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CHROMATOGRAPHIC ANALYSIS AFTER CHEMICAL DEGRADATION OF POLYESTER RESINS IN THE LIQUID AND CURED LAMINATE FORMS*

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SUMMARY

The rapid qualitative and semi-quantitative analysis of the reactant acids and polyols from polyester resins, both in the liquid form usually with styrene monomer and in the cured laminate form, is described. In the liquid form, the styrene monomer is first removed then hydrolytic degradation using molten alkali is carried out, the products being identified as derivatives using gas or liquid chromatography. With cured resins the complete laminate is subjected to the fusion reaction, all difunctional reactants being identified or estimated except that portion of the maleic acid which is copolymerised with styrene by free radical polymerisation during the curing reaction. The polystyrene or maleic copolymer is essentially unaffected at the reaction temperature of 250°C used. The two isomers, *i.e.*, *ortho*- and *isophthalate*, of particular interest with these polyesters are readily separated on a dimethylpolysiloxane column while the three isomers (*ortho*-, *iso*- and *terephthalate*) are conveniently separated on cyanopropyl polysiloxanes. With these columns, the enhancement in retention of the aromatic esters is such that they are eluted after aliphatic dicarboxylic esters of higher molecular weight.

INTRODUCTION

The traditional gravimetric method¹ for the analysis of alkyd resins based on *o*-phthalic acid, glycerol and vegetable oil fatty acids, employing hydrolysis with alcoholic alkali, was early adopted² as a basis for gas chromatographic (GC) analysis. Chromatography has allowed the separation of the considerably wider range of components which have been used in alkyd resins and in particular in polyester resins since the development of the gravimetric procedure. Many of the materials without

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aliphatic vegetable oils but with isophthalic and terephthalic acids require prolonged hydrolysis to effect cleavage.

A review³ of analytical procedures indicates that polyester resins have been cleaved by

(1) Saponifications with alcoholic alkali. After hydrolysis the polyols are recovered and examined as derivatives, while the alkali salts are neutralised and the liberated acids examined as their methyl or trisilyl esters³⁻⁶. These procedures are effectively restricted to alkyd resins or the linear aliphatic esters despite some claims⁶ of wider applicability.

(2) The liberation of polyols by aminolysis with butylamine^{7,8}, benzylamine⁹ and phenethyleneamine^{10,11}. These methods have been employed with polyester and polyurethane foam¹⁰. Reaction periods of up to 42 h are required, and examinations of the constituent acids from the salts formed have not been reported, these being converted into amide derivatives.

(3) Digestion with hydrazine. This is a particular example of aminolysis and has been described as hydrazinolysis¹².

(4) The transesterification of alkyd resins with lithium methoxide¹³⁻¹⁷. With *o*-phthalates, hydrolysis periods of as short as 30 min have been used, while with more resistant esters prolonged methanolysis for 18-42 h is necessary with sodium methoxide. Transesterification with sodium methoxide-methanol-methyl acetate has been used by Jankowski and Garner¹⁸. To expedite the hydrolysis, increased pressure has been used; Rawlinson and Deeley¹⁹ interesterified the sample with an excess of methyl acetate in the presence of a catalyst, under pressure for 1 h. Other procedures involved transesterification with ethanol for periods of 3-16 h in pressure tubes heated to 250°C. Hydrolysis was found to be complete on attainment of a clear solution. Cleavage of polyethylene terephthalate²⁰ was achieved in water by heating for 4 h at 230°C in thick walled tubes.

(5) The analysis of simple carboxylic esters has been carried out by fusion of the sample with a similar amount of sodium hydroxide containing 0.5-1.0% potassium acetate at 320-360°C for 0.5-1.0 h in a furnace associated with the chromatograph. After the fusion the alcohols were flash heated to 230°C and admitted to the chromatograph for analysis. Dialkyl phthalates were examined and the alcohols liberated were identified²¹. It is apparent that with polyhydric alcohols the analysis of a derivative would be necessary and could probably be carried out by an on-column silylation reaction.

In the present work an alternative procedure has been adopted where cleavage is effected external to the chromatograph and the hydroxylic derivatives prepared as well as those of carboxylic components liberated from carboxylates produced by the fusion. Modification of the procedure of Frankoski and Siggia²¹ to allow identification of both functional classes in condensation polymers has previously been reported for polyamide materials both of the nylon²² and fatty polyamide²²⁻²⁴ types, of aromatic polyamides and polyimides^{25,26} and polyhydrazides²⁷.

