 min, the main peaks of the di-HCl adducts (4a and 4b in figure 5) were com-pletely removed, while the smaller pair of peaks (5a and 5b) remained largely unaf-fected. Heating to 220°C for 30 min also reduced them to about half, indicating that they also react, but less easily than the others. Assuming that the smaller peaks rep-resented the normal-abnormal chlorohydrins, probably 6-membered rings had been formed, i.e. the 2-chloro-4-hydroxy-tetrahydropyran shown in figure 4.

After heating to 200°C, the mono-chlorohydrins were completely removed from the 80% HCl sample. This is in contrast to the epoxy pentane reacted with less HCl shown in figure 2 and could be explained by the larger amount of HCl lib-erated by ring formation of the di-chlorohydrins: the HCl reacts with the mono-

80 % HCl

7 % HCl

30 min 220 °C

15 min 200 °C

15 min 200 °C

mono-HCl

mono-H$_2$O (?)

Internal standard

di-HCl

Not heated

Not heated

HCl-H$_2$O

90 °C → 145 °C
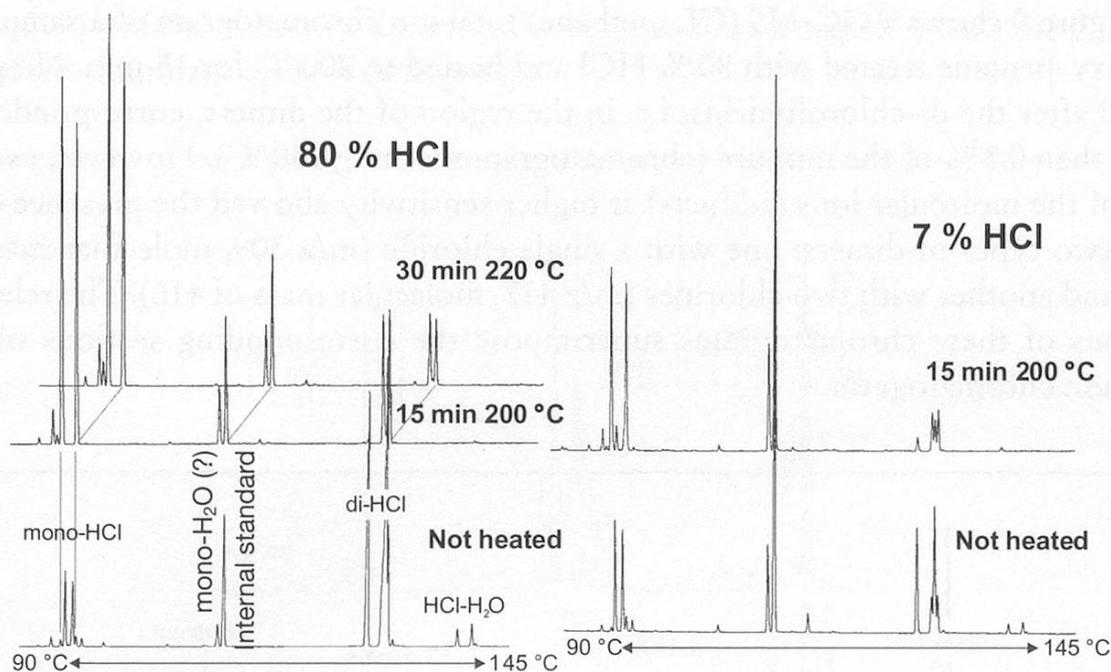
90 °C → 145 °C

90 °C → 145 °C

Figure 8 **Relevant sections of GC-FID chromatograms of diepoxy-pentane partially reacted with HCl at ambient temperature (lower chromatograms) and after heating.** Mixtures reacted with 80 or 7% HCl related to the epoxy functions

chlorohydrins and produces di-chlorohydrins, which in turn degrade to the tetrahydrofurans.

The observation that the di-chlorohydrins more readily undergo ring formation than the mono-chlorohydrins indicates that a hydroxy group more easily substitutes chlorine than attacks an epoxide. This is in agreement with the finding that the chlorohydrin-diols (HCl-H$_2$O in figure 2) were removed already by heating to 200 °C: they are expected to produce 1-hydroxymethyl-2-hydroxy-tetrahydrofuran (not investigated). Conversely the peak eluted shortly before the internal standard, with the molecular mass of the epoxy diol, was hardly affected.

