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GAS CHROMATOGRAPHIC ANALYSIS OF POLYESTER-BASED POLYURETHANE ELASTOMERS AFTER ACID FUSION

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SUMMARY

An analytical procedure is described for the rapid qualitative and quantitative analysis of polyester-based polyurethane elastomers. The elastomers are normally the complex reaction products of an isocyanate-terminated linear polyester prepolymer cross-linked with either a diamine or a diol chain extender. The polymer is cleaved into the corresponding diamine, dicarboxylic acid and glycol acetate fragments by acid fusion using mixed anhydride reagent. These products are analysed by using gas chromatography, after separation using a liquid-liquid extraction procedure. Dicarboxylic acids are converted to dimethyl ester derivatives before gas chromatographic analysis, while diisocyanates are examined as the diamines and diols as acetyl derivatives.

INTRODUCTION

Polyurethanes are a versatile family of polymers used increasingly in recent years, because of their durability, solvent inertness and favourable electrical and thermal properties. A dynamic range of tailored mechanical properties is responsible for the broad use of polyurethane polymers in such varied areas as flexible and rigid foams, elastomers and resins.

The usual method of producing polyurethane is by the polymerization reaction of a diisocyanate and a hydroxy terminated material. The first hydroxy-terminated materials employed were polyesters. Polyesters have been largely replaced by polyethers in flexible and rigid foam areas, as well as in sealant applications. However, they are being used extensively for elastomers, coatings and spandex fibres.

Polyurethanes are, in general, extremely chemically resistant. The urethane linkages are difficult to cleave by simple solution hydrolysis, which is difficult and prolonged as indicated by Dawson *et al.*^{1,2}. Rapid hydrolysis of urethane linkage was reported by Gibian and Siggia³ where only diamines corresponding to diiso-

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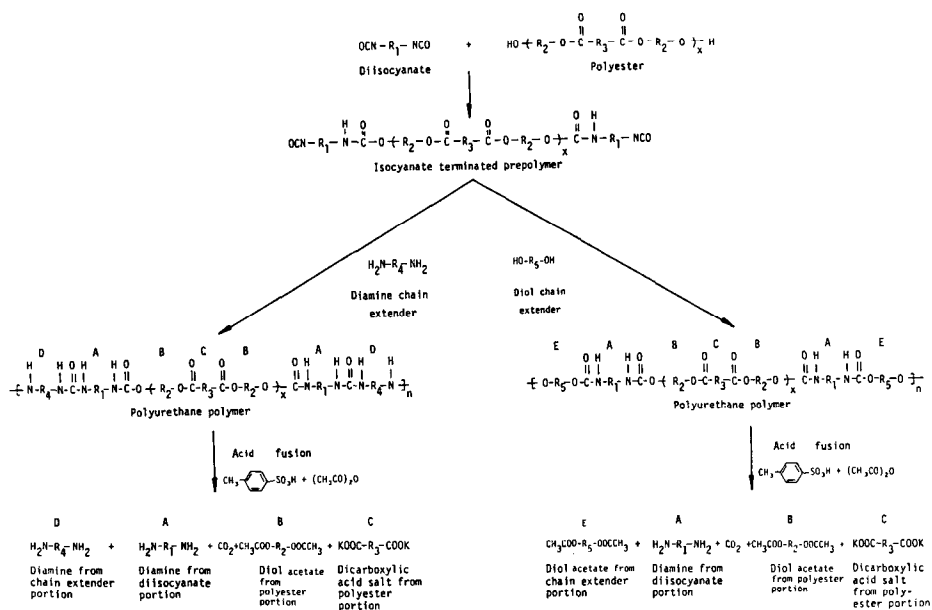


Fig. 1. Reactions involved in the analytical scheme.

cyanate were identified by gas chromatography (GC). We applied an alkali fusion procedure for the analysis of polyether^{4,5} and polyester⁶ based commercial polyurethane materials. We also reviewed the literature relating to the analysis of polyurethanes⁴.

Although alkali fusion successfully cleaved polyester based polyurethanes into diamine, glycol and dicarboxylic acid fragments⁶, the subsequent separation of highly water-soluble glycols is extremely difficult and time consuming. The separation requires an elaborate extraction procedure to be carried out in a continuous liquid-liquid extraction apparatus for at least 5 h. The preparation of suitable derivatives of glycols before the GC analysis requires another hour.

