

CHROM. 7935

## RAPID IDENTIFICATION OF SOLID POLYURETHANE ELASTOMERS

D. THORBURN BURNS

*Loughborough University of Technology, Loughborough, Leics. LE11 3TU (Great Britain)*

and

E. W. JOHNSON and R. F. MILLS

*Triumph Motors, British Leyland UK Ltd., Coventry (Great Britain)*

(Received September 3rd, 1974)

---

### SUMMARY

A procedure based upon pyrolytic gas chromatography and infrared spectroscopy has been developed for the rapid identification of solid polyurethane elastomers. Pyrolytic gas chromatography is used to identify the hydroxyl constituents and the anti-hydrolysis carbodiimide additive, and infrared spectroscopy to identify the diisocyanate.

---

### INTRODUCTION

Solid polyurethane elastomers are elastomeric materials formed by the rearrangement polymerisation of isocyanates and polyols<sup>1</sup>. Their three main constituents are: (i) an aromatic diisocyanate, (ii) a long-chain polyol, either a polyester or a polyether, and (iii) a chain extender, which can be a short-chain glycol, a diamine or water<sup>2</sup>. Physically they are characterised by toughness, excellent tear, and abrasion resistance; the main weakness is generally considered to be their susceptibility to hydrolytic attack, which can be counteracted by the addition of carbodiimide<sup>3</sup>.

The chemical analysis of polyurethanes is difficult because of their three-dimensional polymeric structure. Available classical methods only provide simple qualitative tests for a few specific constituents<sup>2</sup>. Infrared (IR) spectroscopy has been used to identify the type of isocyanate<sup>4,5</sup> and the functional groups<sup>6</sup> present in a polyurethane. Nuclear magnetic resonance shows some potential for the determination of structural groups<sup>7</sup>, but is limited because the sample must be dissolved prior to examination. Hydrolysis of the polyurethane followed by examination of the products is at the present the most complete and proven approach<sup>4,8-10</sup> but the main drawback is that analysis times are long, requiring from 6-24 h for the hydrolysis stage, with further time required for the separation and identification stages.

Pyrolytic gas chromatography (GC) has only recently been applied to polyurethanes. Work by Takeuchi *et al.*<sup>11</sup>, using a small number of samples, appears to show good agreement with IR and mass spectral studies. The procedure is very rapid with both short sample preparation and analysis times.

The purpose of the present study was to develop a rapid method for the identification of solid polyurethane elastomers. The grades of elastomers examined were restricted to those normally encountered in the automobile industry, which in general are polyester urethanes.

Pyrolytic GC was chosen for detailed study in view of the results<sup>11</sup> for polyurethanes, work on other polymers<sup>12,13</sup> and the fact that little sample preparation would be required and given the correct chromatographic conditions, analysis times could be short. Various stationary phases have been examined, *viz.* Apiezon L, Silicone Fluid M.S. 200/12500, Free Fatty Acid Phase (FFAP), Carbowax 6000, Porapak Q, silicone grease, and squalane. Carbowax 6000 proved to be the most suitable phase, and has been successfully used for the identification of polyols, chain extenders, and the anti-hydrolysis additive, carbodiimide. The diisocyanates could not be identified in commercial elastomers using pyrolysis GC; however, IR examination of a cast film allows identification of the aromatic diisocyanate present.

Having identified the polyol, chain extender and the diisocyanate present, the elastomer can be classified. The absence or presence of the carbodiimide allows a further division of class into hydrolysis-unprotected or hydrolysis-protected materials. The specific grade within a class may be ascertained by a shore hardness measurement.

## GAS CHROMATOGRAPHY

### *Experimental*

#### *Apparatus*

The following apparatus was used for GC: a Perkin-Elmer F11 flame ionization gas chromatograph, a Pye "Curie-Point" pyrolyser, and a Hitachi-Perkin-Elmer potentiometric recorder, Model 159.

