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GAS CHROMATOGRAPHIC ANALYSIS OF CROSS-LINKED POLYESTER-BASED POLYURETHANE FOAMS CONTAINING TRI- AND TETRAFUNCTIONAL ALCOHOLS AFTER ALKALI FUSION

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SUMMARY

An analytical procedure is described for rapid qualitative and quantitative analysis of polyester-based polyurethane foams containing tri- and tetrafunctional alcohols. The foams are conventionally the complex reaction products of an isocyanate-terminated partially cross-linked polyester prepolymer further cross-linked with water. The polymer is cleaved into the corresponding diamine, dicarboxylic acid and polyol fragments by molten alkali fusion at high temperature. These products are treated with trimethylsilylimidazole to convert polyols into volatile trimethylsilyl derivatives and hence to eliminate the extraction steps previously employed, which are of limited success with the polyfunctional alcohols. Dicarboxylic acids are converted after extraction into dimethyl ester derivatives. The polyol and acid derivatives and diamines corresponding to the diisocyanates were determined by gas chromatography.

INTRODUCTION

Polyurethane foams are conventionally the complex reaction products of isocyanate-terminated partially cross-linked polyol prepolymers extended with water. During the initial development of polyurethanes, polyesters were the most commonly used type of polyol. Polyesters are still widely used in the manufacture of polyurethanes. The most common ingredients of polyesters for urethane applications are adipic acid, simple glycols and polyols. The glycols used generally include ethylene, propylene, 1,3-butylene, 1,4-butylene, diethylene and dipropylene glycols. The polyols are usually glycerol, 1,2,6-hexanetriol, trimethylolpropane, trimethylolethane and pentaerythritol.

These polymers in general, are extremely resistant to chemicals. The isocyanate linkages are difficult to cleave by simple hydrolysis. Simple solution hydrolysis is

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often incomplete and prolonged. A typical separation procedure after hydrolysis for 16 h, as indicated by Dawson *et al.*[1], involves a lengthy liquid–liquid extraction procedure carried out for 5 h for the recovery of glycols. Even this procedure is not applicable to highly water-soluble polyhydric alcohols, such as glycerol and pentaerythritol.

Although cleavage of the polymer can be achieved by acid fusion[2] with the anhydride reagent of *p*-toluenesulphonic acid and acetic anhydride, there are disadvantages:

(i) Fragments from both glycols and polyglycols (*e.g.* ethylene glycol and diethylene glycol) are the same, therefore glycols cannot be distinguished from polyglycols;

(ii) In the case of polyfunctional alcohols such as pentaerythritol, simultaneous derivatization to acetyl derivatives is incomplete.

Rapid hydrolysis of polyurethanes has been achieved[3–7] by the newly developed technique of alkali fusion, in which hydrolysis fragments were identified by gas chromatography (GC). The literature related to analysis of polyurethanes has been reviewed[5].

This paper reports a rapid procedure for polyester-based polyurethane analysis by the alkali fusion procedure. The hydrolysis fragments were treated with trimethylsilylimidazole (TMSI) to convert polyhydroxy compounds into their trimethylsilyl ether (TMS) derivatives in the presence of other fragments. This enables the subsequent separation of fragments by a simple liquid–liquid extraction procedure (Fig. 1).

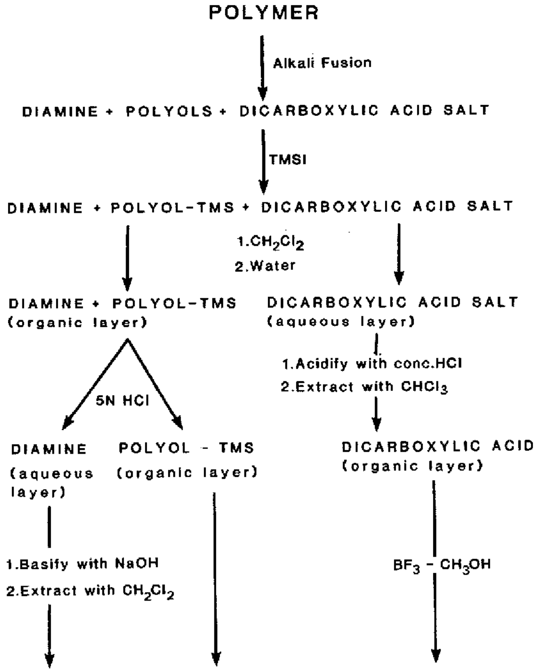


Fig. 1. Analytical scheme.

