

Thin-layer Chromatography of Epoxide Resins

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A simple thin-layer chromatographic technique is described for separating commercial epoxide resins into their various components. A method is described for the quantitative determination of the monomer content of bisphenol A - epichlorohydrin resins. The various components present in epoxide resins are separated on glass plates coated with silica gel G with chloroform as developing solvent. Optimum separation is achieved by giving two developments in chloroform. Details are given of a method for detecting hydrolysable chlorine containing components present in the resin. With the method described it is possible to distinguish between similar resins from different manufacturers.

THE effect of molecular weight on properties of cured epoxide resins of the bisphenol A - epichlorohydrin type has been known for some time when one considers resins ranging from liquids to high molecular weight solids. It has now been found that liquid epoxide resins with the same epoxide equivalent weight exhibit slightly different properties in the cured form, particularly with reference to their crack resistance. Four resins with the same epoxide equivalent were examined for crack resistance, namely, Epikote 828, Epophen EL-5, M 750 and R 18774/1. These differ in monomer content and also in the numbers and proportions of other components present.

Good correlation was found between crack resistance and monomer content. The resin with the highest monomer content (Epikote 828) showed least resistance to cracking, whilst that with the lowest monomer content (R 18774/1) showed greatest resistance to cracking. The two resins with similar monomer contents (Epophen EL-5 and MY 750) showed similar crack resistance, the results falling between those for the other two resins.

A thin-layer chromatographic technique was developed to examine the various commercial liquid epoxide resins and to look for differences in molecular weight distribution. This technique was then extended for use with solid epoxide resins of the bisphenol A - epichlorohydrin type, as well as epoxy novolacs and resins prepared from phenols other than bisphenol A.

A quantitative determination of the monomer content of several of the liquid epoxide resins was obtained by direct comparison of the spot area with that of a known amount of pure monomer. For this purpose an amount of pure monomer (diglycidyl ether of bisphenol A) was prepared as described in this paper.

EXPERIMENTAL

Commercial epoxide resins were chromatographed on glass plates coated with silica gel G, and the chromatogram developed twice in chloroform. The individual components were detected as mauve spots on a white background by spraying the plate with 50 per cent. chromic acid and heating to 105° to 110° C for 15 to 30 minutes. Fig. 1 illustrates the separation obtained with liquid epoxide resins, Fig. 2 illustrates the separation obtained with solid epoxide resins. With solid epoxide resins, on the assumption that the spots labelled $n = 1, 2, 3$, etc., are the normal molecular species (see Discussion and Results), it follows that migration is roughly proportional to molecular weight. This assumption is believed to be valid, although as yet no absolute proof of identity is available. This migration pattern was apparent after one development but less so after two developments, owing to the greater separation of the higher molecular weight species.

METHOD

APPARATUS—

Glass plates, 20 × 20 cm.

Chromatotank—This is obtainable from Shandon Scientific Co. Ltd.

REAGENTS—

All solvents should be of analytical-reagent grade.

Chloroform (*AnalaR*).

Ethanol (*absolute*).

Kieselgel G—This is obtainable from Shandon Scientific Co. Ltd. (E. Merck & Co.).

PQ Universal developer—(Ilford Ltd.).

RESINS—

Epikote 828 (liquid)—(Shell Chemical Co. Ltd.).

Epikote 1040 (solid)—(Shell Chemical Co. Ltd.).

Epikote RX 35 (liquid)—(Shell Chemical Co. Ltd.).

MY 750 (liquid)—(Ciba (ARL) Ltd.).

CT 200 (solid)—(Ciba (ARL) Ltd.).

X33/1189 (tetrafunctional; solid)—(Ciba (ARL) Ltd.).

LY 558 (epoxy novolac; solid)—(Ciba (ARL) Ltd.).

Epophen EL-5 (liquid)—(Leicester Lovell & Co. Ltd.).

Dobekot 502 (liquid)—(Dr. Beck & Co. Ltd.).

R18774/1 (liquid)—(Bakelite Ltd.).

DER 332 (liquid)—Obtainable from R. W. Greef & Co. Ltd. (Dow Chemical Co. Ltd.).

DER 542 (tetrabrominated; solid)—Obtainable from R. W. Greef & Co. Ltd. (Dow Chemical Co. Ltd.).

DER 511 (partially brominated; solid)—Obtainable from R. W. Greef & Co. Ltd. (Dow Chemical Co. Ltd.).

Bisphenol A—(Ciba (ARL) Ltd. and Shell Chemical Co. Ltd.).