The optimised conditions for analysis, determined in preliminary studies, were: column, 1 m  $\times$  3.2 mm O.D.; stationary phase, 10% Carbowax 6000 on Chromosorb W, 80-100 mesh; oven temperature, 40° for 0 min, to 210° at 15°/min; injection block temperature, 350°; air pressure, 28 lbs./sq. in.; hydrogen pressure, 15 lbs./sq. in.; carrier gas, nitrogen; nitrogen flow-rate, 30 ml/min; recorder, 2.5 mV; attenuation, various; pyrolysis temperature, 770°; pyrolysis time, 10 sec; pyrolysis wire, coiled pure iron<sup>14</sup>.

#### *Materials*

The following chemicals were obtained from Dunlop (Leicester, Great Britain): Polyols—polyethylene adipate (PEA) and polycaprolactone. Chain extenders—1,4-butanediol and hydroquinone-diethyl ether (30:10). Diisocyanates—4,4'-diphenylmethane (MDI), 1,5-naphthalene (NDI) and 2,4- and 2,6-tolylene (TDI). Anti-hydrolysis additive—polycarbodiimide (Stabaxol).

Elastomer Products (Leicester, Great Britain) supplied the following chemicals: Polyols—polyethylene adipate (PEA) (Polyol 2000), polyethylene adipate/polypropylene adipate (PEA + PPA) (Polyol 2001) and polycaprolactone (Niax 560). Chain extenders—1,4-butanediol (Agent B) and hydroquinone-diethyl ether (30:10). Diisocyanate—4,4'-diphenylmethane (MDI). Anti-hydrolysis additive—polycarbodiimide (Stabaxol).

TABLE I  
FORMULATIONS

*A series*

<b>A1</b>		<b>A2</b>	
PEA	100 parts	PEA	100 parts
MDI	30 parts	TDI	9 parts
Hydroquinone- diethyl ether	14 parts	Hydroquinone- diethyl ether	1 part
<b>A3</b>		<b>A4</b>	
Polycaprolactone	100 parts	PEA	100 parts
MDI	50 parts	NDI	30 parts
1,4-Butanediol	12.5 parts	1,4-Butanediol	14 parts
Polycarbodiimide	2 parts		

*B series*

<b>B1</b>	<b>B2</b>	<b>B3</b>	<b>B4</b>
Polyol 2000	Polyol 2001	Polyol 2000	Polyol 2000
MDI	MDI	MDI	MDI
1,4-Butanediol	1,4-Butanediol	Hydroquinone- diethyl ether	Hydroquinone- diethyl ether
	Polycarbodiimide		Polycarbodiimide
<b>B5</b>	<b>B6</b>	<b>B7</b>	<b>B8</b>
Polyol 2001	Polyol 2001	Niax 560	PEA
MDI	HDI	MDI	MDI
Hydroquinone- diethyl ether	1,4-Butanediol	1,4-Butanediol	Hydroquinone- diethyl ether
Polycarbodiimide	Polycarbodiimide	Polycarbodiimide	

*Formulations*

In addition to the polyurethane constituents various grades of solid polyurethane elastomers were obtained. Information on the per cent formulation of some of the grades (A1–A4) was supplied and used to further check the validity of the identification, in other cases only the components were given (B1–B8) (Table I).

*Results*

The hydroxyl constituents and the polycarbodiimide were subjected to pyrolysis GC, under the conditions summarised above, and the pyrograms are examined and the peaks are listed for identification purposes as shown in Table II. Relative peak sizes are not given as these vary with the grades, batch of components and exact pyrolysis conditions (large > 15% maximal peak, minor < 2% are indicated). Reference pyrograms, although not essential, are helpful in identifying unknown samples.

Formulations A1–A4 and B1–B8 were pyrolysed and in each case the constituents were identified using the data in Table II as follows:

*Polyols*

- (1) PEA —Major peak at 4.3 min and no peak at 3.5 min.
- (2) PEA + PPA —Major peak at 4.3 min plus a small peak at 3.5 min and a medium-sized peak at 0.6 min.
- (3) Polycaprolactone —Major peak at 11.5 min.