The chromatograms at the right in figure 8, from a sample of diepoxy-pentane reacted with only 7% HCl, are about three times less attenuated (larger peak of the internal standard). Heating to 200 °C for 15 min neither completely removed the mono-chlorohydrins, nor the di-chlorohydrins, but the reaction paths were the same.

There did not seem to be substantial elimination of water or HCl resulting in unsaturated compounds. Such products are expected to have a short retention time. Search by the molecular ion (adduct) in CI total ion chromatograms did not reveal significant peaks.

Formation of dimers

Figure 9 shows a GC-MS (CI, methane) total ion chromatogram of a sample of diepoxy-pentane treated with 80% HCl and heated to 200°C for 15 min. No peak eluted after the di-chlorohydrins, i.e. in the region of the dimers, corresponded to more than 0.3% of the mixture (chromatogram reaching 250°C). However, extraction of the molecular ions (adducts) at higher sensitivity showed the presence of at least two types of dimers: one with a single chlorine (m/z 309, molecular mass of 308) and another with two chlorines (m/z 417, molecular mass of 416). The relevant sections of these chromatograms superimpose the corresponding sections of the total ion chromatogram.
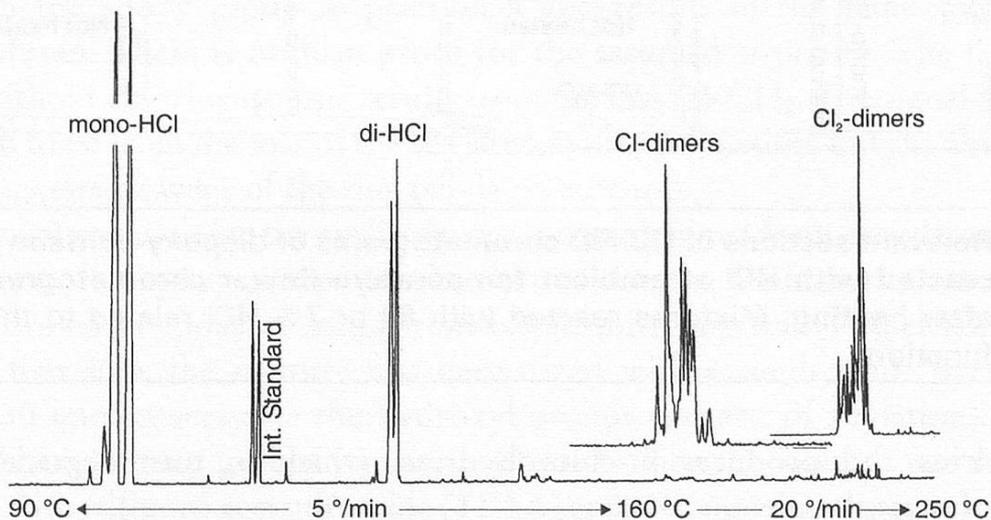

Figure 9 **GC-MS (CI) total ion chromatogram of diepoxy-pentane partially reacted with HCl at ambient temperature and heated to 200°C for 15 min; single ion chromatograms of two types of (silylated) dimers recorded at higher sensitivity above the corresponding region of the total ion chromatogram**

At the bottom of figure 10, the region of the GC-MS (CI) total ion chromatogram comprising the dimers is shown, starting immediately after elution of the water/HCl reaction products (HCl-H_2O in figure 2). Compared to figure 9, attenuation is strongly reduced. Above the TIC, the extract of m/z 173 is shown. The fragment m/z 173 is common to the epoxy-hydroxy-pentanes and 3-hydroxy-methylene-tetrahydrofurans and is formed by loss of a chlorine or a trimethyl siloxy function from a reacted epoxy group. It is an important or even the dominant fragment observed for all components eluted in the region of the mono-chlorohydrins (loss of chlorine) and the assumed epoxy diol, but is not observed for the di-chlorohydrins. In the rear part of the chromatogram, the section shown in figure 10, m/z 173 is a fragment from a majority of the compounds, indicating that most of these contain the epoxy-hydroxy-pentane or hydroxy-methylene-tetrahydrofuran

