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APPLICATION OF ALKALI AND ACID FUSION REACTIONS TO THE GAS CHROMATOGRAPHIC ANALYSIS OF SILICONE-POLYESTER RESINS

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SUMMARY

An application of alkali and acid fusion reactions to the gas chromatographic (GC) analysis of silicone-polyester resins is described. The resins are cleaved into polyol, dicarboxylic acid and fatty acid fragments by means of hydrolytic fusion and then these fragments after separation and derivatisation are analysed using GC. The organic pendant groups on the siloxane part of the polymer are split off as the corresponding hydrocarbons. The methane and benzene thus formed is estimated by gas–solid chromatography.

INTRODUCTION

Silicone-polyester resins are of considerable commercial importance and due to their excellent properties and experior durability are used in coil coatings, appliance and high temperature finishes. They can be prepared by simple condensation using various hydroxy or methoxy functional, low-molecular-weight silicone resins co-reacted with polyesters. The common ingredients of polyester resins used in these applications with a hydroxy functional silicone intermediate[1], are: polyols, such as glycerol, penthaerythritol and trimethylolethane; carboxylic acids, such as phthalic anhydride and adipic acid; vegetable oils, such as linseed, sunflower, safflower and dehydrated castor oil.

The characterization of polymer and coating materials using gas chromatography (GC) and chemical degradation has been widely reviewed by Haken[2,3]. Development of alkali and acid fusion reactions for the characterization of other polymers and coating materials has been reported by Siggia and co-workers[4–6] and by Haken and co-workers[7–20] and others as mentioned later in this paper[2,21]. However the application of alkali and acid fusion reaction gas chromatography to the complete analysis of silicon polyester resins has not been previously reported.

An alkali fusion procedure was reported[15] using a fusion flux reagent (prefused

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mixture of potassium hydroxide containing 5% sodium acetate prepared according to the method of Siggia and co-workers[4,5]) to cleave polyester resins to the corresponding acid salt and glycol fragments. The fusion was carried out in sealed Pyrex tubes at 250°C for 30 min. After separation using solvent extraction, filtration and vacuum distillation, derivatisation was employed for GC analysis. Trifluoroacetic anhydride (TFAA) and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) were used to obtain the corresponding esters and silyl ethers respectively from the glycols. While boron trifluoride–methanol was used for derivatisation of the liberated carboxylic acids to produce the corresponding methyl esters.

A recent paper[20] showed acid fusion reactions for the analysis of polyester based polyurethanes. The polymer was cleaved to form the corresponding diamine, or carboxylic acid and polyol acetate fragments using mixed anhydride reagent prepared according to the method of Tsuji and Konishi[21,22]. Derivatisation of the liberated dicarboxylic acid was carried out using boron trifluoride–methanol. The polyol acetate fragments were used directly for GC analysis after separation and concentration.

Determination of polyols in silicone polyester resins has been achieved[23] using small scale saponification with tetramethylammonium hydroxide (TMAH) at 100°C for 20 min followed by derivatisation of the polyols to the corresponding trimethylsilyl ethers. There were no apparent interferences from silicone fragments or reagent peaks.

Instrumental analysis such as UV–IR spectrometry and NMR are commonly used for identification but there is often difficulty in achieving complete analysis. An alternative to the analysis of substituent groups in silicone polymers has been reported[6] using alkali fusion to cleave, forming the corresponding hydrocarbons, which are trapped and then analysed by GC. Fusion using a powdered potassium hydroxide reagent was carried out from 100 to 300°C over 10 min. Separation was conducted by injecting 0.5 ml of gas collected over the reaction medium into a Porapak column with temperature programmed from 90 to 260°C at 8°C/min.

A technique to elucidate the functional group substitutents on siloxane chains has also been reported[24–26] by alkaline hydrolysis using potassium hydroxide. The hydrolysis decomposes the polymer into monomers and these were converted into trimethylsilyl (TMS) derivatives, which were then identified by capillary GC–mass spectrometry (MS). This technique is simple and rapid but cannot be used for quantitative determination of functional groups as the hydrolysis was not complete.

This paper describes the application of alkali and acid fusion reaction GC for the analysis of polyol, carboxylic acid and fatty acid fragments derived from silicone polyester resins. The analysis of alkyl and aryl groups bonded to siloxane intermediates by means of both acid alkali fusion reaction is also reported.

