

## THE IDENTIFICATION OF COMMERCIAL ACRYLIC FIBRES USING THERMOGRAVIMETRIC ANALYSIS

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(Received 7 September 1978)

### ABSTRACT

The thermal analysis of acrylic fibres is discussed and a procedure for the characterisation of 28 commercial fibres by thermogravimetry and derivative thermogravimetry is described. The classification of these 28 fibres into about 17 groups, and in some instances the identification of individual fibres, is achieved by using a combination of thermal analysis data and consideration of cross-sectional shapes.

### INTRODUCTION

The classification of acrylic fibres into specific groups based on qualitative and quantitative copolymer composition is an important problem in the identification of textiles, more particularly in crime investigations because of the large scale production of these fibres by numerous manufacturers. A number of analytical procedures are available. These include the examination of physical characteristics, solubility tests, use of staining reagents<sup>1</sup>, pyrolysis gas chromatography (unpublished results) and infrared spectroscopy<sup>2</sup>. Each individual technique is, however, subject to some limitations and in most instances a combination of these techniques is required for satisfactory identification. Pyrolysis mass spectrometry has proved useful in the characterisation of nylons<sup>3</sup> and in the analysis of nylon copolymers<sup>4</sup> but no similar success has been reported from studies on acrylic fibres.

Acrylic fibres by definition, must contain polymer chains composed of at least 85% by weight of acrylonitrile units. The thermal decomposition of polyacrylonitrile (PAN) resin has been the subject of extensive investigation due to the unusual chemical processes which occur and the nature of the final residue. Results from a series of papers on this topic have been summarised<sup>5</sup> and several different techniques have been employed in the study<sup>6, 7</sup>. In the temperature range 170-250°C, oligomerisation of nitrile groups through cross linking of polymer chains results in the formation of heterocyclic structures, while no weight loss is detected. Decomposition

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commences at approximately 290°C being initially rapid, and then gradually slowing. After 550°C, when a 45% weight loss has occurred, little further breakdown takes place. During the transformation, chain stripping processes form a highly conjugated heterocyclic network with the evolution of such materials as hydrogen cyanide, alkyl nitriles and simple hydrocarbons. The final carbonised residue at 600°C acts as a semiconductor, this property persisting even at room temperature.

The considerable interest shown in the degradation of PAN, and to a lesser extent its copolymers, is not reflected in studies on commercial acrylic fibres. Reports on the thermal analysis of such fibres are rather isolated, usually being incorporated into investigations on a variety of synthetic fibres<sup>8, 9</sup>. Ten commercial acrylic fibres have been examined by differential thermal analysis (DTA), glass transition points, melting points and decomposition temperatures having been used for the purposes of comparison<sup>10</sup>. Some instances of discrimination were obtained but large areas of overlap of data for fibres of differing composition were evident, and the report could not be considered as an exhaustive examination of acrylic fibres. This paper describes the degree to which thermogravimetry (TG) and derivative thermogravimetry (DTG) can be employed in the characterisation of acrylic fibres.

## EXPERIMENTAL

A Stanton-Redcroft TG 750 Thermobalance (Stanton Redcroft Ltd., Copper Mill Lane, London, SW 17 OBN) equipped with a DTG 750 time derivative unit was used for all analyses at a heating rate of 50°C min<sup>-1</sup>. The purge gas was helium (99.9%) at a flow rate of 10 ml min<sup>-1</sup>.

A selection of 28 commercially available acrylic fibres was made, from the collection obtained from manufacturers<sup>2</sup> and held at the Home Office Central Research Establishment, to give as wide a range of composition and manufacturer as possible. The fibres ranged from 2–6 denier, some were delustered and two dyed.

Sample sizes between 500 and 800 µg were used. The fibres were coiled into a tight ball with the aid of forceps and pressed onto the bottom of the sample crucible to ensure uniform heating by efficient thermal contact. At least two separate analyses were conducted for each sample.

## RESULTS AND DISCUSSION

### *Analytical considerations*

The heating rate used for this investigation (50°C min<sup>-1</sup>) is appreciably faster than that used by most workers in the field of TG analysis who use rates varying between 5°C min<sup>-1</sup> and 20°C min<sup>-1</sup>. Apart from the obvious advantage of a considerable reduction in the time required for an analysis, this faster heating rate gives a rapid rate of decomposition which is reflected in the excellent sensitivity obtained for the DTG curves, even with samples down to 100 µg. Indeed, the use of a heating rate of 20°C min<sup>-1</sup>, although increasing the resolution obtained on the TG curve,

results in a drastic reduction in the sensitivity of the DTG unit, an adequate DTG trace being essential to the analysis. In one study heating rates as rapid as  $100^{\circ}\text{C min}^{-1}$  were found to be preferable in DTA studies of acrylic fibres<sup>10</sup>.