This paper reports a rapid and reliable analytical procedure for the analysis of polyester-based polyurethanes after acid fusion using mixed anhydride reagent. The procedure developed does not have the disadvantages present in alkali fusion due to simultaneous cleavage and derivatization of the glycol fragment. Hence lengthy liquid-liquid extraction procedures and derivatization procedures are avoided. Therefore, the total analysis would require only a fraction of the time required for the procedure using alkali fusion⁶.

The reactions involved in the analytical procedure are shown in Fig. 1.

EXPERIMENTAL

Samples

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

TABLE I
COMMERCIALY AVAILABLE POLYESTER-BASED POLYURETHANE SAMPLES

TDI = toluene diisocyanate (80:20; 2,4 and 2,6 isomer mixture); MDI = *p,p'*-diphenylmethane diisocyanate; MBCA = methylenebis(*o*-chloroaniline).

Sample No.	Diisocyanate	Polyester	Cross-linker
1	TDI	Ethylene glycol adipate	MBCA
2	TDI	Ethylene glycol 1,4-butanediol adipate	MBCA
3	TDI	Ethylene glycol, 1,2-propanediol, 1,4-butanediol adipate	MBCA
4	MDI	Ethylene glycol adipate	1,4-Butanediol
5	TDI	Ethylene glycol, 1,2-propanediol adipate	MBCA

Preparation of mixed anhydride reagent^{7,8}

The anhydride reagent was prepared by adding 10 g of acetic anhydride to 19 g of *p*-toluenesulphonic acid (which had been dried for 24 h under reduced pressure) contained in a 100-ml round-bottomed flask. The mixture was refluxed at 125°C for 0.5 h. The product consisting of mixed anhydrides of acetic acid and *p*-toluene sulphonic acid was used without further purification.

Acid fusion

Acid fusion was carried out using 200 mg of polymer and 30 g of mixed anhydride reagent prepared according to the method of Tsuji and Konishi^{7,8}. The reaction was carried out by refluxing the polymer reagent mixture at 125°C for 3 h.

Separation procedure

After cooling, the contents of the flask were dissolved in 20 ml of dichloromethane and neutralized with a saturated solution of sodium carbonate. Then the mixture was transferred to a separating funnel where the contents were extracted three times with 20-ml portions of dichloromethane.

The aqueous sodium carbonate solution was rendered slightly acidic using concentrated hydrochloric acid and the liberated dicarboxylic acid was extracted three times with 15-ml portions of chloroform. Dibasic acid extracted was converted to its dimethyl ester by adding 5 ml of boron trifluoride-methanol reagent and refluxing for 1 h. The unreacted reagent was destroyed by adding water (20 ml) and the methyl ester was extracted twice with 10-ml portions of chloroform and concentrated to a small volume (1 ml) under reduced pressure for GC analysis of dicarboxylic acid corresponding to the polyester backbone.

The combined dichloromethane extract was extracted three times with 15-ml portions of 5 *M* aqueous hydrochloric acid. The combined aqueous extract was rendered slightly basic by adding sodium hydroxide pellets and liberated diamines were extracted three times with 15-ml portions of dichloromethane and concentrated for GC analysis of diamines corresponding to diisocyanate portion and chain extender portion of the polymer.

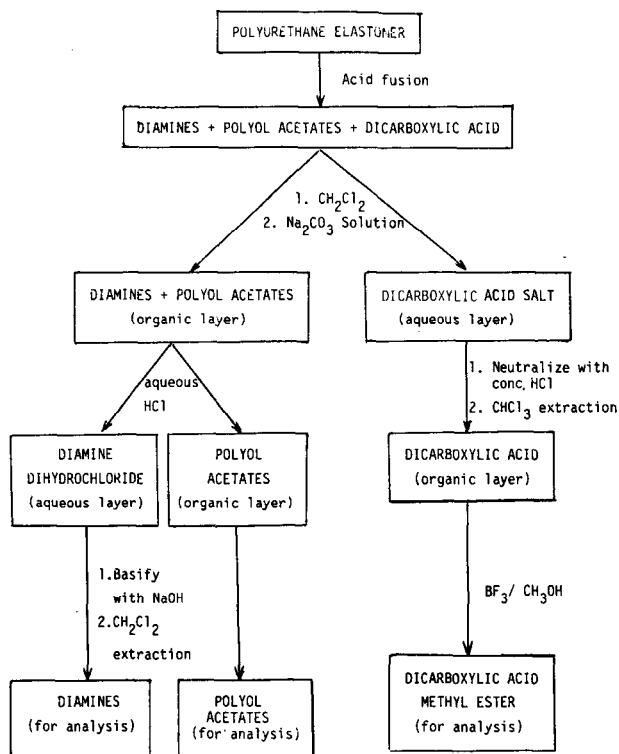


Fig. 2. Analytical scheme.

