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Note

Quantitative determination of dicarboxylic acids and polyols in silicone–polyester resins

J. K. HAKEN*, N. HARAHAP and R. P. BURFORD

Department of Polymer Science, The University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

Alkyd and polyester resins are produced by the condensation of a wide variety of mono- and dicarboxylic acids with polyols. These resins may be variously modified but when silicone intermediates are incorporated products used in the paint industry exhibit excellent exterior durability and are described as silicone–polyester resins.

The determination of carboxylic and polymeric esters has been reported using alkali and acid reaction[1,2]. Phthalate[3] and polyvinyl esters[4] have been hydrolysed with molten potassium hydroxide in a reactor attached to the injection port of a gas chromatograph. Similar alkali fusion procedures conducted externally to the chromatograph have been used for the identification of dicarboxylic acids and polyols in polyester resins in the liquid and cured laminate form[5]. The qualitative analysis of vegetable oil based[6] and linear[7] silicone–polyester resins has recently been reported. The microfusion was conducted at 250°C for 1 h after which the polyols were identified as their trifluoracetamide derivatives and the carboxylic acids as their methyl or dimethyl esters. The organic pendant groups on the co-condensed siloxane intermediate were estimated simultaneously using gas solid chromatography. The analysis of silicone polyesters has been extended[8] to allow simultaneously estimation of the silicon content which converted to silicate is reacted to form a trimethylsilyl derivative.

Acid reactions were used with cellulose esters by Williams and Siggia[9] in the *in situ* chromatographic reactor and by Haken *et al.*[6,7] with various polyesters. The acidic cleavage of oil modified and linear silicone polyesters[6,7] has been carried out by reaction for 2 h at 125°C of the polymer (200 mg) with 15 ml of mixed anhydride reagent consisting of an equimolar mixture of the anhydrides of acetic and *p*-toluenesulphonic acids[10,11].

Before the recent work of Haken *et al.*[6,7] the analysis of silicone polyester resins had not been widely studied. Quantitative analysis of polyols in silicone polyester resins and paint films has been reported by McFadden and Scheuing[12] using a method involving a small-scale saponification with tetramethyl ammonium hydroxide at 100°C for 2 min followed by the formation of polyol derivatives with silylation reagents and subsequent gas chromatography (GC).

The analysis of polyester resins has followed from that of alkyd resin[13] where the functional classes have been separated, and identified separately. This procedure was first followed with the application of alkali and acid fusion but it has been

established[14] that while these reactions effect complete hydrolysis, losses occur with the extraction steps.

The hydrolysis of simple alkyd resins using 1 N ethanolic hydroxide followed by acetylation to form derivatives of the liberated polyols has been reported[15]. The analysis of phthalic anhydride and polyols was performed simultaneously on a column packed with 5% nitrile silicone oil and 22% orthophosphoric acid 85% on Chromaton N. The method is of limited use as few resins are as readily hydrolysed while few dicarboxylic acids are succcessfully examined as the free acids.

This paper reports the quantitative determination of dicarboxylic acids and polyols in linear silicone–polyester resins using acid fusion reaction GC. GC is readily performed simultaneously for the both functional classes of compounds as their appropriate derivatives.

The hydrocarbons, *i.e.* methane and benzene, corresponding to the organic pendant groups on the silloxane intermediate have been previously examined and are not repeated here. The quantitative nature of these cleavages has been previously reported for dimethyl polysiloxanes by Haken *et al.*[16].

EXPERIMENTAL

Samples

Polyester resins based on adipic acid, isophthalic acid, neopentyl glycol and trimethylol propane, modified with silicone-intermediate SY231 [a methoxy functional methyl phenyl polysiloxane (Wacker Chemie)], with a silicone content of 30% were used in this work. The resins were prepared to the intermediate manufacturer's formulation and their composition is shown in Table I.