EXPERIMENTAL

Samples

Silicone-polyester resins examined were prepared by simple condensation according to the formulation shown in Table I and using a procedure developed by Dow Corning[1] employing Dow Corning 2-6018 intermediate (a hydroxy functional, low-molecular-weight silicone resin).

TABLE I

FORMULATION OF SILICONE POLYESTER SAMPLES

Ingredient	*Wt. %*				
	1	*2*	*3*	*4*	*5*
Dow Corning 2-6018 intermediate	25	25	25	25	30
Pentaerythritol (mono)	14	14	14	14	–
Glycerol	6	6	6	6	–
Trimethylolethane	–	–	–	–	23
Phthalic anhydride	16	16	16	16	26
Stearic acid	39	4	–	–	–
Sunflower fatty acid	–	35	39	–	–
Linseed fatty acid	–	–	–	39	–
Dehydrated castor oil	–	–	–	–	21

Alkali fusion and separation

Alkali fusion was carried out using 200–300 mg of polymer with 1–3 g of a prefused mixture of potassium hydroxide and 5% sodium acetate[4,5]. The reaction was achieved by heating the polymer reagent mixture in a stainless-steel screw capped pressure tube at 250°C for 1 h according to the technique of Haken and Rohanna[15]. After cooling the contents were transferred to a round-bottom flask containing 25 ml of chloroform and then TFAA (5 ml) was added to the mixture. After refluxing for 1–2 h, distilled water was added to dissolve the potassium salt of the carboxylic acid and destroy the excess TFAA. Chloroform containing TFA derivatives of polyols were separated using a separating funnel. A 20-ml aliquot of chloroform was then added to the flask to recover the remaining TFA esters of the polyols. The mixture in chloroform was concentrated to 1 ml prior to analysis.

The aqueous layer containing the acid salts was adjusted to a pH of 1 with dilute hydrochloric acid to liberate the carboxylic acids. These were then recovered by solvent extraction using two 20-ml portions of chloroform. The organic layer was dried with anhydrous magnesium sulphate and concentrated by vacuum distillation. Boron trifluoride methanol reagent (10 ml) was added to the concentrated chloroform extract and the mixture refluxed for 1–2 h. The resulting ester solution was transferred to a separating funnel containing 30 ml of water and extracted twice with chloroform (20 ml). The extract was dried over anhydrous magnesium sulphate and vacuum distillation was then employed to concentrate the extract to 1 ml for analysis. The detailed separation scheme using alkali fusion reaction GC is shown in Fig. 1.

For the analysis of pendant alkyl and aryl groups in the polysiloxane part of the samples, alkali fusion was applied. The apparatus used was the stainless-steel fusion tube, the screw cap being fitted with a serum cap to allow a syringe to withdraw the reaction gases through a rubber–PTFE septum. About 0.5 ml of gas collected from the tube was injected into a Porapak column for GC analysis.

Acid fusion and separation

Acid fusion was carried out in a 50-ml round bottom flask using approximately

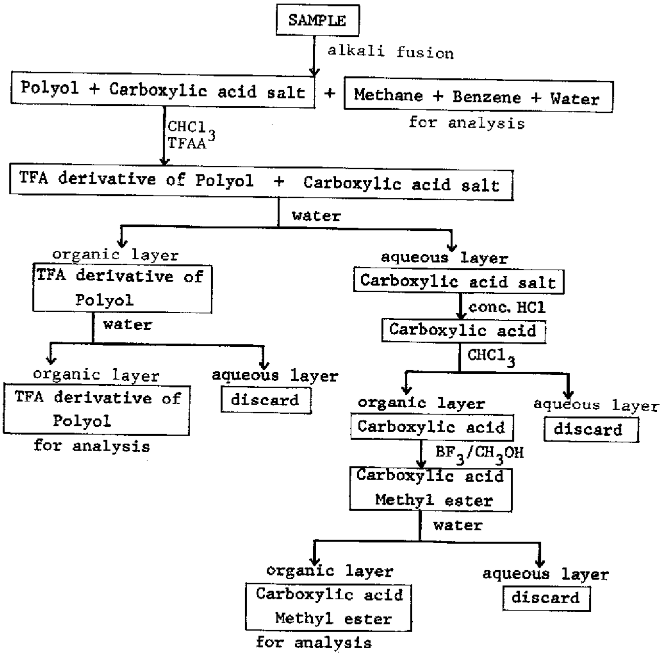


Fig. 1. Analytical scheme for alkali fusion.