moiety. Above the m/z 173 extract, the relevant sections of the mono-chloro dimers (m/z 309) and the di-chloro dimers (m/z 417) are shown together with the CI spectra of the dominant peak of each group.
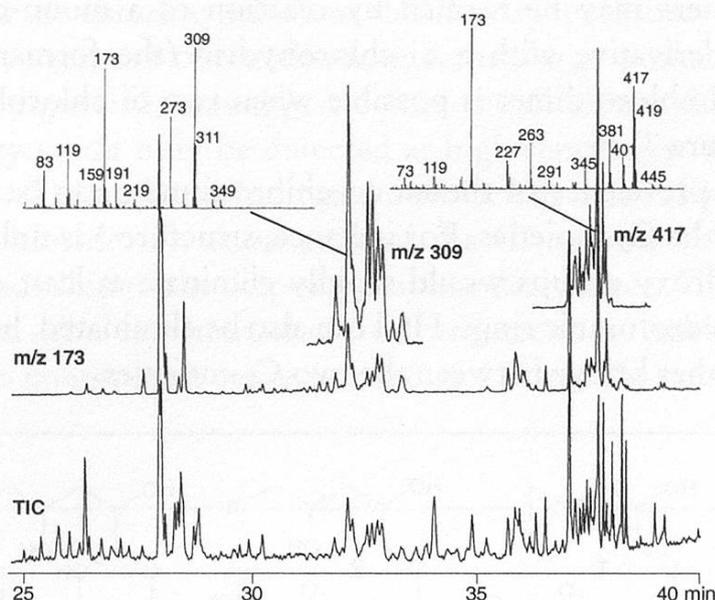

Figure 10 **Region of the dimers shown at high sensitivity: total ion chromatogram (CI-TIC), mass selective extracts of m/z 173 and the molecular adducts of two types of dimers, and CI mass spectra of the dominant compound of each group of dimers**

The two groups of dimers consist of a large number of compounds of similar structure. The most basic mono-chloro dimer results from the reaction of the hydroxy group of a mono-chlorohydrin with a diepoxy-pentane, opening the epoxy ring. To obtain structure 1 in figure 11, a normal chlorohydrin attacks the epoxy group of the diepoxy-pentane in the normal way. It must be assumed that there are three more products from abnormal reactions. For linoleic acid in ESBO, all 4 structures might be of similar importance, since there is no normal and abnormal attack. There are, of course, many diastereomers and enantiomers of these structures. The fragment m/z 173, representing the silylated epoxy-hydroxy-pentane, results from cleavage of the dimer at the ether bond, i.e. is from the upper part of the structure 1 in figure 11. Fragment m/z 119 is from the chlorine-containing lower half of the molecule. The same dimer is obtained from the reaction between two normal mono-chlorohydrins, the hydroxy group of the first substituting the chlorine of the second.

Since heat treatment rapidly forms the cyclic products, first of all the substituted tetrahydrofurans, cyclic structures are likely to be more important than the open chain structures: the hydroxy function of the tetrahydrofuran derivatives reacts

with a diepoxy-pentane or a mono-chlorohydrin (structure 4). Also the reverse is possible: the hydroxy group of the mono-chlorohydrin reacts with a tetrahydrofuran, substituting chlorine (structure 5). In this case, m/z 173 is from the hydroxy-methylene tetrahydrofuran. Also structure 6 should be expected, i.e. the hydroxy group of one tetrahydrofuran substituting the chlorine of another.

Di-chloro dimers may be formed by reaction of a mono-chlorohydrin or a tetrahydrofuran derivative with a di-chlorohydrin (the former shown in structure 2). Even a tri-chloro dimer is possible when two di-chlorohydrins react with each other (structure 3).