EXPERIMENTAL

Chromatography

The chromatography was carried out using a Hewlett-Packard 5750 Research

Chromatograph fitted with flame ionisation detectors. The separations were achieved with (1) a 6 ft. \times 1/8 in. O.D. stainless-steel column packed with 5% DEGS on Chromosorb W AW DMCS (80–100 mesh), (2) a 12 ft. \times 1/4 in. O.D. aluminium column packed with 10% SE-30 on Celatom AW DMCS (Eagle Picher Corp., Cincinnati, OH, U.S.A.) and (3) a 6 ft. \times 1/8 in. O.D. stainless-steel column packed with 10% SILAR 10CP on Chromosorb W AW DCMS (100–120 mesh).

Alkali fusion

Approximately 0.1 g of polymer was used with *ca.* 1.0 g of potassium hydroxide–sodium acetate reagent prepared as indicated by Whitlock and Siggia²⁸. The reaction was carried out in 9 mm O.D., 6 mm I.D. Pyrex tubes sealed under vacuum. The samples were heated in a cylindrical block of stainless steel containing four suitably sized holes. The block was heated with a resistance heater. temperatures of 250, 300 and 350°C were used and in most cases a heating period of 30 min at 250°C was satisfactory.

Separation procedure

After the alkali-fusion reaction, and subsequent cooling, the tube was opened, and distilled water was added to the mixture to dissolve the potassium salt of the carboxylic acid. At this stage the alcohol was dispersed in the aqueous medium. The alcohol was then extracted using two 20-ml portions of a suitable solvent, *i.e.*, chloroform, to give aqueous and organic layers which contain the salt of the acid and alcohol components respectively. Vacuum distillation was then applied to the organic layer to remove the excess of solvent and to concentrate the alcohol.

N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) or trifluoroacetic anhydride (TFAA) (1–5 ml) was added to the alcohol to yield the ether in the case of BSTFA or the trifluoroacetyl (TFA) ester in the case of TFAA. A 0.3- μ l volume of the trimethylsilyl ether could be immediately injected into the gas chromatograph for analysis. In the case of the TFA derivative, water (5 ml) was then added to destroy the excess of reagent, yielding two layers. The bottom layer contains the TFA derivative while the top layer containing trifluoroacetic acid was discarded. A 0.3- μ l volume of the TFA derivative was injected into the chromatograph.

To the aqueous layer containing the salt of the carboxylic acid, dilute hydrochloric acid was added to adjust the pH to 1, thus liberating the free carboxylic acid. Vacuum filtration was applied, and the acid crystals were dried in an oven for 30 min at 100°C. BSTFA or BF₃–methanol (1–5 ml) was added to the carboxylic acid to yield the trimethylsilyl ester with BSTFA or the corresponding methyl ester with BF₃–methanol. A 0.3- μ l volume of the trimethylsilyl ester was immediately injected into the chromatograph for analysis.

In the case of the BF₃–methanol reagent, the free carboxylic acid crystals (0.1 g) were mixed with 10 ml of the BF₃–methanol solution and heated to boiling for 20 min. (Aromatic acids require reflux for 1 h.) The resultant ester solution was transferred to a separating funnel containing 30 ml of water and was extracted twice with toluene (20 ml). The toluene extract was dried over anhydrous magnesium sulphate, and then vacuum distilled to remove the excess of toluene and concentrate the methyl ester of the carboxylic acid. A 0.3- μ l volume of the methyl ester was then injected into the chromatograph.

Fig. 1 illustrates the detailed separation and derivatization procedure.

