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### Pyrolysis-gas chromatography of flexible polyether and polyester urethane foams

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The pyrolysis-gas chromatography (Py-GC) of flexible polyurethanes has not been extensively reported, although the technique is routinely used to advantage in industrial laboratories. The analysis of polyurethane materials has largely concerned the identification of the reactants or their derivatives that have been produced by chemical degradation of the polymer.

Chemical cleavage has been applied to polyurethanes using acidic<sup>1</sup> or alkaline hydrolysis<sup>2-8</sup> or aminolysis<sup>9-12</sup>, one procedure indicating reaction firstly with hydrochloric acid and then hydrazine<sup>12</sup>.

The reaction times requires are usually long and the hydrolysis is frequently conducted in a Parr bomb or similar apparatus. The reaction products have been identified by a variety of chromatographic and spectroscopic techniques. Some considerable reduction in the degradation time has been achieved by Gibian<sup>7</sup> and by Birbira and Haken<sup>8</sup>, both of whom used alkali fusion with potassium hydroxide. The former worker conducted the reaction in an apparatus attached to a gas chromatograph and rapidly identified any volatile products amenable to gas chromatography. The second group conducted the fusion separately and identified the reaction products or their derivatives by gas, liquid or gel-permeation chromatography as appropriate.

Py-GC has been reported by several workers<sup>13-18</sup>. Takeuchi *et al.*<sup>13</sup> pyrolysed flexible polyurethane foams based on polypropylene glycol-based polyethers, tolylene diisocyanate and polyaryl isocyanates and identified volatile products obtained at 850°C. Burns *et al.*<sup>14</sup> studied solid polyurethane elastomers using a combination of pyrolysis gas chromatography and infrared spectrophotometry to identify the diisocyanates.

A recent report<sup>19</sup> has indicated the inability to differentiate between flexible polyurethane foams of the two major and widely variant chemical types based on reaction of isocyanates with polyethers and polyesters. This work shows programmes that readily allow the qualitative identification of the two types, both of which in practice are usually based on tolylene diisocyanate. The similarities in the pyrograms

are in agreement with criteria suggested in the literature<sup>20</sup> to be necessary for the identification of variant chemical types.

#### EXPERIMENTAL

The polyester foam used was prepared by the reaction of a diol based on polyethylene glycol and adipic acid with tolylene diisocyanate. The polyether foam was prepared by the reaction of a triol based on ethylene glycol-propylene glycol-glycerol with tolylene diisocyanate.

Py-GC was conducted using a Hewlett-Packard Model 7620A gas chromatograph fitted with 10 ft.  $\times$  1/8 in. O.D. stainless-steel columns containing Porapak Q with dual flame-ionization detection. Operation was isothermal at 100°C for 1 min, then programmed to 240°C at 20°C/min. Nitrogen was used as the carrier gas. A sample (0.012–0.3 mg) was pyrolysed at 610°C for 10 sec using a Philips Curie-point pyrolyser. Reproducibility tests were carried out on sample sizes ranging from 0.012 to 0.3 mg.