Epichlorohydrin—(Ciba (ARL) Ltd.).

PROCEDURE—

Preparation of plates—A slurry was prepared by adding 70 ml of distilled water to 30 g of dry Kieselgel G and mixing them thoroughly. This was immediately used to coat the plates with a 250 to 300- μ thick layer of Kieselgel G with a conventional spreader.¹ The plates were air dried for 30 minutes at room temperature and then activated for 30 to 45 minutes at 105° to 110° C in an air-circulating oven. The activated plates were cooled and stored in a desiccator for at least 2 hours before use.

Pure monomer—Epikote RX 35 was distilled twice through an Edwards 2-inch falling-film molecular still at a pressure of 5 μ and a distillation temperature of about 175° C. The distillate obtained was then re-crystallised from absolute ethanol to which had been added up to 10 per cent. of distilled water. By choosing the re-crystallisation conditions correctly, crystals of pure monomer could be grown (m.p. 44.5° to 46° C; $C_{21}H_{24}O_4$ was found to contain 73.9 per cent. of carbon and 7.2 per cent. of hydrogen, actual values being 74.1 per cent. of carbon and 7.1 per cent. of hydrogen).

Chromatography—All the resins examined were prepared as 2 per cent. solutions in chloroform, and 0.015 ml of each solution spotted about 1.5 cm from the bottom edge of the plate. The plate was developed vertically in chloroform to a height of 15 cm in a tank lined with filter-papers. After development the plate was removed from the tank and the chloroform allowed to evaporate. When the tank atmosphere was unsaturated with chloroform one development was sufficient, but if the tank atmosphere was fully saturated two developments were found necessary for optimum separation. The separated components were detected as mauve spots by spraying the chromatogram with 50 per cent. chromic acid and heating to 105° to 110° C for 15 to 30 minutes.

Species containing hydrolysable chlorine were detected by spraying the dried chromatogram with aqueous N potassium hydroxide and heating to 150° C for 30 minutes. The chromatogram was then cooled and sprayed with ethanolic silver nitrate (0.05 N) and heated to 150° C for 15 minutes, cooled and sprayed with a mixture of equal volumes of concentrated nitric acid and 100 volume hydrogen peroxide. The chromatogram was then carefully developed in a dilute solution of nitric acid (1 + 30) and finally sprayed with concentrated PQ universal developer. (During this development the absorbent below the level of the developing solvent tended to flake off.) The hydrolysable chlorine containing species showed as black spots on a faintly grey background.

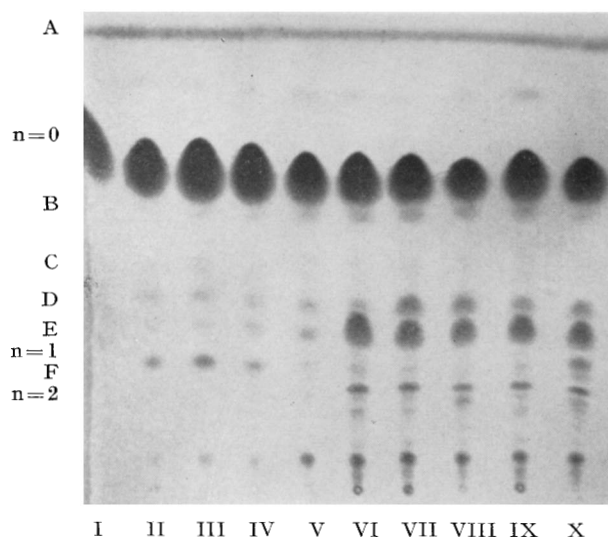


Fig. 1. The liquid epoxide resins examined and separated into their various components: I, monomer; II, twice distilled RX 35; III, once distilled RX 35; IV, RX 35; V, DER 332; VI, Epikote 828; VII, Epophen EL-5; VIII, MY 750; IX, Dobeck 502; X, R 18774/1. Spots A, B, C and D are probably due to products of the various isomers to be found in bisphenol A, spots E contain hydrolysable chlorine and are probably the chlorohydric derivative of the epoxy monomer