The procedure developed (i) does not have the disadvantages present in acid fusion, (ii) eliminates the necessity of using an elaborate, lengthy liquid–liquid extraction procedure to recover glycols, and (iii) allows us to separate and identify polyfunctional alcohols, such as glycerol and pentaerythritol, which are impossible to separate and identify by the procedures described previously[1].

EXPERIMENTAL

Commercially available polyester-based polyurethane samples, with the compositions listed in Table I, were used for the analysis.

TABLE I

COMPOSITION OF POLYESTER-BASED POLYURETHANE SAMPLES ANALYSED

Sample No.	*Diisocyanate**	*Polyester*
1	TDI	Diethylene glycol, pentaerythritol adipate
2	MDI	Diethylene glycol, pentaerythritol adipate
3	TDI	Ethylene glycol, propylene glycol adipate
4	TDI	Ethylene glycol, 1,4-butanediol adipate
5	MDI	Ethylene glycol, 1,4-butanediol adipate

* TDI = Toluene diisocyanate (80:20 mixture of 2,4 and 2,6 isomers); MDI = *p,p'*-diphenylmethane diisocyanate.

Alkali fusion

Alkali fusion was carried out using 100 mg of polymer with 10 g of fusion flux reagent a prefused mixture of potassium hydroxide containing 5% sodium acetate, prepared according to the method of Frankoski and Siggia[8]. The hydrolysis was achieved by placing finely ground polymer–reagent mixture in a stainless-steel pressure tube heated at 200°C for 2 h.

Separation and derivatization procedure

After the stainless-steel tube had been cooled and opened, the contents were transferred to a 50-ml vial containing 5 ml of trimethylsilylimidazole (TMSI) (Tri-Sil® Z, Pierce) with 20 ml of dichloromethane. The mixture was continuously shaken for *ca.* 15 min, and the contents were transferred to a separating funnel. About 25 ml of water were added to destroy the excess TMSI, and the mixture was extracted with another two 15-ml portions of dichloromethane.

The combined dichloromethane extracts were extracted with three 15-ml portions of 5 *N* aqueous hydrochloric acid, and the remaining dichloromethane extract was concentrated as above for the GC analysis of TMS derivatives of polyols corresponding to the polyester portion of the polymer.

The combined hydrochloric acid extracts were rendered slightly basic by adding sodium hydroxide pellets, and liberated diamines were extracted with three 15-

ml portions of dichloromethane and concentrated for the GC analysis of diamines corresponding to diisocyanate portion of the polymer.

The remaining aqueous solution was rendered slightly acidic with concentrated hydrochloric acid, and liberated dicarboxylic acid was extracted with three 15-ml portions of chloroform. The dibasic acid was converted into its dimethyl ester by adding 5 ml of boron trifluoride–methanol to the chloroform extract and refluxing it for 1 h. The unchanged reagent was destroyed by adding *ca.* 15 ml of water, and the methyl ester remaining in the chloroform layer was concentrated under reduced pressure to a small volume (*i.e.* 1 ml) for the GC analysis of dicarboxylic acid corresponding to the polyester backbone.

Gas chromatography

Gas chromatography was carried out using Hewlett-Packard 5830A Research Model chromatograph with flame ionization detection.

