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GAS CHROMATOGRAPHIC ANALYSIS OF POLYETHER-BASED POLYURETHANES AFTER ACID FUSION

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SUMMARY

An analytical procedure is described for rapid qualitative and quantitative analysis of polyether-based polyurethanes. Polyurethane foams are conventionally the complex reaction product of an isocyanate terminated branched polyether prepolymer extended with water. The polymer is cleaved into the diamine corresponding to the polyether portion of the polymer, by using mixed anhydride reagent. These products are analysed using gas chromatography after separation using liquid-liquid extraction procedure. The procedure is discussed and compared with an earlier reported scheme where the polymer was first fragmented by alkali fusion and the liberated polyether subsequently degraded using mixed anhydride reagent.

INTRODUCTION

Polyurethanes for the last two decades have been one of the fastest growing segments of the polymer industry. Polyurethanes are characterized by the urethane $[-NH-(CO)-O-]$ linkage although other groups such as ether, ester, biuret, allophanate, amide and other groups may be present in the polymer molecule.

The method of manufacture of polyurethane includes the reaction of di- or polyfunctional hydroxy compounds, such as hydroxy terminated polyethers or polyesters with di- or polyisocyanate. Because of the many structural variations that are possible in their manufacture, urethanes may be considered as the most versatile polymers.

The most widely used and versatile types of hydroxy component are hydroxy-terminated polyethers. They are prepared commercially by the base-catalysed addition of alkylene oxides such as propylene, ethylene and butylene oxide to di- or polyfunctional alcohols¹.

As instrumental techniques such as infrared spectrometry (IR)²⁻⁴ and nuclear magnetic resonance spectroscopy (NMR)^{5,6} were found to be unsuitable for the complete analysis of polyurethanes, the methods based on chemical degradation followed

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by the analysis of fragments were found to be the most proven approach. Chemical degradation is usually carried out under aqueous acidic⁷⁻¹⁰ and alkaline^{5,6,11-15} conditions.

The method described by Haslam and co-workers^{8,9} with 50% aqueous hydrochloric acid was found to give incomplete hydrolysis despite longer reaction times (60 h) and yielded some undesirable side products. Alkaline hydrolysis has subsequently been carried out using aqueous sodium and potassium hydroxide reagents. Despite longer reaction time^{5,6} (*i.e.* 16 h at 150°C), the hydrolysis of only urethane linkage occurs while ether linkages remain unreacted, in the case of polyether based polyurethanes. Therefore, the analysis was restricted only to the identification of diamine corresponding to diisocyanate portion of the polymer. The analytical scheme recently developed by Haken and co-workers^{16,17} described a procedure for the complete analysis of polyether based polyurethanes where alkali fusion is used for the rapid high temperature hydrolysis of the polymer followed by acidic cleavage of the polyether fragment formed.

Acid fusion reactions have been successfully used to cleave polyvinyl esters and cellulose esters by Siggia and co-workers¹⁸⁻²⁰. The reagents used include orthophosphoric acid, sodium bisulphate monohydrate, *p*-toluenesulphonic acid and benzene sulphonic acid. *p*-Toluenesulphonic acid was found to be the most suitable of all reagents available for acid fusion due to its high thermal stability (*i.e.* up to 200°C) and excellent compatibility with the polymers. *p*-Toluenesulphonic acid could be used alone or in combination with acetic anhydride for acid fusion. Several such mixed anhydrides of carboxylic and sulphonic acid have been used by Karger and Mazur²¹ for the cleavage of ether linkages. Mixed anhydride reagent of *p*-toluenesulphonic acid and acetic anhydride reagent has been used to cleave polyether polyols and hydroxy terminated polyols based on diamines and alkylene oxides.

We present a one-step simple rapid reliable analytical procedure for the complete analysis of polyurethane foam based on polyethers. Polymer is cleaved using mixed anhydride reagent and the reactions involved are shown in Fig. 1.

The advantages of using this reagent are:

(i) Complete cleavage of both urethane linkage and ether linkage could be achieved in a single step.

(ii) Complete cleavage of the polymer is achieved in 6 h at 125°C whereas days of refluxing is required under aqueous acidic conditions^{5,6}.