200 mg of polymer with 15 g of mixed anhydride reagent, an equimolar mixture of the anhydrides of acetic acid and *p*-toluenesulphonic acid prepared according to the method of Tsuji and Konishi[21,22]. 0.5 ml of N-methyl imidizole was added to the flask before refluxing at 125°C for 2 h. After cooling, the contents were transferred to a separating funnel and a saturated solution of sodium carbonate was added followed by chloroform. The resulting organic layer was separated, dried and concentrated under reduced pressure for the polyol analysis.

The aqueous sodium carbonate solution was slightly acidified using concentrated hydrochloric acid and the liberated carboxylic acids recovered by solvent extraction using two × 20-ml portions of chloroform. The extract was concentrated under reduced pressure and 10 ml of boron trifluoride methanol reagent was added for derivatisation, by refluxing for 2 h. After cooling, excess reagent was destroyed with 20 ml water and the mixtures was extracted using two times 20 ml portions of chloroform. After drying with anhydrous magnesium sulphate the extract was concentrated by vacuum distillation to 1 ml for analysis. The detailed separation scheme using the acid fusion technique is shown in Fig. 2.

Gas chromatography

GC was carried out using a Hewlett-Packard Model 5750 research gas chromatograph with flame ionization detection and with helium as carrier gas.

TFA esters and acetates of polyols

These were separated on an aluminium column (12 ft. × ¼ in. O.D.) packed

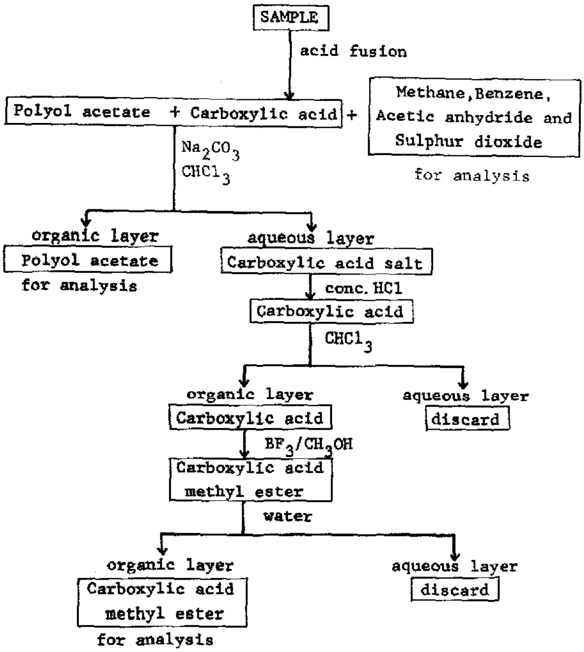


Fig. 2. Analytical scheme for acid fusion.

with 5% (w/w) neopentyl glycol succinate on Chromsorb W DMCS. The column was temperature programmed between 120 and 220°C at 10°C/min and held at the initial and final temperature for 6 and 10 min respectively.

Methyl esters of carboxylic acids

These were separated isothermally at 185°C on an aluminium column (12 ft. × ¼ in. O.D.) packed with 5% (w/w) diethylene glycol succinate on Chromosorb W HMDS.

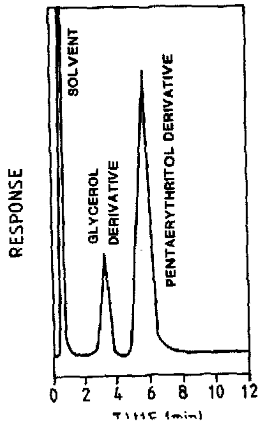


Fig. 3. Gas chromatogram showing separation of TFA derivatives of glycerol and pentaerythritol.

Methane and benzene

Separation was carried out on a 6 ft. × 1/8 in. O.D. stainless-steel column packed with Porapak Q. The column was operated for 2 min isothermally a 72°C and then temperature programmed at 40°C/min to 181°C and held for 10 min for the headspace gases after alkali fusion.

The corresponding gases after acid fusion were separated on the same column which was operated isothermally for 1 min at 130°C and was then programmed at 10°C/min to 230°C.

RESULTS AND DISCUSSION

The silicone polyester resin samples were successfully cleaved into the corresponding polyol and carboxylic acid fragments by means of alkali or acid fusion reactions. Methane and benzene fragments were similarly obtained by both reaction from the siloxane components.