Diamines

These were separated on a 4 ft. × 1/8 in. .O.D. stainless-steel column packed with 3% XE-60 on Chromosorb W-HP, 100–120 mesh, with helium as the carrier gas at a flow-rate of 25 ml/min. The detector and injection ports were maintained at 250°C and 260°C, respectively. The column was operated for 1 min isothermally at 70°C, and then temperature-programmed at 8°C/min to 240°C and held at 240°C for 6 min.

Trimethylsilylether derivatives of polyols

These were separated on a 6 ft. × 1/8 in. O.D. stainless-steel column packed with 5% SE-30 on Chromosorb W-HP, 100–120 mesh, with helium as the carrier gas ast a flow-rate of 25 ml/min. The detector and injection ports were maintained at 200°C and 250°C, respectively. The column was operated for 6 min isothermally at 100°C and then temperature-programmed at 6°C/min to 230°C and held at 230°C for 6 min.

Trimethylsilylether derivatives of polyols from Sample No. 1

These were separated on the same column, operated for 1 min isothermally at 160°C and then temperature-programmed at 15°C/min to 230°C and held at 230°C for 2 min. All the other conditions remained the same as above.

Dicarboxylic acid methyl ester

These were separated on the same column, operated isothermally at 150°C. All the other conditions remained the same as above.

RESULTS AND DISCUSSION

Polyester-based polyurethane foams can be successfully cleaved into diamine, dicarboxylic acid and polyol fragments by alkali fusion[6], but the subsequent separation of polyols before identification is often difficult or impossible. Although some glycols can be separated by an elaborate liquid–liquid extraction procedure, it is not possible to separate trifunctional alcohols (such as glycerol) and tetrafunctional alcohol (such as pentaerythritol), which are often found in rigid foam formulations. This problem was overcome by the derivatization of polyols before separation. The derivatization reagent trimethylsilylimidazole (TMSI) was used for the derivatization of polyols into their TMS derivatives. The advantages of using TMSI are that:

(i) It derivatizes hydroxy compounds without derivatizing diamines; (ii) It can be used in the presence of a certain amount of water in the reagent as long as sufficient of the reagent is used to react with both the water and the polyols. Therefore we were able to develop a simple analytical scheme (Fig. 1) for the analysis of polyester-based urethane foams.

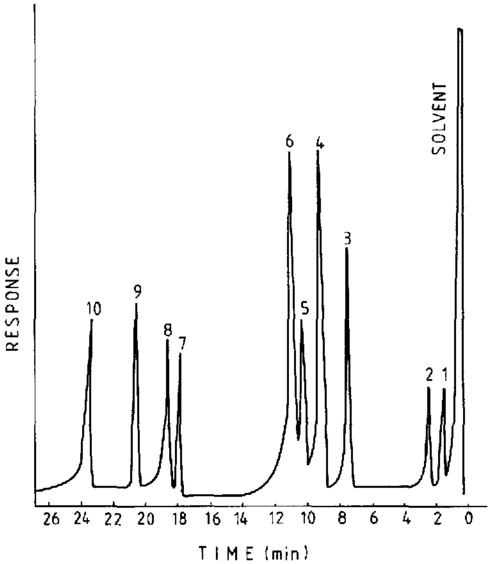


Fig. 2. Gas chromatogram showing separation of diamines. Peaks: 1 = ethylenediamine (EDA); 2 = hexamethylenediamine (HDA); 3 = *o*-phenylenediamine (*o*-PDA); 4 = *p*-phenylenediamine (*p*-PDA); 5 = *m*-phenylenediamine (*m*-PDA); 6 = toluenediamines (TDA); 7 = 1,5-naphthylenediamine (NDA); 8 = methylenebis(cyclohexylamine) (HMDA); 9 = *p,p*′-diphenylmethanediamine (MDA); 10 = methylenebis(*o*-chloroaniline) (MBCA).

Fig. 2 shows the GC separation of diamines corresponding to all commercially available diisocyanates and common diamine chain extenders. This was used to identify the diamines obtained from all five polymer samples analysed.