The instrument has been modified for interfacing to a VG Micromass 16F mass spectrometer and this imposes certain restrictions on the operating conditions of the thermobalance. Helium is used as the inert purge gas in preference to nitrogen to maintain a sufficiently low pressure within the source of the mass spectrometer. The flow rate has been optimized at  $10\text{ ml min}^{-1}$  to permit the bulk of the decomposition products to be transferred to the mass spectrometer for analysis while minimising the amount of air which diffuses into the system.

Some fibre samples were available in 2–6 denier, with and without delustrant

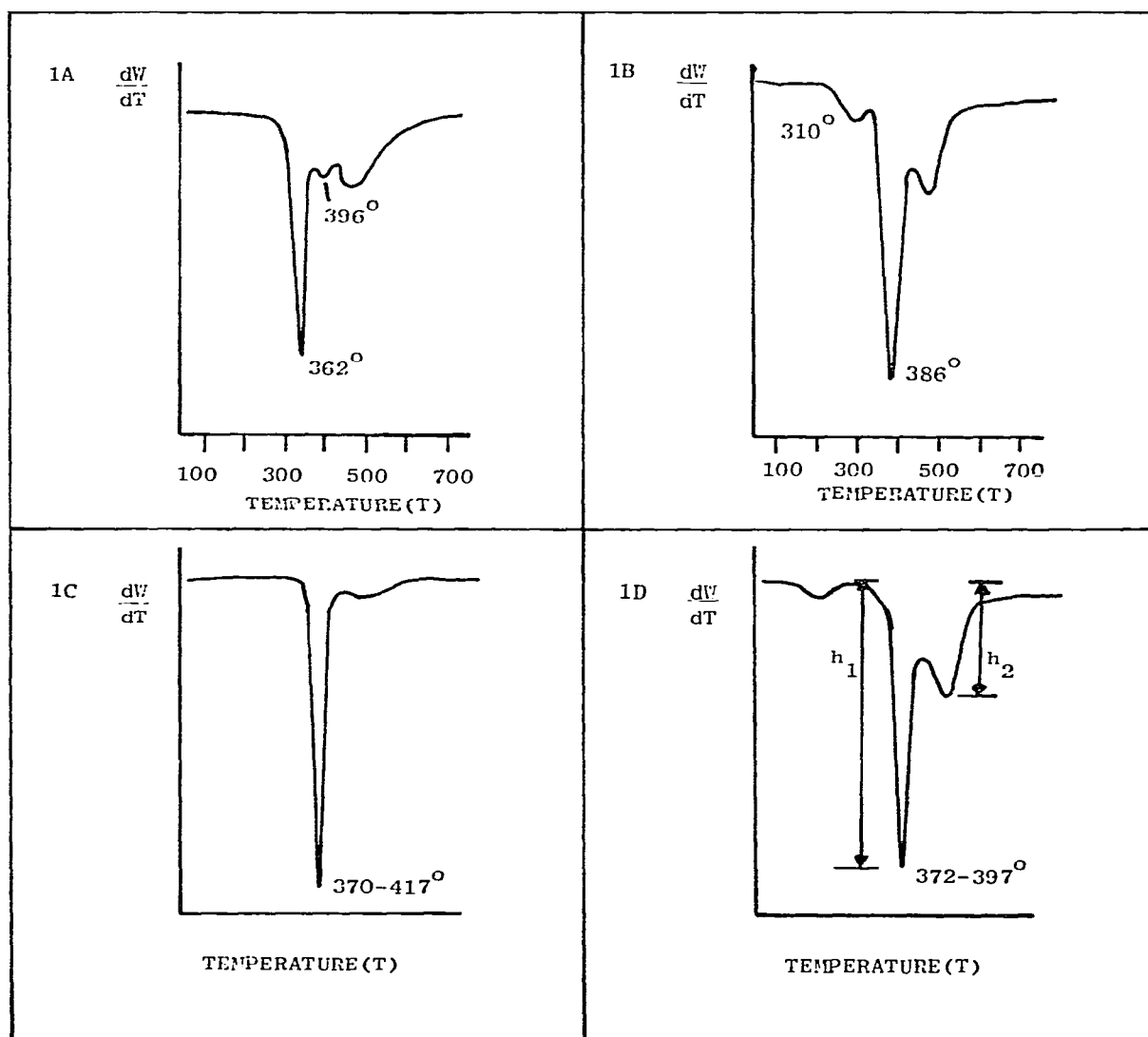


Fig. 1. The four types of DTG trace obtained during the analysis of 28 acrylic fibres (see Table 2). The range of temperatures encountered are marked in C and D.

and after dyeing but these factors did not influence the TG and DTG results obtained sufficiently to affect the classification scheme described here.