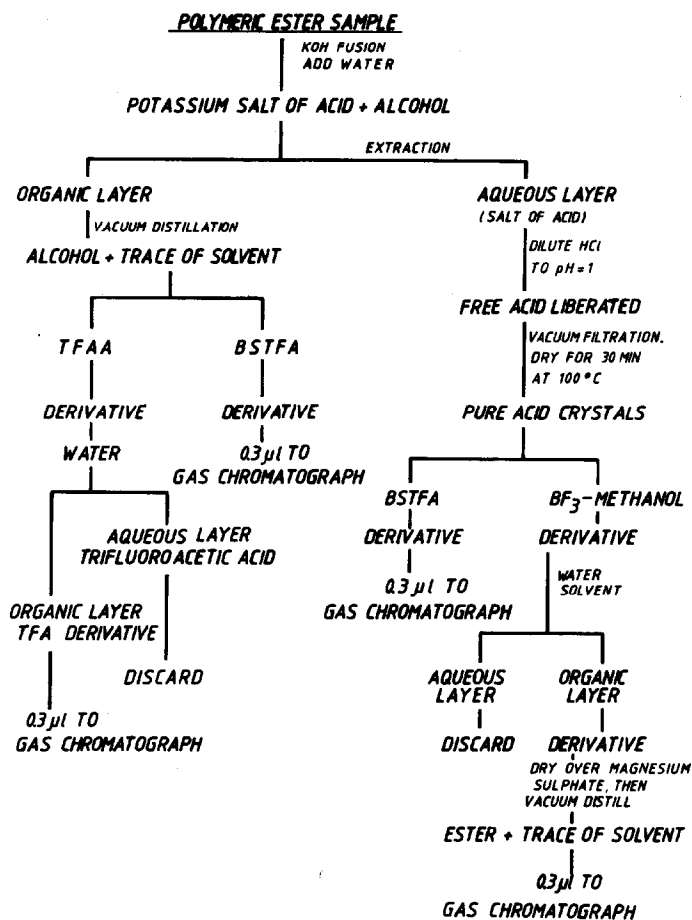


Fig. 1. Scheme for polyester analysis.

Samples

The polymeric esters examined had the following compositions: 1, polyethylene terephthalate (DuPont); 2, polybutylene terephthalate (DuPont); 3, medium activity *o*-phthalic polyester resin (*o*-phthalic acid-maleic acid = 1:1, propylene glycol, 67% resin in styrene); 4, medium activity isophthalic, adipic polyester resin (saturated acid-unsaturated acid = 1.4:1, diethylene glycol, 72% resin in styrene); 5, high activity *o*-phthalic polyester resin (*o*-phthalic acid-maleic acid = 1:3, propylene glycol, 70% resin in styrene); 6, medium activity isophthalic polyester resin (isophthalic acid-maleic acid = 1.5:1, propylene glycol, 67% resin in styrene); 7, medium activity isophthalic polyester resin, isophthalic acid-maleic acid = 1:1, diethylene glycol, 72% resin in styrene); 8, low activity, isophthalic polyester resin, isophthalic acid-maleic acid = 1.8:1, propylene glycol, 67% resin in styrene); 9, medium activity, isophthalic polyester resin, (isophthalic acid-maleic acid = 1:1, propylene glycol, 67% resin in styrene); 10, medium activity isophthalic polyester resin (isophthalic acid-maleic acid = 1:1.5, dipropylene glycol, neopentyl glycol, 62% resin in styrene); 11, high activity

isophthalic polyester resin (isophthalic acid–maleic acid = 1:2, propylene glycol, neopentyl glycol, 60% resin in styrene).

RESULTS AND DISCUSSION

The polyethylene and butylene terephthalate samples were readily cleaved by fusion and the derivatives formed according to Fig. 1. The TFA derivatives of the alcohols were prepared and a composite chromatogram with both alcohols is shown in Fig. 2. The formation of dimethyl terephthalate requires extended reaction with BF_3 -methanol, the acid reacting much more readily with BSTFA. Fusion does not appear to have been employed previously with either of the polymers, although several dialkyl phthalates were examined by Frankoski and Siggia²¹. The analysis of polybutylene terephthalate has not previously been reported.

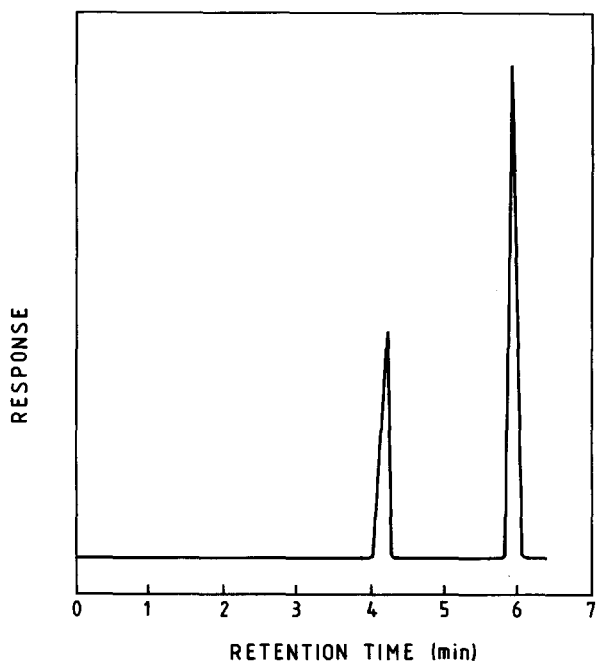


Fig. 2. Chromatogram showing separation of trifluoroacetyl derivatives of ethylene and propylene glycols.