Fig. 3 shows the separation of TMS derivatives of the common polyhydric alcohols contained in polyesters used in polyurethane applications, on an SE-30 column. This can also be used for the qualitative and quantitative analysis of the compositions of polyols used in polyesters. Fig. 4 shows a separation of TMS derivatives of polyols separated from sample No. 1.

Derivatization of dicarboxylic acids into their methyl esters was used for the GC identification of dicarboxylic acids. Adipic acid was converted into its dimethyl ester by boron trifluoride–methanol. Separation of dimethyl adipate on an SE-30 column is shown in Fig. 5.

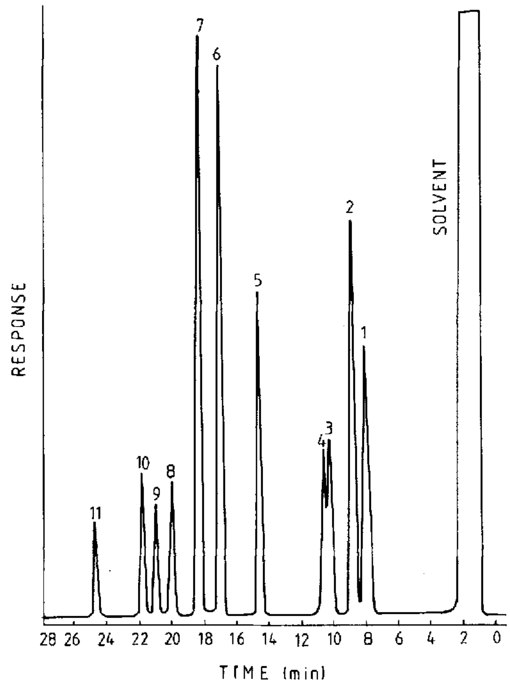
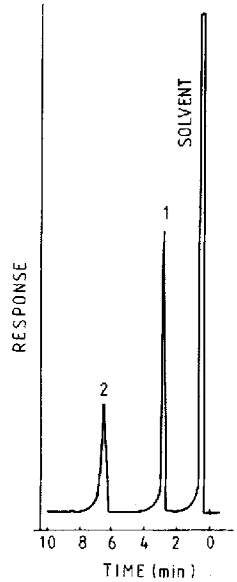


Fig. 3. Gas chromatogram showing separation of trimethylsilyl derivatives of polyols. Peaks: 1 = ethyleneglycol; 2 = 1,2-propyleneglycol; 3 = 1,2-butyleneglycol; 4 = 2,3-butyleneglycol; 5 = 1,4-butyleneglycol; 6 = diethyleneglycol; 7 = dipropyleneglycol; 8 = glycerol; 9 = trimethylol ethane; 10 = trimethylol propane; 11 = pentaerythritol.



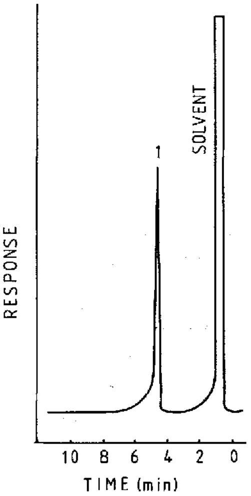


Fig. 4. Gas chromatogram showing separation of diethyleneglycol TMS (peak 1) and pentaerythritol TMS (peak 2).

Fig. 5. Gas chromatogram showing separation of dimethyl adipate (peak 1).

CONCLUSIONS

Alkali hydrolytic fusion of polyester-based polyurethane foams is much faster than conventional solution hydrolysis methods. The hydrolysis fragments are treated with TMSI to convert polyols into their TMS derivatives, which enable the separation and subsequent GC analysis of polyols. Non-volatile fragments, such as dicarboxylic acids, are also converted into a suitable derivative before GC analysis. Complete qualitative and semi-quantitative analysis of polyurethane foams can be achieved in a fraction of the time required for methods described previously.

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