Derivatisation of polyols after the alkali fusion reaction into the corresponding esters using TFAA was performed before dissolving the carboxylic acid salts in water. The solution was used for GC analysis of the polyols. Similar chromatograms of glyceryl trifluoroacetate and pentaerythritol tetrafluoroacetate were obtained with each sample, as shown in Fig. 3.

Alkyl and aryl substituents in the polysiloxane components of the samples were cleaved successfully by means of alkali fusion. Separation was achieved successfully by injecting the reactant gases trapped in the reaction tube, into a Porapak Q column as shown in Fig. 4A.

Polyol acetates produced by acid fusion and corresponding to the polyol por-

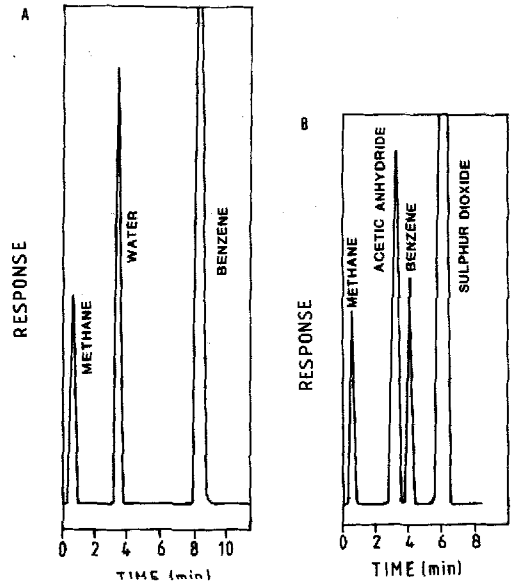


Fig. 4. (A) Gas chromatogram showing separation of methane, water and benzene. (B) Gas chromatogram showing separation of methane, acetic anhydride, benzene and sulfur dioxide.

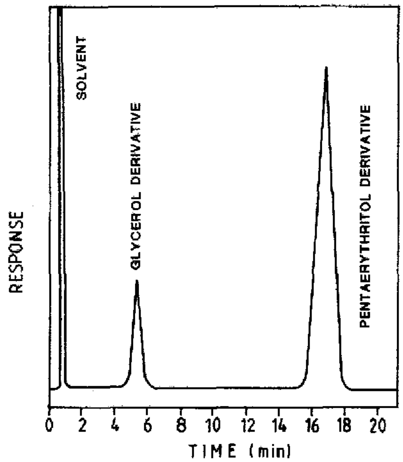
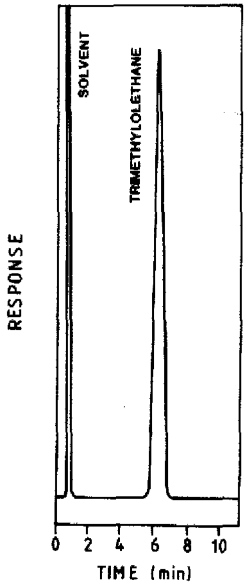


Fig. 5. Gas chromatogram showing separation of acetylated derivatives of glycerol and pentaerythritol.

tion of the samples were successfully separated on the packed column previously described and temperature programmed. Fig. 5 shows a chromatogram of the derivatives of glycerol and pentaerythritol for sample No. 1, which is similar to the chromatograms obtained for sample Nos. 2, 3 and 4. Fig. 6 shows a chromatogram of the derivative of trimethylol methane from sample No. 5.

Derivatisation of the carboxylic acid fragments using boron trifluoride–methanol reagent into their methyl esters after either alkali or acid fusion was used for GC analysis of dicarboxylic acids and fatty acids Fig. 7 shows the separation of



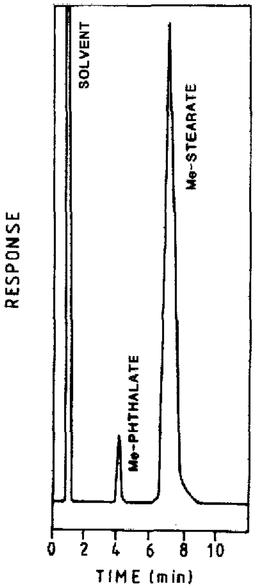
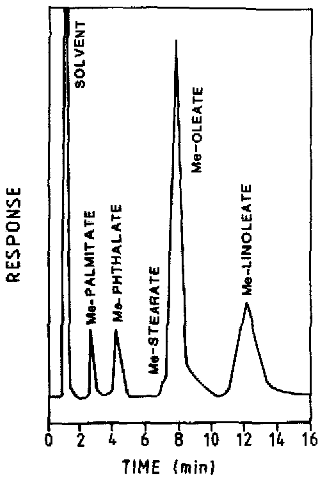


Fig. 6. Gas chromatogram showing separation of triacetylated derivative of trimethylolethane.