The dichloromethane extract remained after hydrochloric acid extraction was concentrated as above for GC analysis of polyol acetates corresponding to the chain extender portion and glycol portion of the polyester backbone. The complete separation scheme is shown in Fig. 2.

Gas chromatography

GC was carried out using a Hewlett-Packard 5830A Research Model gas chromatograph with flame ionization detection.

Diamines. These were separated on a 4 ft. \times 1/8 in. O.D. stainless-steel column packed with 3% XE-60 on Chromosorb W HP, 100–120 mesh, using helium as carrier gas at a flow-rate of 25 ml/min. The detector and injection port were maintained at 250°C and 260°C, respectively. The column was operated 4 min isothermally at 130°C and then temperature programmed at 20°C/min to 240°C and held at 240°C for 5 min.

Acetates of polyols. These were separated on a 6 ft. \times 1/8 in. O.D. stainless-steel column packed with 10% SE-30 on Chromosorb WHP, 100–120 mesh, using helium as carrier gas at a flow-rate of 25 ml/min. The detector and injection port were maintained at 200°C and 250°C, respectively. The column was operated 6 min isothermally at 100°C and then temperature programmed at 10°C/min to 180°C and held at 180°C for 2 min.

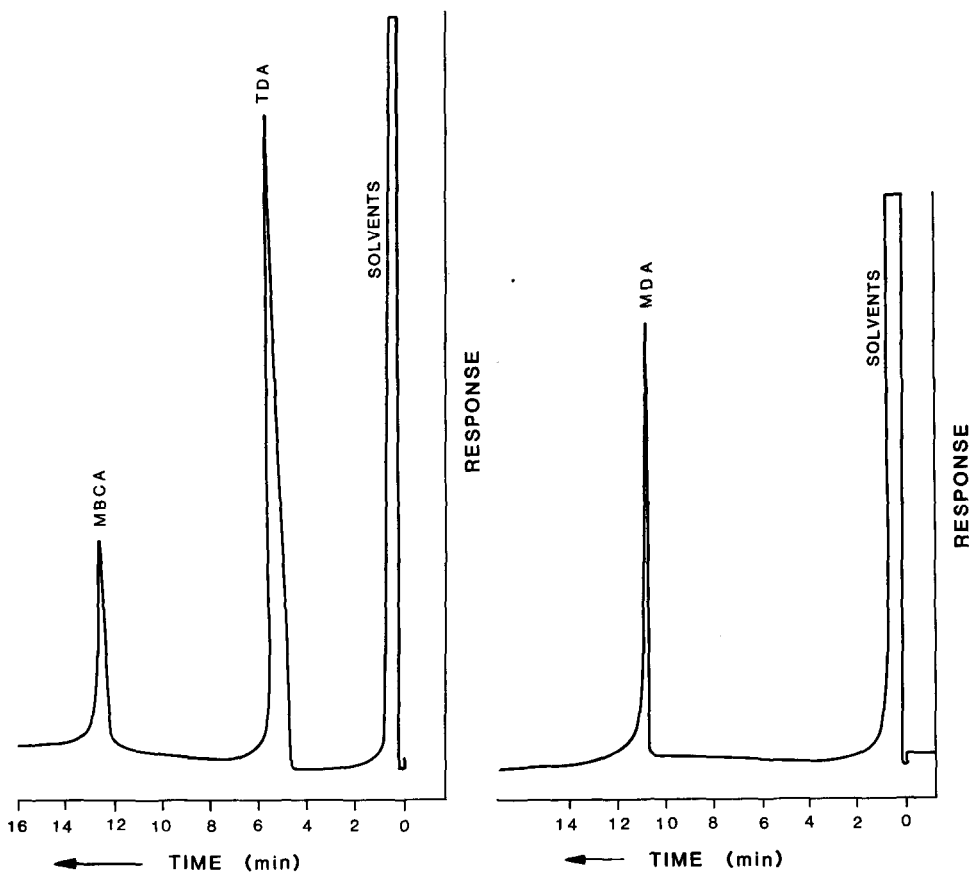


Fig. 3. Gas chromatogram showing separation of toluene diamines (TDA) and methylenebis(*o*-chloroaniline) (MBCA). Conditions: 4 ft. \times 1/8 in O.D. stainless-steel column packed with 3% XE-60 on Chromosorb WHP, 100–120 mesh; helium carrier gas at a flow-rate of 25 ml/min. The detector and injection ports were maintained at 250°C and 260°C, respectively. The column was operated 2 min isothermally at 130°C and then temperature programmed at 20°C/min to 240°C and held at 240°C for 5 min.

Fig. 4. Gas chromatogram showing separation of *p,p'*-diphenylmethane diamine (MDA). Conditions as in Fig. 3.

Dicarboxylic acid methyl ester. These were also separated on the same column operated isothermally at 150°C. The other conditions remained as above.

RESULTS AND DISCUSSION

Polyester-based polyurethane elastomers were successfully cleaved into diamine, dicarboxylic acid and polyol acetate fragments by acid fusion using mixed anhydride reagent. Before the GC analysis, these fragments were successfully separated using the liquid–liquid extraction procedure shown in Fig. 2.

The diamines corresponding to the diisocyanate portion and chain extender portion of the polymer were successfully separated by GC on a XE-60 column. Fig.

3 shows the separations of toluene diamines (*i.e.* 2,4 and 2,6 isomers) and methylenebis(*o*-chloroaniline) (MBCA) from sample 1. Similar chromatograms were obtained for all the other samples except sample 4. Fig. 4 shows the separation of *p,p'*-diphenylmethane diamine (MDA) corresponding to *p,p'*-diphenylmethane diisocyanate (MDI). Although separation of 2,4 and 2,6 isomers of toluene diamine was unsuccessful using GC, it could be achieved using liquid chromatography as shown in our previous report⁶.

Derivatization of dicarboxylic acids into their methyl esters was used for GC identification of dicarboxylic acids. Adipic acid present in all the samples was converted to its dimethyl ester using borontrifluoride-methanol reagent. Separation of dimethyl adipate on a SE-30 column is shown in Fig. 5.