TABLE II

## PEAKS FOR HYDROXYL CONSTITUENTS AND POLYCARBODIIMIDE

Abbreviations: L = large; M = minor.

<i>Retention time (min)</i>	<i>PEA</i>	<i>PEA + PPA</i>	<i>Polycaprolactone</i>	<i>1,4-Butanediol</i>	<i>Hydroquinone-diethyl ether</i>	<i>Stabaxol</i>
0.3	L	L	L	M	L	
0.4	L	L			L	
0.6		L	M	M		
1.0- 1.2			M			
3.5		M				
4.0- 4.3	L	L	L			
5.0- 5.1			M			
5.5	M	M				
6.3- 6.5	M	M	M			
7.7- 7.9	M	M	M	M		
8.3- 8.5			M			
9.0- 9.1	L	L		M		
10.0			M			
11.0-11.2	M	M				
11.4-11.8		L	L	L		
11.8-11.9	M	M				
13.2-13.4	M	M				
15.7-16.3	M	M	M			
22.0-22.5	M	M	M			
29.0-29.3						L
35.3-36.4						L
39.0-40.0						L

*Chain extenders*

(1) 1,4-Butanediol in the presence of PEA —indicated by peak at 11.5 min.

(2) 1,4-Butanediol in the presence of PEA + PPA —increase in relative peak area must be used for the peak at 11.5 min compared with the pyrogram of PEA + PPA alone.

(3) Butanediol in the presence of polycaprolactone —increase in relative peak area must be used for the peak at 11.5 min compared with the pyrogram of polycaprolactone alone.

(4) Hydroquinone-diethyl ether in the presence of PEA —the relative increase in the peak area of the first two peaks (0.3 and 0.4 min) compared with the pyrogram of PEA alone. Plus the negative information of no significant peak at 11.5 min.

(5) Hydroquinone-diethyl ether in the presence of PEA + PPA —increase in relative peak area must be used for the peaks at 0.3 and 0.4 min compared with the pyrogram of PEA + PPA.

*Anti-hydrolysis additive*

Polycarbodiimide —indicated by the presence of peaks after 29.0 min.

## IDENTIFICATION OF THE DIISOCYANATES BY IR SPECTROSCOPY

The three main aromatic diisocyanates NDI, TDI and MDI were finger-

TABLE III  
DIAGNOSTIC ABSORPTIONS OF AROMATIC DIISOCYANATES

<i>Diisocyanate</i>	<i>Diagnostic IR absorption band</i>
TDI	1785 cm <sup>-1</sup> (5.6 μ) and 758 cm <sup>-1</sup> (13.2 μ)
MDI	815 cm <sup>-1</sup> (12.25 μ) and 782 cm <sup>-1</sup> (12.8 μ)
NDI	779 cm <sup>-1</sup> (12.85 μ)

printed by IR spectroscopy using the method outlined below. Commercial polyurethane elastomers were then fingerprinted in the same manner and the diisocyanate used was identified by comparison with the diisocyanate fingerprints.

### *Experimental*

Approximately 0.2 g of solid polyurethane elastomer was cut up into small pieces and transferred to a 5-ml beaker. 90% formic acid was added and the whole was heated to boiling by means of a hot plate. After the solid had gone into solution, which took from 15–60 min, depending on the type of elastomer, the contents of the beaker was allowed to cool. A film was cast on a sodium chloride plate and the excess of formic acid was dried off in an air-circulated oven at 100°. The IR spectra of the films were recorded over the range 4000–650 cm<sup>-1</sup> (2.50–15.0 μ) by the use of a recording IR spectrophotometer. Regular wavelength calibrations were made using a standard polystyrene film.

The aromatic diisocyanates were readily identified by the diagnostic absorptions listed in Table III.