(iii) Acetylation of fragments occurs simultaneously with the cleavage hence derivatation before gas chromatographic (GC) analysis of non volatile fragments would not be required and the subsequent separation of ester of glycols by liquid-liquid extraction is much easier than glycol itself.

(iv) Total analysis time using this procedure is a fraction of that required for the procedure using alkali fusion due to the elimination of one degradation step and the subsequent separation step using liquid-liquid extraction.

EXPERIMENTAL

Samples

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

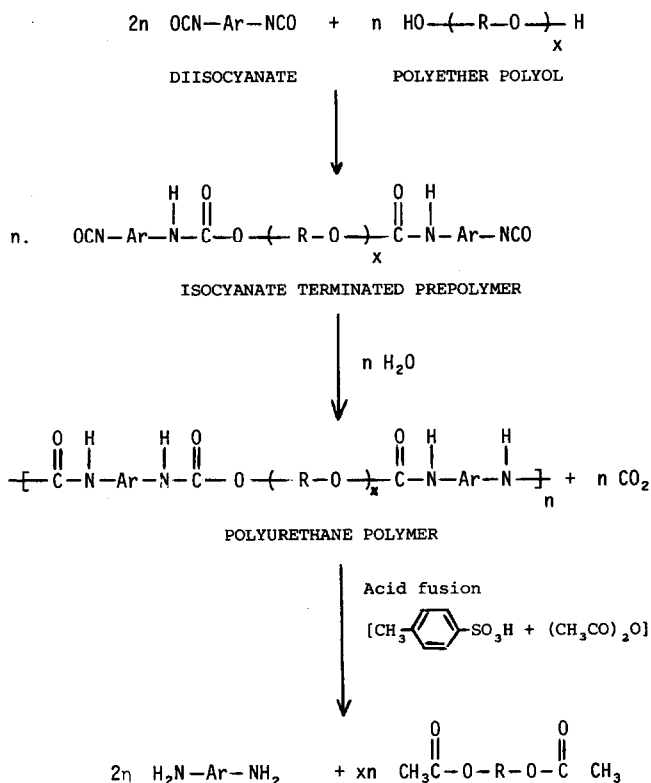


Fig. 1. Reactions involved in the analytical scheme.

Acid fusion

Acid fusion was carried out using approximately 200 mg of polymer with 30 g of mixed anhydride reagent prepared according to the method of Tsuji and Konishi^{22,23}. The reaction was carried out by placing finely ground polymer into the boiling reagent in a flask connected to a reflux condenser. The mixture was allowed to reflux at 125°C for 6 h.

TABLE I

COMPOSITION OF POLYURETHANE SAMPLES

TDI = toluene diisocyanates (80:20 mixture of 2,4- and 2,6-isomers); MDI = 4,4'-diphenylmethane diisocyanate; NDI = 1,5-naphthalene diisocyanate.

Sample No.	Isocyanate	Polyether polyol
1	TDI	Propylene oxide adduct of glycerol
2	TDI	Ethylene oxide adduct of glycerol
3	TDI	Ethylene oxide-propylene oxide adduct of glycerol
4	MDI	Polytetramethylene ether glycol
5	MDI	Propylene oxide adduct of glycerol
6	NDI	Propylene oxide adduct of glycerol

Preparation of mixed anhydride reagent^{22,23}

Mixed anhydride reagent was prepared by refluxing 0.1 mole of acetic anhydride and 0.1 mole of *p*-toluenesulphonic acid (which had been dried under reduced pressure for 24 h) at 125°C for 0.5 h.

Separation procedure

After cooling the reaction mixture, the contents were dissolved in dichloromethane and then neutralized with a saturated solution of sodium carbonate, followed by another three extractions with 10-ml portions of chloroform. The combined organic extracts were dried over anhydrous sodium sulphate and extracted three times with 10-ml portions of 5 *M* hydrochloric acid. The organic layer remained after hydrochloric acid extraction was dried and treated with 1-methylimidazole²⁴ (0.2 ml) and acetic anhydride (2 ml). After 10 min at room temperature, water (10 ml) was added to destroy the excess reagent and the organic layer was separated, dried and concentrated to give about 1 ml of solution of which 1 μ l was injected into the gas chromatograph for the analysis polyol acetates corresponding to polyether portion of the polymer.