The observed prevalence of the mono-chloro dimers can be explained by ring formation within the C_5-moieties. For instance, structure 3 is unlikely to be important since the hydroxy groups would rapidly eliminate at least one HCl, forming one or two tetrahydrofuranic rings. HCl can also be eliminated, however, by formation of a second ether bridge between the two C_5-moieties.
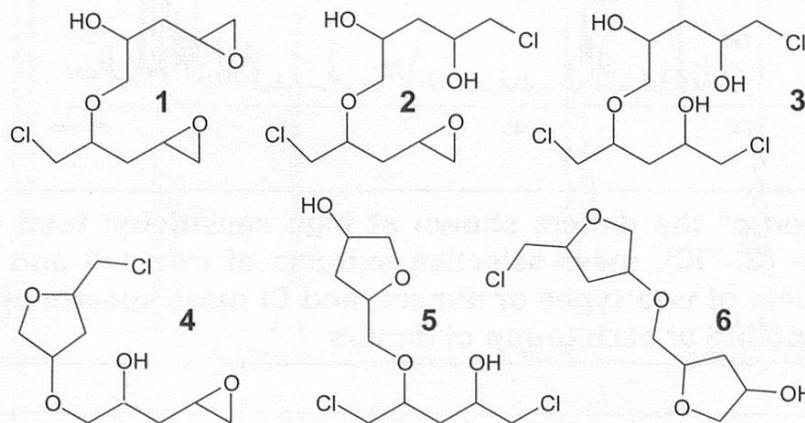

Figure 11 **Some possible structures of dimers starting from normal addition to epoxy groups**

The first group of peaks eluted at about 26–28 min in the total ion chromatogram and the m/z 173 fragmentogram of figure 10 represents components with a molecular mass of 280. Their structure was not identified. The group of peaks eluted at about 36.5 min, i.e. between the two types of dimers described above, is from the dimers containing a hydrolyzed epoxy group (diol) and, hence, from an epoxy-chlorohydrin reacted with an epoxy-diol building block.

This incomplete survey of possible dimers shows the complexity of the dimerisation process: the number of components formed is high and renders a quantitative determination of the dimers difficult. Adding up all peaks of the TIC in figure 10 without application of a response factor suggests the presence of 1–2% dimers. Analysis by size exclusion chromatography, grouping all these components to a single signal, showed that the dimers of ESBO fatty acids were below 10% (9, 10).

The analogous chromatograms from diepoxy-pentane treated with only 7% HCl were similar (GC-FID chromatogram in figure 12). Again, the peaks of the complex mixture of dimers could only be observed when sensitivity was massively increased. The mono-chloro dimers strongly dominated the di-chloro dimers (in the 80% HCl sample, the two were similar), presumably because the abundant reaction partner of the chlorohydrins was the diepoxy-pentane.

There are, however, the two additional, rather large peaks in the rear of the chromatogram of figure 12, eluted just before the di-chloro dimers. In the 80% HCl product, they could only be detected at high sensitivity. Their spectra were virtually identical. CI (methane) indicated a molecular mass of 328 Dalton and the presence of one chlorine. The base peak of the CI spectra was m/z 173, which confirms the relationship to the diepoxy-pentane derivatives. The structures could not be elucidated. The fact that there do not seem to exist diastereomers is puzzling. The two compounds corresponded to 11% of the converted material or 3.7% of the total.
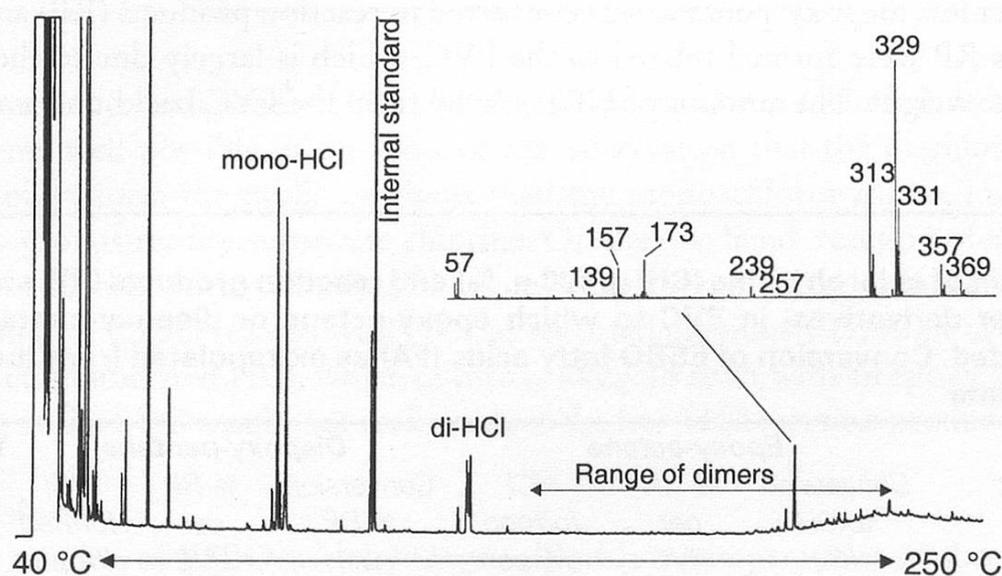
Figure 12 **GC-FID chromatogram of diepoxy-pentane treated with 7% HCl and heated to 200 °C for 15 min, showing two unidentified peaks in the range of the dimers, characterized by the CI mass spectrum**