In addition, the hydroquinone–diethyl ether may be confirmed by a characteristic absorption doublet at 1070 cm<sup>-1</sup> (9.35 μ) and 1085 cm<sup>-1</sup> (9.22 μ). The aliphatic HDI cannot be satisfactorily identified by this technique since HDI does not give a diagnostic absorption band. Its presence is normally indicated in elastomers by the absence of an aromatic absorption at 1600 cm<sup>-1</sup> (6.25 μ).

## DISCUSSION AND CONCLUSIONS

The elastomers examined in the present study can be classified by reference to

TABLE IV  
CLASSIFICATION OF THE ELASTOMERS

<i>Type</i>	<i>No.</i>	<i>Polyol</i>	<i>Diisocyanate</i>	<i>Chain extender</i>
Thermoplastic	1	PEA	MDI	1,4-Butanediol
	2	PEA	MDI	Hydroquinone–diethyl ether
	3	PEA + PPA	MDI	1,4-Butanediol
	4	PEA + PPA	MDI	Hydroquinone–diethyl ether
	5	Polycaprolactone	MDI	1,4-Butanediol
Millable	6	PEA + PPA	HDI	1,4-Butanediol
	7	PEA	TDI	Hydroquinone–diethyl ether
Castable	8	PEA	NDI	1,4-Butanediol

their three main chemical constituents. The various types of material examined are listed in Table IV.

Each class can be further divided into hydrolysis-protected or hydrolysis-unprotected elastomers depending on the absence or presence of the carbodiimide.

The specific grade within a particular class of polyurethane elastomer is determined by the ratio of the polyol, chain extender and diisocyanate in the formulation. However, it is not considered necessary to determine the constituents quantitatively in order to identify the specific grade. After classification the grade of the elastomer is more readily assessed by a shore hardness measurement<sup>15</sup>. For example the shore hardness for three grades in type No. 1 (Table IV) is given in Table V.

TABLE V  
VARIATION OF HARDNESS WITH COMPOSITION

Shore hardness	PEA	MDI	1,4-Butanediol
75A	100	33	7
90A	100	53	13.5
60D	100	90	26.8

Future studies will involve GC carried out under subambient conditions in order to try and resolve the early peaks used for the identification of the hydroquinone-diethyl ether.

#### REFERENCES

- 1 J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology, Part I, Chemistry*, Interscience, New York, 1962.
- 2 P. Wright and A. P. C. Cumming, *Solid Polyurethane Elastomers*, MacLaren, London, 1969.
- 3 J. M. Buist and H. Gudgeon (Editors), *Advances in Polyurethane Technology*, MacLaren, London, 1968.
- 4 P. J. Corish, *Anal. Chem.*, 31 (1959) 1298.
- 5 A. G. Fogg, R. Griffiths, W. P. Hayes and D. T. Burns, *Lab. Pract.*, 19 (1970) 475.
- 6 R. E. Kirk and D. F. Othmer (Editors), *Encyclopaedia of Chemical Technology*, Vol. 12, Wiley, New York, 2nd ed., 1967.
- 7 E. G. Brame, C. Ferguson and G. J. Thomas, *Anal. Chem.*, 39 (1967) 517.
- 8 J. L. Mulder, *Anal. Chim. Acta*, 38 (1967) 563.
- 9 E. Shroeder, *Plaste Kautsch.*, 9 (1962) 121, 186.
- 10 B. Dawson, S. Hopkins and P. Sewell, *J. Appl. Polym. Sci.*, 14 (1970) 35.
- 11 J. Takeuchi, S. Tsuge and T. Okumoto, *J. Gas Chromatogr.*, 6 (1968) 542.
- 12 A. Fiorenza and G. Bonomi, *Rubber Chem. Technol.*, 36 (1963) 1129.
- 13 G. L. Coulter and W. C. Thompson, *Column*, 3, No. 3 (1970) 6.
- 14 W. C. Thompson, *Lab. Pract.*, 18 (1969) 1074.
- 15 *British Standard*, B.S. 903, Part A7, 1957.