The samples 3–11 all contained styrene as a reactive component and this was removed as a thin film by preliminary heating for 1 h at 100°C before the fusion was conducted. Preliminary experiments involving solution of the resins after heating and preparation of films which were examined using infra-red spectrophotometry did not show any absorption bands due to styrene.

Several of the samples were converted into a solid laminate by the use of benzoyl peroxide as catalyst. Finely divided laminate was subjected to the fusion reaction and degradation of the ester component occurred. In those locations where the double bond of the maleic acid had been copolymerised with the monomeric styrene, the acid was not liberated by the fusion reaction.

The seven polyols present in the samples were all resolved and as is apparent in Fig. 3 no overlapping occurred. The conditions used for gas chromatography, *i.e.*, 120°C, were the same as used for the separations shown in Fig. 2.

The diesters were separated on either the polyester or silicone columns, the elution sequence in either case being maleate, adipate and phthalate.

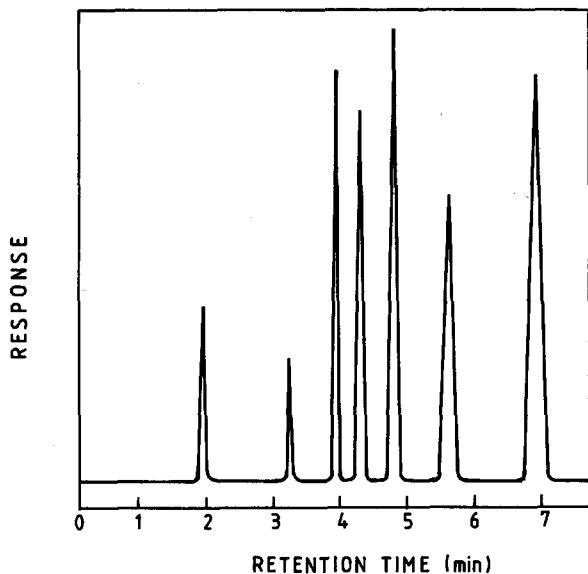


Fig. 3. Chromatogram showing in increasing elution order the separation of trifluoroacetyl derivatives of neopentyl glycol, propane-1,2-diol, propane-1,3-diol, ethylene glycol, dipropylene glycol, butane-1,4-diol and diethylene glycol.

The isomeric phthalate esters are not readily separated on a simple stationary phase due largely to the similarity of their boiling points. On the SE-30 columns the *ortho* isomer is well resolved, while the *iso*- and *terephthalates* appear as a single peak. The resolution of all three isomers has been reported with a column containing Bentone 34¹⁸, but the separation was not shown and it has not been achieved in this laboratory or by Rawlinson and Deeley¹⁹. Bentone 34 is modified, naturally occurring material which is of variable composition and performance, and like other industrial materials its use should be avoided.

The separation shown in Fig. 4 is superior to that of Rawlinson and Deeley who reported the same relative retention values for a three isomers on both polyester, *i.e.*, 1,4-butanediol succinate, and Apiezon L columns.

A recent report²⁹ concerning the separation of various benzenecarboxylic acids and their esters has shown that on an essentially identical, *i.e.*, SE-30, column, dimethyl *o*-phthalate has a retention index value of 1400 units while dimethyl *isophthalate* and dimethyl *terephthalate* have values of 1495 and 1519 units respectively. In admixture the latter two isomers are not resolved, the index value of the composite peak being between that of the individual compound peaks. The corresponding val-