Polyol acetates corresponding to the glycol portion of the polyesters were suc-

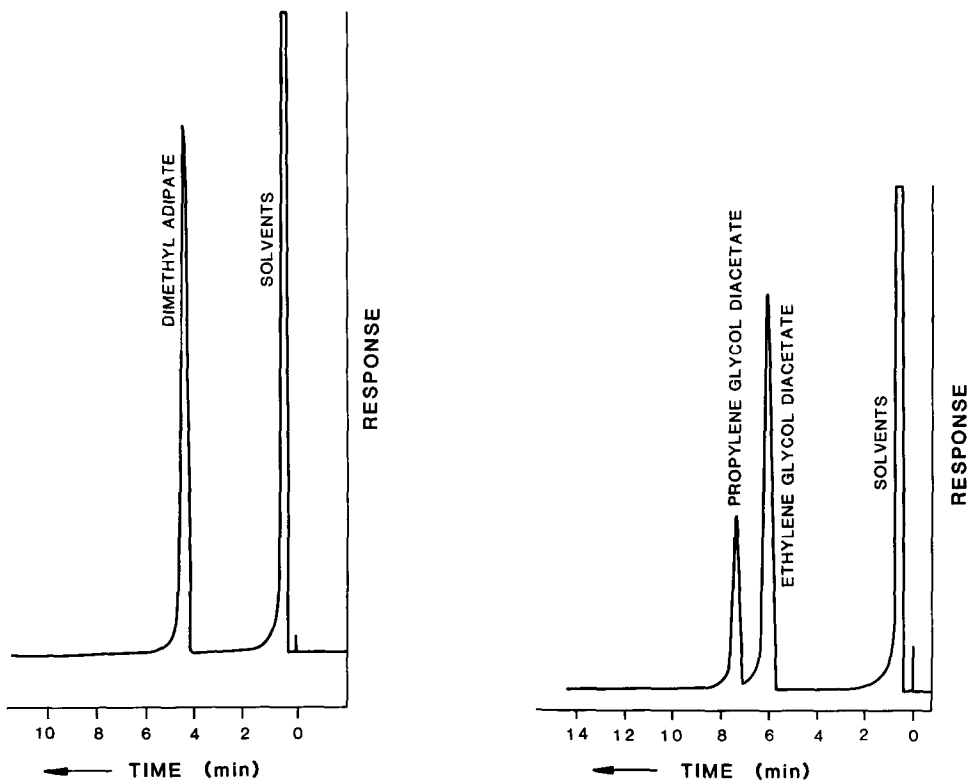


Fig. 5. Gas chromatogram showing the separation of dimethyl adipate. Conditions: 6 ft. \times 1/8 in. O.D. stainless-steel column packed in 10% SE-30 on Chromosorb WHP, 100–120 mesh; helium carrier gas at a flow-rate of 25 ml/min. The detector and injection ports were maintained at 200°C and 250°C, respectively. The column was operated isothermally at 150°C.

Fig. 6. Gas chromatogram showing the separation of ethylene glycol diacetate and propylene glycol diacetate. Conditions: 6 ft. \times 1/8 in. O.D. Stainless-steel column packed with 10% SE-30 on Chromosorb WHP, 100–120 mesh; helium carrier gas at 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 6 min isothermally at 100°C and temperature programmed at 10°C/min to 180°C and held at 180°C for 2 min.

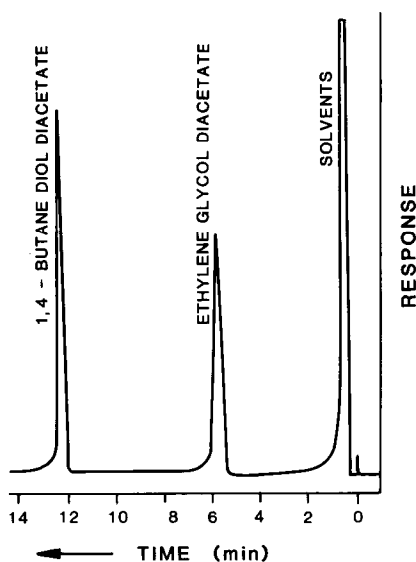


Fig. 7. Gas chromatogram showing separation of ethylene glycol diacetate and 1,4-butane diol diacetate. Conditions as in Fig. 6.

cessfully separated on a SE-30 column. Figs. 6 and 7 show the separation of glycol acetates from samples 4 and 5, respectively. These chromatograms could be used for the quantitative estimation of glycol proportions used in polyester manufacture. If monoacetate products appear in the chromatograms, the method of Blakeney *et al.*⁹ could be used to achieve complete acetylation of glycols before the GC analysis.