Reaction in PVC

Epoxy-octane and diepoxy-pentane were added to PVC (mixed into dissolved PVC) in order to test their behavior in the matrix of interest. 12 g/100 g of the epoxy compounds were added, i.e. some three to four times less than ESBO is admixed to the PVC gaskets, taking into account the higher proportion of the epoxy functions on the molecular weight.

The experiment with epoxy-octane showed the formation of the two chloro-hydrins observed in figure 1. With heating to 200 °C for 15 min, 5 % of the epoxy-octane was converted to the chlorohydrins (table 1). This means that 0.6 % epoxy-octane was consumed related to the PVC or 0.15 g/100 g HCl was cleaved from the PVC (assuming full conversion to chlorohydrins). After heating to 220 °C for 30 min, 18 % of the epoxy-octane was converted to the chlorohydrins, correspon-ding to 0.6 g/100 g HCl released from the PVC. These results might be somewhat too low because there remained an insoluble residue, possibly enclosing some reac-tion products.

The analogous experiment with diepoxy-pentane primarily produced deriva-tives eluted from GC in the region of the mono-chlorohydrins (figure 13), i.e. mono-chlorohydrins and cyclic compounds. Some 5 times less di-chlorohydrins were observed, despite their rapid formation shown in figure 6, confirming that they rapidly react by ring formation and loss of HCl. The HCl probably reacts with another epoxy group. This means that the diepoxy compounds (diepoxy-pentane or diepoxy linoleic acid) essentially absorb merely one mole of HCl.

As shown in table 1, the quantitative data was similar to that of epoxy-octane: somewhat less diepoxy-pentane was converted to reaction products (RP) and some-what less RP were formed related to the PVC, which is largely due to the smaller molecular weight. The amount of HCl cleaved from the PVC backbone was almost identical.

Table 1

Formation of chlorohydrins (CH; g/100 g, %) and reaction products (RP; sum of CH and other derivatives) in PVC to which epoxy-octane or diepoxy-pentane have been added. Conversion of ESBO fatty acids (FA) as extrapolated from the epoxy-octane data

Heat treatment	Epoxy-octane			Diepoxy-pentane			ESBO-FA
	Conversion to CH (%)	% CH per PVC	HCl formed (% per PVC)	Conversion to RP (%)	% RP per PVC	HCl formed (% per PVC)	% RP per PVC extra-polated
200 °C, 15 min	5	0.6	0.15	3.3	0.4	0.15	1.3
220 °C, 30 min	18	2.2	0.6	11	1.3	0.5	4.7