Fig. 7. Gas chromatogram showing separation of methyl esters of sample No. 1.



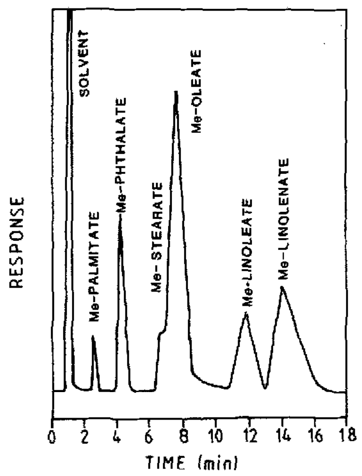


Fig. 8. Gas chromatogram showing separation of methyl esters of sample No. 3.

Fig. 9. Gas chromatogram showing separation of methyl esters of sample No. 4.

methyl orthophthalate and methyl stearate. Figs. 8–10 show the separation of the esters obtained from sunflower, linseed and dehydrated castor oils.

The separations can be improved if required but those presented allow ready separation of the methyl orthophthalate. The chromatograms of the fatty esters after fusion are virtually identical with those prepared from the unreacted oils and readily allow the costituent oil to be identified.

In the analysis of polyester resins using alkali fusion[15], solvent extraction was employed to separate glycols and dicarboxylic acid salts followed by derivatisation of glycols to esters and ethers using TFAA and BSTFA respectively. Such a method could not be employed for the analysis of polyols in silicone-polyester samples due to the insolubility of the polyols in the available solvents. Alternatively, derivatisation

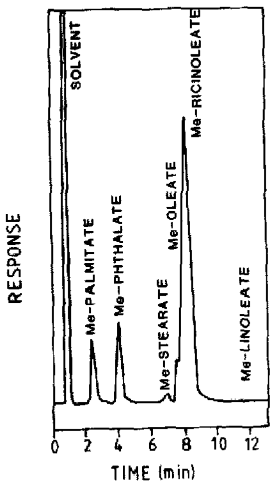


Fig. 10. Gas chromatogram showing separation of methyl esters of sample No. 5.

TABLE II

ANALYSIS OF ALKYL AND ARYL SUBSTITUTED POLYSILICONE-POLYESTER RESINS BY ALKALI FUSION GC

Volatile alkali fusion products	*Retention time (min)*	*Elution temp. (°C)*
Methane	0.64	73
Water	3.30	107
Benzene	8.4	180

of polyols was carried out before extraction, as used previously[7–12]. It was found that the preferred method of analysis of such polyols is acid fusion. Acid fusion is faster (*cf.* 1.5 h) while alkali fusion requires *cf.* 5 h for the analysis. Polyol acetates obtained are very stable while derivatives prepared after alkali fusion reaction using TFAA reagent are very unstable and must be examined promptly.

Schlueter and Siggia[6] have reported the determination of methane from the alkali fusion of a polymethyl siloxane on a Porapak Q column. The separation is similar to that shown in this work although temperature programming was employed to allow separation of benzene and water, which by the headspace technique used is the major volatile component. Fig. 4B show the chromatogram after acid fusion, with the presence of acid components, namely acetic anhydride and sulphur dioxide, formed by some degradation of the *p*-toluenesulphonic acid.

Table II shows retention data of the components observed during the analysis of alkyl and aryl substituted silicone polyester resins by alkali fusion reaction GC while Table III shows the products of acid fusion.

TABLE III

ANALYSIS OF ALKYL AND ARYL SUBSTITUTED SILICONE-POLYESTER RESINS BY MEANS OF ACID FUSION REACTION GC

Volatile alkali fusion products	*Retention time (min)*	*Elution temp. (°C)*
Methane	0.24	130
Acetic anhydride	3.0	163
Benzene	4.0	203
Sulfur dioxide	6.12	216

CONCLUSIONS

The application of alkali and acid fusion reaction GC has been demonstrated for the analysis of polyols, carboxylic acids and oils/fatty acids in silicone-polyester resins. Moreover, the analysis of alkyl and aryl groups in the siloxane component of the resins has been achieved concurrently by both fusion reaction procedures.

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