Mixed anhydride reagent is an excellent reagent for acid fusion due to its high compatibility with polymers, indicated by the instantaneous solubility of all polymer samples analysed in the hot reagent. This reagent completely cleaves polyester-based polyurethanes in 3 h at 125°C, with the simultaneous conversion of polyhydroxy compounds into the corresponding acetates, whereas with other acidic reagents (*i.e.* 50% aqueous hydrochloric acid), several days of refluxing are required for the complete cleavage¹⁰.

The hydrolysis of polyester-based polyurethanes will always give polyhydroxy compounds (such as glycols and tris) which are extremely difficult to separate, and hence require a continuous liquid-liquid procedure to be carried out at least for 5 h, and these polyhydroxy compounds must be converted to a suitable derivative before the GC analysis. The mixed anhydride reagent not only affects the complete cleavage of the polymer, but also simultaneously acetylates polyhydroxy compounds formed. Therefore, neither the lengthy liquid-liquid extraction procedure nor the derivatization procedure is required for the method using acid fusion, hence the total analysis would require only a fraction of the time required for alkali fusion.

CONCLUSIONS

Acid fusion of polyester-based polyurethanes using mixed anhydride reagent is much faster than conventional solution hydrolysis methods. Complete qualitative

and semi-qualitative analysis of polyurethane polymer could be achieved in a few hours. The degradation fragments are conveniently analysed by GC. Non-volatile fragments such as dicarboxylic acids are converted to a suitable volatile derivative before GC analysis.

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