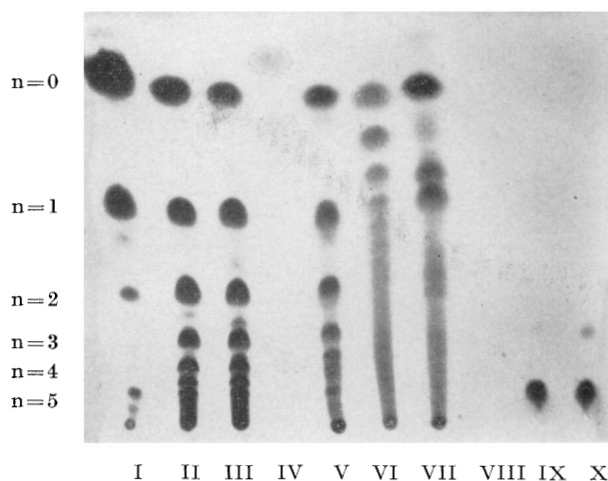
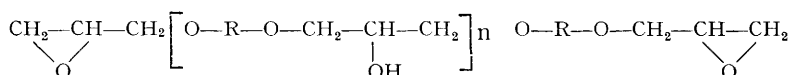


Fig. 2. The solid epoxide resins examined with a sample of a liquid resin for comparison: I, Epikote 828; II, Epikote 1040; III, CT 200; IV, DER 542; V, DER 511; VI, LY 558; VII, X 33/1189; VIII, Epichlorohydrin; IX, Bisphenol A; X, Bisphenol A

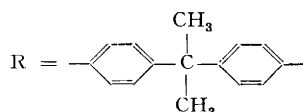
Quantitative chromatography—A plate was prepared by spotting alternately 0.015 ml of a 2 per cent. solution of the liquid resin under investigation and decreasing amounts of monomer solution. The first plate was run with 0.020, 0.018, 0.016, 0.014, 0.012 and 0.010 ml of 2 per cent. monomer. After developing and detecting as described above, the spots of monomer corresponding most closely in area with those of the actual resin were taken as an indication of the monomer content of that resin. This process was repeated with volumes of monomer solution differing by 0.001 ml and arranging for the closest match to occur in the centre of the plate. From the results obtained it was possible to determine the concentration of monomer in the resin. For the solid resins a more dilute solution (0.4 per cent.) of monomer was used.

DISCUSSION AND RESULTS

The bisphenol A-epichlorohydrin resin can be represented by the following theoretical formula—



where



$n = 0$ gives a monomer; $n = 1$ gives a dimer; $n = 2$ gives a trimer; $n = 3$ gives a tetramer; and so on.

Table I gives the values obtained for the monomer content of the liquid and solid resins examined.

TABLE I
QUANTITATIVE RESULTS OF MONOMER DETERMINATIONS

Resin	Epoxide equivalent	Monomer, per cent.
Epikote 828	196	85 to 90
Epophen EL-5	196	80 to 85
MY 750	196	80 to 85
R 18774/1	195	70 to 75
Dobcockot 502	195	80 to 85
CT 200	454	17 to 22
Epikote 1040	455	22 to 27

Fig. 1 is a photograph of the liquid epoxide resins examined and separated into their various components. The rows of spots designated $n = 1, 2, 3$, etc., are believed to correspond to the various molecular species as given in the formula above. The spots designated A, B, C, etc., are as yet unidentified although they are probably due to products of the various isomers² to be found in bisphenol A. The row of spots designated E contains hydrolysable chlorine and is probably the chlorohydrin derivative of the epoxy monomer. From the chromatograms obtained it is possible to distinguish between resins of the same type obtained from different manufacturers.

Epichlorohydrin cannot be detected under these circumstances.

From Fig. 1 it can be seen that although molecular distillation causes an increase in the monomer content of an epoxide resin it does not remove all of the other components. Indeed, in order to obtain pure monomer it is necessary to resort to re-crystallisation.

Fig. 2 is a photograph of the solid epoxide resins examined, with a sample of a liquid resin included for comparison. Here it is possible to distinguish between resins derived from bisphenol A (Epikote 1040 and CT 200) and those derived from (i) tetrabromo bisphenol A (DER 542), (ii) a partially brominated resin (DER 511), (iii) an epoxy novolac LY 558 and (iv) a tetrafunctional epoxide resin (X33/1189). The tetrabrominated epoxide resin (DER 542) and the epoxy novolac (LY 558) give brown and orange spots on detecting with chromic acid, while the tetrafunctional epoxide resin (X33/1189) gives spots ranging from yellow

through various shades of pink to mauve. The spots formed by the tetrabrominated epoxide resin (DER 542) are very much fainter than those for the other resins and can hardly be seen on the photograph.

Good reproducibility of results could be obtained providing care was taken in preparing the chromatograms, and that fresh resin solutions were used. Changes in monomer content and the proportions of the other components were found to occur after the resin had been in contact with chloroform for several days.

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