Procedure

Approximately 200 mg of the resin sample was hydrolysed with 5 ml acetic anhydride containing 15% water in a round bottom flask with reflux for about 1 h. As internal standards, stearic acid (12–15 mg) and glycerol (13–17 mg) were added before the reaction. Acetic acid formed during the reaction and the remaining acetic anhydride in the mixture were carefully distilled out, and the residue was then allowed to cool at room temperature. About 8 ml of bromine trifluoride–methanol reagent was added into the flask and the mixture was then refluxed again for 1 h. After cooling, the mixture was concentrated under reduced pressure and followed by the

TABLE I

COMPOSITION OF SILICONE–POLYESTER RESINS

Polyester components	*wt.-%*	
	Sample 1	*Sample 2*
Adipic acid	32.4	21.4
Isophthalic acid	14.3	26.3
Neopentyl glycol	—	7.9
Trimethylol propane	53.3	44.4

SAMPLE

| +internal standards
| acid fusion

DICARBOXYLIC ACIDS   + POLYOL ACETATES

| BF$_3$-methanol

DIMETHYL CARBOXYLATES + POLYOLS

| acetic anhydride

DIMETHYL CARBOXYLATES + POLYOL ACETATES

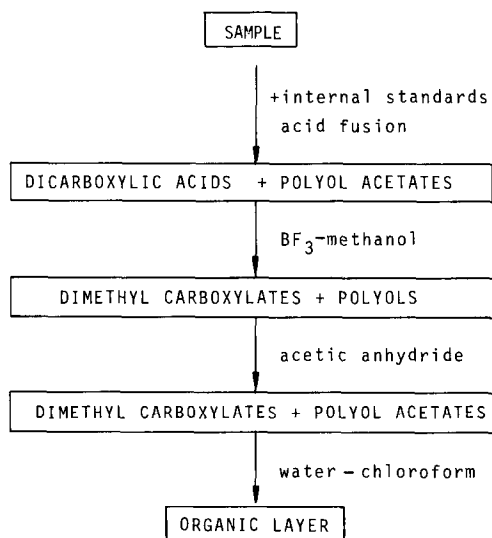| water – chloroform

ORGANIC LAYER

Fig. 1. Analytical scheme.

addition of 5 ml of acetic anhydride and 0.5 ml of 1-methylimidazole. The excess of acetic anhydride and the methylacetate formed were distilled out withcare and then the remaining solution was transferred into a separating funnel containing 25 ml of distilled water and was extracted twice with dichloromethane (20 ml). The dichloromethane extract was dried over anhydrous magnesium sulphate and concentrated under reduced pressure to about 1 ml. Finally 1 μl of this resultant mixture was injected into the gas chromatograph for simultaneous analysis of both functional classes. The analytical scheme is shown in Fig. 1.

Gas chromatography

GC was carried out using a Hewlett-Packard 5750 Research Model gas chromatograph equipped with a flame ionisation detector. Helium was used as carrier gas at a flow-rate of 60 ml/min.

The separations were performed on a column (10 ft. $\times$ $\frac{1}{4}$ in. O.D., aluminium) packed with Silar 10% 10 CP on Chromosorb W AW DCMS (100–200 mesh), temperature programmed at 6°C/min from 185 to 224°C and held at upper limit for 4 min.

RESULTS AND DISCUSSION

The qualitative analysis of the acid and polyol components of silicone polyesters may be identified simultaneously by effecting the hydrolytic cleavage with the mixed anhydride reagent and subsequently esterifying the liberated free acids[17]. Some competing transesterification reactions occur with a partial reduction in the concentration of the polyol acetates and the formation of minor amounts of sulphonic esters. It has been shown that linear polyester resins cross-linked with aminoplasts

TABLE II

ANALYSIS OF SILICONE–POLYESTER RESINS CONTAINING THREE COMPONENTS

Component	Analysis (wt.-%)	Standard deviation	Expected (wt.-%)	Recovery (%)
Adipic acid	31.3	1.25	32.4	96.6
Isophthalic acid	13.3	0.5	14.3	97.6
Trimethylol propane	51.8	1.36	53.3	97.2

are degraded by reaction with acetic anhydride and acetic acid. A re-esterification step ensures that all polyols are converted to their acetates[18,19].