The combined aqueous hydrochloric acid layers were neutralized by adding sodium hydroxide pellets and liberated diamines were extracted with three times 10-ml portions of dichloromethane. The combined organic extracts were dried, concentrated and used for the GC analysis of diamine corresponding to diisocyanate portion of the polymer. The separation scheme is shown in Fig. 2.

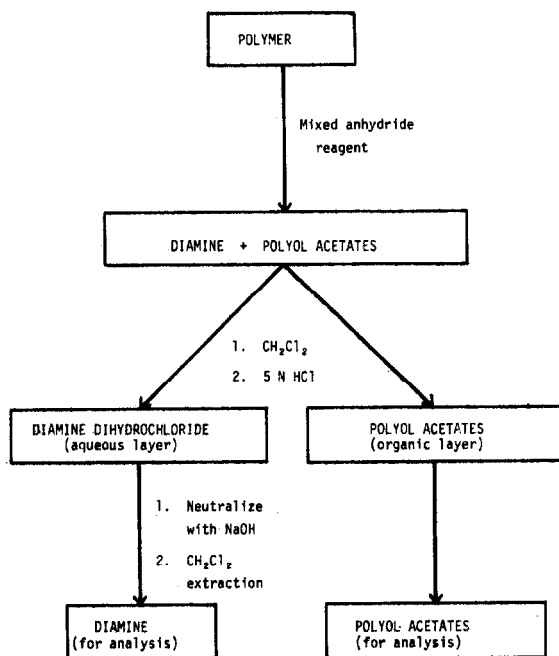


Fig. 2. Analytical scheme.

Gas chromatography

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

Diamines

Diamines were separated on 4 ft. \times 1/8 in. O.D. stainless-steel column packed with 10% XE-60 on Chromosorb W AW DMCS 80–100 mesh, using helium carrier gas at a flow-rate of 25 ml/min. The detector and injection ports were maintained at 225 and 250°C, respectively. The column was operated 1 min isothermally at 150°C and then temperature programmed at 15°C/min to 240°C and held at 240°C for 5 min.

Polyol acetates

Polyol acetates were separated on a 6 ft. \times 1/8 in. O.D. stainless-steel column packed with 10% SE-30 on Chromosorb W HP, 80–100 mesh, using helium carrier gas flow-rate at 25 ml/min. The injection port and detector were maintained at 200 and 220°C, respectively. The column was operated 6 min isothermally at 100°C and then temperature programmed at 15°C/min to 200°C and held at 200°C for 5 min.

RESULTS AND DISCUSSION

Polyether based polyurethanes were successfully cleaved into diamine and polyol acetate fragments using acid fusion. Although quantitative cleavage of ether linkages could be achieved by refluxing the polymer and reagent mixture at 125°C for 3 h, the quantitative cleavage of urethane linkages was only achieved by extending the reaction time to 6 h.

The diamine fragment corresponding to the diisocyanate portion of the poly-

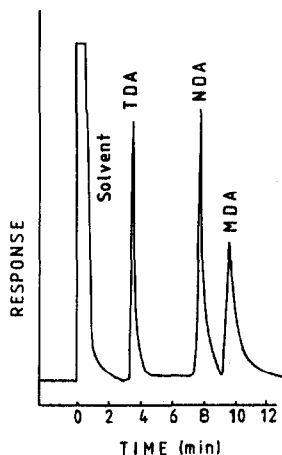


Fig. 3. Gas chromatogram showing separation of toluene diamines (TDA) 1,5-naphthalene diamine (NDA) and 4,4'-diaminodiphenylmethane (MDA). Conditions: 4 ft. \times 1/8 in. O.D. stainless-steel column packed with 10% XE-60 on Chromosorb W-AW-DMCS 80–100 mesh, helium carrier gas flow-rate 25 ml/min. The detector and injection ports at 225 and 250°C, respectively. The column was operated 1 min isothermally at 150°C and then temperature programmed at 15°C/min to 240°C and held at 240°C for 5 min.