From the HCl reacted with epoxy-octane, the amount of ESBO fatty acids was calculated which would have been converted in this particular PVC: after heating to 200 °C for 15 min, the PVC would have contained 1.3 g/100 g of HCl-reacted ESBO fatty acids. With 10 g/100 g ESBO in a PVC film or coating, 13 % of the ESBO fatty acids had reacted. Since migration of the reacted ESBO fatty acids is assumed to be the same as that of the other ESBO fatty acids, this also means that 13 % of the migrating ESBO fatty acids had consisted of HCl derivatives. In a gasket containing 30–50 g/100 g ESBO, some 3 % of the ESBO fatty acids had been converted.
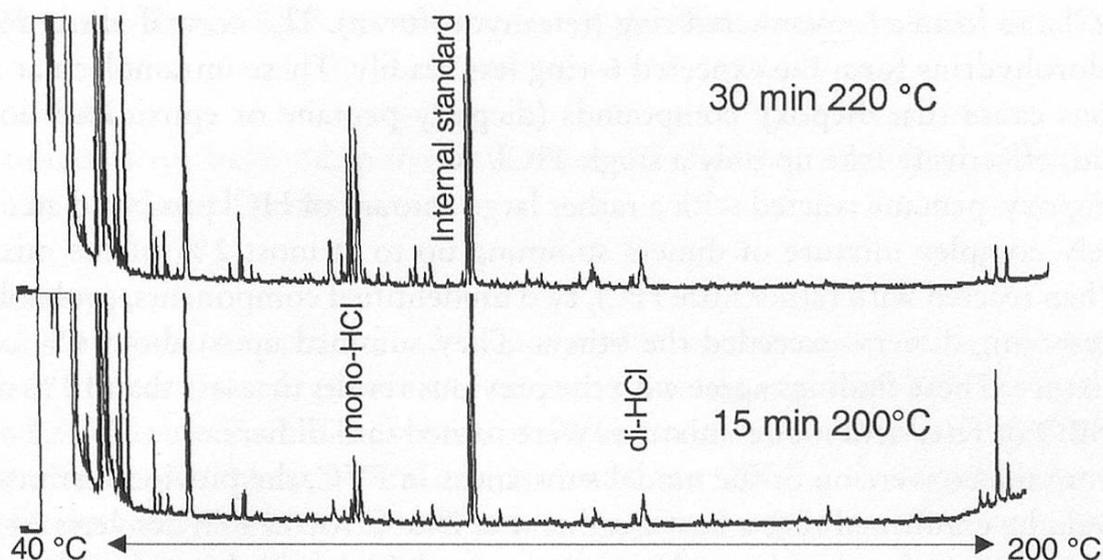
Figure 13 **GC-FID chromatograms of diepoxy-pentane admixed to PVC and heated to 200 or 220 °C. Internal standard corresponding to 5 g/100 g of the diepoxy-pentane**

It was not investigated whether HCl reaction products were bonded to PVC. This seems well possible in the light of the observation that the di-chlorohydrins more rapidly form the cyclic products than the mono-chlorohydrins, i.e. that the hydroxy groups readily substitute chlorine. On the one hand, reaction of a hydroxy group of a chlorohydrin with the PVC would explain the "disappearance" of epoxy compounds or ESBO reacted with HCl, as reported previously (9, 10). On the other, such reaction liberated HCl, which in turn is likely to react with an epoxy group, i.e. bonding to the PVC would not really reduce the free HCl reaction products.

Conclusions

The reaction of ESBO with hydrogen chloride at temperatures of about 200 °C, as commonly applied for curing PVC, was studied. Since the mixture of the reaction products seemed to be too complex to be analyzed for the fatty acids, first of all the epoxidized linoleic acid, model compounds were used: 1,2-epoxy-octane simulated oleic acid, 1,2-4,5-diepoxy-pentane linoleic acid. The results can be summarized by the following points:

1. Epoxy octane formed two chlorohydrins (positional isomers), which resisted 200 °C without relevant further modifications (including formation of dimers).
2. The reactions of the methylene-interrupted diepoxide (diepoxy-pentane, simulating linoleic acid) are more complex. At ambient temperature, HCl rapidly forms the di-chlorohydrins, even when the amount is small compared to the epoxy groups available (as in the real application of ESBO in PVC). This suggests that the two epoxy groups do not react independently of each other.

3. Upon heating to 200 °C for 15 min, the normal-normal di-chlorohydrins lose HCl and form a 5-membered ring (tetrahydrofuran). The normal-abnormal di-chlorohydrins form the expected 6-ring less readily. These intramolecular reactions cause that diepoxy compounds (diepoxy-pentane or epoxidized linoleic acid) effectively take up only a single HCl.
4. Diepoxy-pentane reacted with a rather large amount of HCl produced an extremely complex mixture of dimers summing up to at most 2 % of the mixture. When reacted with rather little HCl, two unidentified components, probably representing dimers, exceeded the others. They summed up to about 4 % of the mixture. These findings agree with the previous results that less than 10 % of the ESBO or fatty acid model mixtures were turned into dimers.
5. From the conversion of the model substances in PVC, the previous estimations could be confirmed that a heat treatment at 200 °C for 15 min converts 3–15 % of the ESBO fatty acids to chloro derivatives. It should, however, be kept in mind that the amount of HCl cleaved from PVC depends on several other factors, such as the purity of the polymer and the activity of the support surface.