The non-volatile reaction products, *i.e.* excluding methane and benzene from the polysiloxane intermediate, of the silicone–polyester resin samples based on adipic acid, isophthalic acid, neopentylglycol and trimethylol propane were analysed simultaneously using the acid fusion reaction GC procedure described.

Good agreement between observed and expected values was obtained as summarised in Tables II and III. The calibration for this analysis was by the internal standard method using stearic acid and glycerol as the added components. Quantitative determinations of the carboxylic acids were obtained by measuring the areas under the corresponding acid derivatives and comparing them to the internal standard derivative peak run under the same analytical conditions, while determinations of polyols were obtained by comparison with acetylated glycerol.

All of the results presented in Tables II and III were obtained from eight individual determinations. The analysis values are 93.7–97.6%. However apart from experimental error, some material losses during the synthesis of the resin could occur and this fact must be taken into consideration when evaluating the results as this affects the concentration of that material in the resin. Further, the initial materials are not 100% pure, and as pilot batches of any new resin are required the results are considered satisfactory. Reproducibility of the analysis is found very good as shown by the standard deviations.

Derivative formation of dicarboxylic acids and polyols was maximised by refluxing for 1 and 0.5 h respectively. Occasional shaking of the reaction mixture was found necessary to prevent premature sample particle aggregation. All of the derivatives were relatively stable and under appropriate conditions, were readily separated by GC. Trimethylsilyl derivatives of neopentyl glycol, trimethylol ethane, trimethylol

TABLE III

ANALYSIS OF SILICONE–POLYESTER RESINS CONTAINING FOUR COMPONENTS

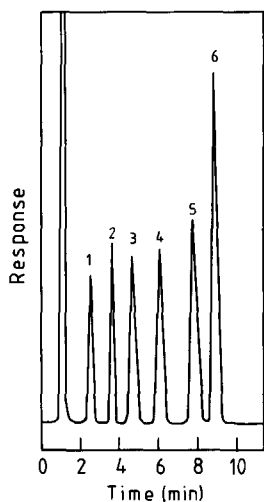| Component	Analysis (wt.-%)	Standard deviation	Expected (wt.-%)	Recovery (%)
Adipic acid	20.4	1.14	21.4	95.3
Isophthalic acid	25.3	1.97	26.3	96.2
Neopentyl glycol	7.4	0.62	7.9	93.7
Trimethylol propane	42.3	1.25	44.4	95.3

Fig. 2. Gas chromatogram showing separation: 1 = neopentyl glycol diacetate; 2 = dimethyl adipate; 3 = methyl stearate; 4 = glycerol triacetate; 5 = dimethyl isophthalate; 6 = trimethylol propane diacetate.

propane, adipic acid and isophthalic acid have been successfully separated on the SE-30 column[16]. The later derivatives are separated more effectively on Silar 10 CP and the separation achieved here are shown in Fig. 2.

Acetic acid formed during the first step of the procedure should be distilled out to avoid both the avoid formation of methyl acetate and an excessive use bromine trifluoride–methanol reagent. During the reaction of dicarboxylic acids and bromine trifluoride–methanol whilst hot polyol acetates were found to be cleaved with to the formation of methyl acetate and polyols, therefore, the acetylation was repeated with 1-methylimidazole as catalyst by refluxing for 0.5 h. Methyl acetate previously formed and the excess of the acetic anhydride reagent should be distilled out prior to GC. Water was used to destroy the excess of the remaining reagents, especially that of the 1-methylimidazole. There were no apparent interferences from silicone intermediate fragments or reagent peaks throughout this GC analysis.

Acid fusion reaction GC with acetic anhydride–acetic acid has been demonstrated as a satisfactory method for a single-step quantitative determination of common dicarboxylic acids and polyols in silicone polyester resins. The analysis procedure is simple, rapid, accurate and precise. The determination of the organic pendant groups on the siloxane intermediate may be conducted simultaneously as previously reported.

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