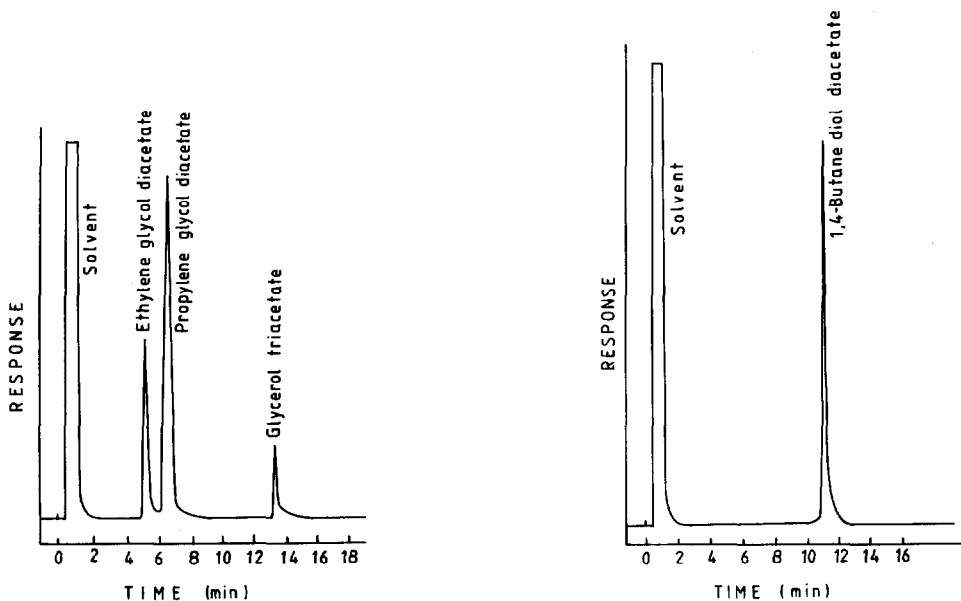


Fig. 4. Gas chromatogram showing separation of ethylene glycol diacetate, propylene glycol diacetate and glycerol triacetate. Conditions: 6 ft. \times 1/8 in. O.D. stainless-steel column packed with 10% SE-30 on Chromosorb W HP, 80–100 mesh, Helium carrier gas flow-rate at 25 ml/min. The detector and injection ports at 200 and 220°C, respectively. The column was operated 6 min isothermally at 100°C and temperature programmed at 15°C/min to 200°C and held at 200°C for 5 min.

Fig. 5. Gas chromatogram showing separation of 1,4-butanediol diacetate. Conditions as in Fig. 4.

mer was successfully separated by GC on a XE-60 column. The diamines were identified by comparing their retention times with authentic standards separated under the same conditions. Fig. 3 shows the separation of such diamines corresponding to all three diisocyanates present in the samples.

Successful separation of the isomers of diamine corresponding to TDI was not achieved by using GC and liquid chromatography was used for isomers separation. Conditions used were similar to those reported in our previous work²⁵.

Polyol acetates corresponding to the polyether portion of the polymer were successfully separated using GC with a SE-30 column. Figs. 4 and 5 show the separation of polyol acetates corresponding to the polyether portion of the polymer sample Nos. 3 and 4, respectively. These chromatograms could be used for the qualitative and quantitative identification of the polyether.

Mixed anhydride reagent is not capable of acetylating the polyol fragments completely. As a result, peaks corresponding to monoacetate derivatives were also obtained²⁵. Therefore the acetylation method of Blakeney *et al.*²⁴ using 1-methylimidazole and acetic anhydride was used to obtain only di- or tri-acetylated polyols. This will facilitate the quantitative composition analysis of polyether polyol.

CONCLUSIONS

Acid fusion using mixed anhydride reagent is a rapid and reliable method

available for the complete chemical degradation of polyether-based polyurethane. Unlike alkali fusion, the cleavage of both urethane and ether linkages occur simultaneously. Fragments formed undergo acetylation, hence derivatization before the GC analysis is not required.

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