The study left open the following points:
1. The identification of most components is plausible, but not irreproachably proven. Since mass spectrometry does not seem to be sufficiently specific, the key components should be isolated and investigated by other techniques.
2. It was not possible to determine whether or not material "disappeared" upon heat treatment. Owing to the volatility of the diepoxy-pentane and the unknown response factors of the derivatives, no balance could be calculated between the derivatives observed in the chromatogram and the diepoxide consumed.
3. It was not investigated whether chlorohydrins react with the PVC polymer. However, this is not relevant for the estimation of migrating reaction products since the reaction of a chlorohydrin with PVC liberates HCl and thus replaces the reacted chlorohydrin.
4. For structural reasons, the number of isomers resulting from the reaction of epoxidized linoleic acid is likely to be substantially higher than for the diepoxy pentane. For instance, there is no preference of the "normal" to the "abnormal" reaction product.
5. The mixture of the reaction products of linolenic acid with HCl is likely to be even more complex.
6. There remained unidentified peaks, such as the pair among the mono-chlorohydrins summing up to some 2 %, a not satisfactorily identified peak eluted just before the internal standard (suggested to be the epoxy-diol), the two peaks among the dimers (some 4 %) and others in the range of up to about 1 % of the mixture. If, for instance, 10 % of ESBO is converted and 50 mg/kg of ESBO migrates into food, 1 % unidentified material corresponds to 50 µg/kg in food, which may still exceed the threshold of toxicological concern (12).

Key words

Epoxidized soya bean oil, poly(vinyl chloride), lids for glass jars, epoxy-octane, diepoxy-pentane, chlorohydrins

Summary

1,2-Epoxy-octane and 1,2-4,5-diepoxy-pentane were used as chemical models to study the reactions of epoxidized oleic and linoleic acid with HCl, as they occur when ESBO is used as HCl scavenger in PVC. Epoxy-octane formed chlorohydrins which remained stable at typical curing conditions (200 °C, 15 min). Diepoxy-pentane formed mono and di-chlorohydrins. Heating caused ring formation, presumably with 2-chloromethyl-4-hydroxy-tetrahydrofuran as the main product. A complex mixture of dimers was observed, but the concentration of the sum of these remained below 5 % of the converted material. From the amount of derivatives formed it is deduced that heating to 200 °C for 15 min converts 5–15 % of the ESBO fatty acids into chloro-containing derivatives. This proportion should also be expected in the migrates.

Zusammenfassung

1,2-Epoxy-Octan and 1,2-4,5-Diepoxy-Pentan dienten als chemische Modelle zur Untersuchung der Reaktionen von Epoxyöl- und Diepoxylinolsäure mit HCl, wie sie mit ESBO ablaufen, das als HCl-Fänger in PVC eingesetzt wird. Epoxy-Octan bildete Chlorhydrine, die bei den normalerweise verwendeten Einbrennbedingungen (200 °C, 15 min) stabil blieben. Diepoxy-Pentan bildete Mono- und Dichlorhydrine. Erhitzung führte zu Ringbildung, mit 2-Chlormethyl-4-Hydroxy-Tetrahydrofuran als vermutetem Hauptprodukt. Eine komplexe Mischung von Dimeren wurde beobachtet, doch die Summe blieb unter 5 % des umgesetzten Materials. Aus der Menge der Derivate wird extrapoliert, dass sich bei 200 °C/ 15 min im PVC 5–15 % der ESBO-Fettsäuren zu chlorhaltigen Derivaten umsetzen und auch entsprechend im Migrat vertreten sind.

Résumé

1,2-Epoxy-octane et 1,2-4,5-diepoxy-pentane ont été utilisés comme modèles chimiques pour étudier les réactions des acides oléique et linoléique époxydés avec HCl, comme elles déroulent quand ESBO est employé comme scavenger de HCl dans le PVC. Epoxy-octane a créé des chlorhydrines, qui sont restés stables aux conditions du traitement typique du PVC (200 °C, 15 minutes). Diepoxy-pentane a formé mono- et di-chlorohydrines. Le traitement thermique les a converti en substances cycliques, probablement avec 2-chloromethyl-4-hydroxy-tetrahydrofurane comme produit principal. Un mélange complexe des dimères a été observé, mais la

concentration de la somme de ces composés était en dessous de 5 % du matériel converti. De la quantité des dérivés formées, il est déduit que chauffage du PVC a 200 °C pour 15 min convertit 5–15 % des acides gras d'ESBO dans des dérivés chlorées. Dans les migrats ils sont présent dans le même pourcentage.

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