#### RESULTS AND DISCUSSION

Figs. 1 and 2 show pyrograms of flexible polyether- and polyester-based poly-

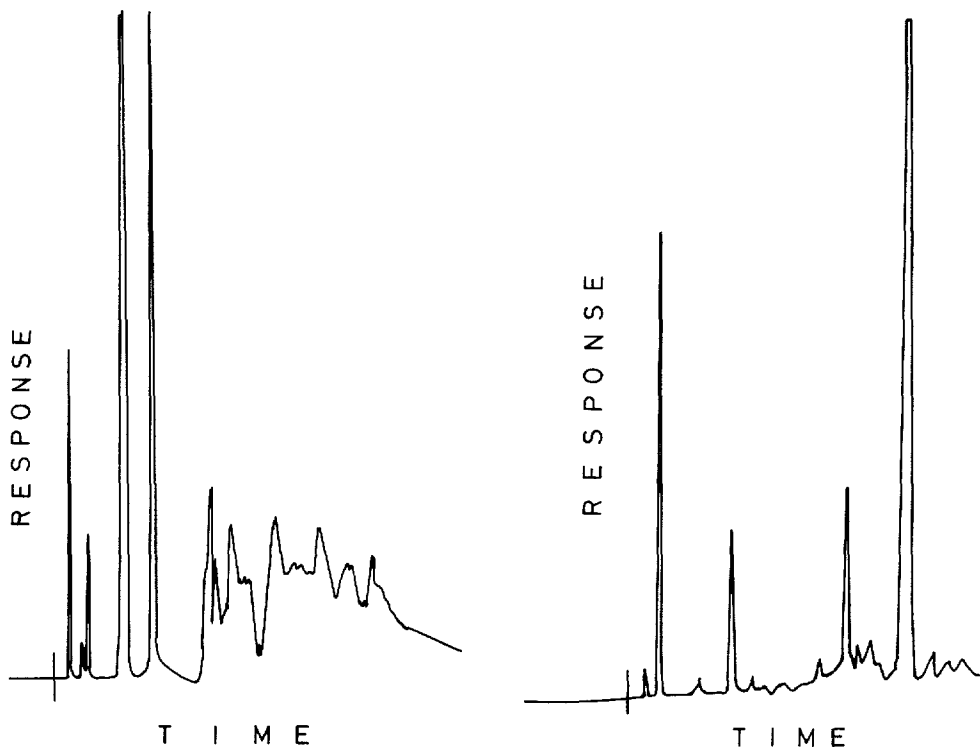


Fig. 1. Pyrogram of flexible polyether-based polyurethane foam.

Fig. 2. Pyrogram of flexible polyester-based polyurethane foam.

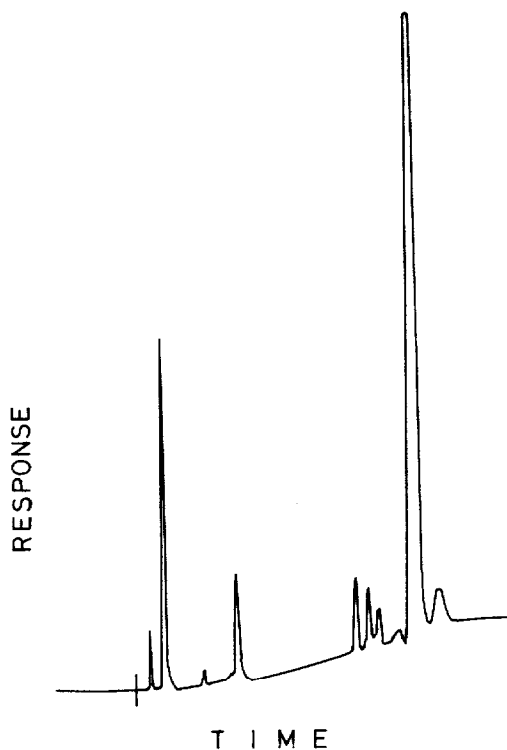


Fig. 3. Pyrogram of flexible polyester-based polyurethane lining from an exhibit in a criminal matter.

urethane foams of known composition. The major peak in one type is absent from the other type. The peak of second abundance in the polyether is present as a minor peak in the polyester, while several other minor peaks are coincident. Some agreement is to be expected as both types are based on tolylene diisocyanate.

In contrast to Figs. 1 and 2, it is evident that Figs. 2 and 3 possess marked similarities of some of the major component peaks. Fig. 3 is a pyrogram of an unknown foam taken from a coat in a criminal matter and described by the manufacturer as an ester interlining. The four major peaks are common, the two most abundant in the same relative amounts and the other two in similar concentrations but in slightly reversed proportions.

The requirements for the qualitative identification of polymers of different functional classes are conveniently based on a fingerprint comparison, and identification for forensic purposes has been discussed by May and co-workers<sup>20,21</sup>. These authors provided a small library<sup>21</sup> of polymer pyrograms and developed an index system to reduce the number of comparisons required. The retention times of the three "highest peaks" in the pyrogram are noted in order of increasing retention. The one or more rows in the index tabulation into which the three retention times can be fitted give pyrograms that are used for comparison. Although the procedural value of the approach has been demonstrated, some care is necessary in the inter-

pretation in the absence of extensive testing owing to the common occurrence of particular reactants in widely variant polymer types.

Although the pyrograms shown readily allow identification, it is obvious that capillary chromatography will allow the examination of very much smaller samples; casework studies have been carried out for some years with samples as small as 0.5  $\mu\text{g}^{22}$ .

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