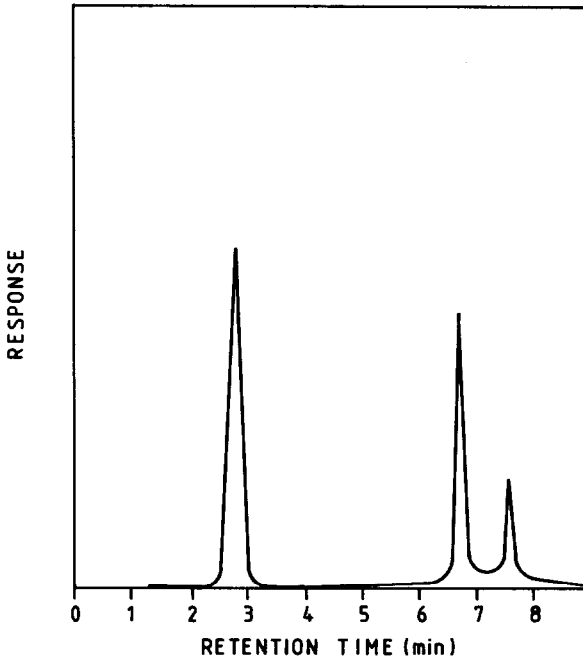


Fig. 4. Chromatogram showing the separation of methyl esters of benzoic acid, *o*-phthalic acid and the superimposed peak of iso- and terephthalic acids.

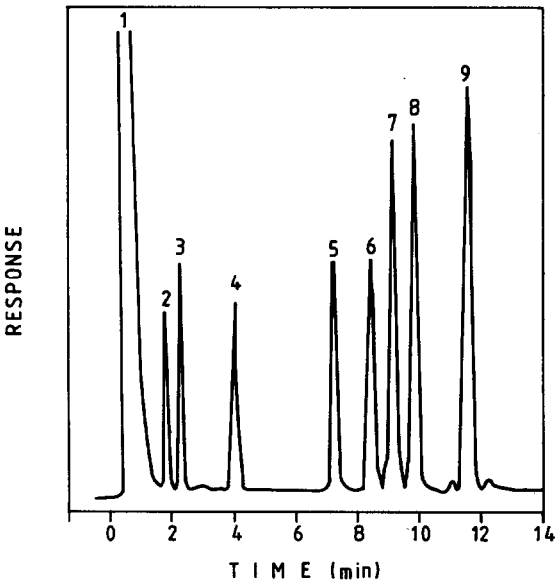


Fig. 5. Chromatogram showing the separation of isomeric phthalate esters and common aliphatic dibasic esters on 10% SILAR 10 CP programmed from 170 to 220°C at 4°C/min. Peaks: 1 = solvent; 2 = dimethyl maleate; 3 = dimethyl succinate; 4 = dimethyl adipate; 5 = dimethyl azelate; 6 = dimethyl sebacate; 7 = dimethyl terephthalate; 8 = dimethyl isophthalate; 9 = dimethyl *o*-phthalate.

ues on a polyester column, *i.e.*, cyclohexanedimethanol succinate, are 2012 (*ortho*), 2053 (*iso*-) and 2012 units (terephthalate).

In a report of a recommended IUPAC method for the analysis of alkyd resins¹⁷, on a dimethylpolysiloxane, *i.e.*, DC-11, column, the relative retention values of the *ortho*, *iso* and *tere* esters were 1.20, 1.33 and 1.30 respectively, while on a mixed polyester (DEGS) Carbowax 20M column the corresponding values were 1.3, 1.31 and 1.22.

The three isomeric phthalate esters have been separated using two specialty polyesters³⁰ of high polarity and stabilized with phosphoric acid. On SP-222-PS³¹ and SP-216-PS³² with temperature programming, the esters were eluted in the sequence *tere*, *iso* and *ortho*. Better separations are achieved using cyanopropylpolysiloxanes³³. Fig. 5 shows the separation of the three aromatic esters using 10% SILAR 10 CP. The elution order is the same as on the polyesters and again the esters are eluted after the C₁₀ dicarboxylic ester.

The three isomers could not be separated using liquid chromatography, although separation may be effected using spectrophotometry. An A.S.T.M. procedure adopted in 1961³⁴ and extended in 1976, suitable for mixtures of the three isomers using ultra-violet spectrophotometry, or a differential infra-red analyser may be employed³⁵.

The procedure presented is generally applicable to polyester resins as exemplified by the polyethylene and polybutylene terephthalates used in fibre and plastic applications, linear polyesters based on *o*-phthalic and isophthalic acids with aliphatic modifiers or with maleic anhydride to enhance reactivity, as used in reinforced plastics.

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