#### *Thermal decomposition of acrylic fibres*

Courtelle and Courtelle Latent Crimp gave very characteristic DTG traces (Fig. 1A). The DTG trace obtained from Tacryl (Fig. 1B) is also unique but this results mainly from the presence of a residual solvent peak at 310°C, as will be discussed later. The remaining 25 fibres could be classified into one of two groups on the basis of the general shape of their DTG curves (Figs. 1C and 1D).

For most of the fibres studied, initial decomposition commences at approximately 350°C with a rapid weight loss, reflected in the height and shape of the first DTG peak, followed by a considerably slower second phase of decomposition. This second phase produces a much broader DTG peak, reaching a maximum approximately 100°C higher than the first and terminating at approximately 550°C. Further heating to 700°C results in a very slow weight loss, this failing to register on the DTG trace, and a highly carbonised residue remains. It is clear from the comparison of the DTG curves that the modes of decomposition are rather different.

Fibres giving DTG curves resembling Fig. 1C show an initial weight loss of approximately 50–60% and then a second phase of decomposition during which a small weight loss occurs. In many analyses this second weight loss is so slow as to barely register on the DTG trace. None of the fibres in this group has a second DTG peak with a height greater than 6% of that of the first peak. The fibres AF500 and Zefkrome, reported as being pure polyacrylonitrile<sup>2</sup>, are classified in this group. However the shape of the DTG curve is in marked contrast to that obtained from pure PAN resin<sup>7</sup>.

The second group, giving DTG curves resembling Fig. 1D, show two main decomposition steps each of which represents an approximately equal weight loss with the second DTG peak being very prominent. The height of this peak is between 19 and 63% of the first peak.

#### *Residual spinning solvents*

Many of the fibres examined contain up to 1% by weight of residual spinning solvent which is apparent as a small gradual loss in the temperature range 160–240°C (e.g. Fig. 1D). Dimethylformamide (DMF) and dimethylacetamide (DMA) are the solvents most commonly employed in the manufacture of acrylic fibres<sup>11</sup> but it is not possible to differentiate between these two solvents using TG alone. A heavy petroleum fraction in the kerosene range is used as the spinning solvent for the fibre Tacryl and a significant weight loss (2–3%) is observed at a temperature of about 310°C (Fig. 1B) which clearly distinguishes this fibre from all the others examined. Such a solvent could well persist for some time in the finished product unlike DMF and DMA which are known to wash out in water<sup>4</sup>.

### Classification scheme for acrylic fibres

Factors which can be used for the discrimination of acrylic fibres by TG and DTG are as follows.

(a) The shape of the DTG curve. As previously discussed all but two of the fibres studied can be placed into one of two categories (Figs. 1C and 1D).

(b) Temperature at maximum rate of weight loss ( $T_{\max}$ ). This is measured at the apex of the main DTG curve and the temperatures are found to be reproducible with a standard deviation of  $\pm 2^{\circ}\text{C}$  by duplicate determinations on all fibres. A difference of  $8^{\circ}\text{C}$  or more between samples is therefore deemed significant for the purpose of discrimination.

(c) Percentage weight loss up to  $700^{\circ}\text{C}$ . This is readily calculated from the TG curve and all weight losses have concluded by this temperature. Results obtained are found to have a standard deviation of  $\pm 1\%$ , this value again obtained by duplicate determinations on all fibres. Differences of more than  $4\%$  between samples have therefore been considered to be significant for discrimination.

(d) Ratio of DTG heights. For samples having an appreciable second weight loss in the DTG trace (Fig. 1D) the ratio  $h(2)/h(1)$ , where

$$\frac{h(2)}{h(1)} = \frac{\text{height of peak 2}}{\text{height of peak 1}}$$

can be characteristic. It appears that this ratio is dependent to some degree on the percentage of copolymer in the fibre. Few details of the exact percentage composition of commercial fibres are available, but those published enable the comparisons shown in Table 1 to be made. It appears that the ratio of peak heights increases with the copolymer content and this factor can serve as an aid in the discrimination of closely related fibres. The DTG trace often shows appreciable noise, both electronic and from external vibrations, and thus the ratios obtained were subject to considerable error. Nevertheless, the ratios show a standard deviation of  $\pm 0.03$  and differences of 0.12 or more in this ratio have been considered significant for discrimination.

(e) Cross-sectional shape. This physical property is easily determined and should therefore form part of any identification scheme for acrylic fibres.

TABLE 1

COMPARISON OF PERCENTAGE COPOLYMER WITH DTG PEAK HEIGHT RATIOS

<i>Fibre</i>	<i>Methyl acrylate</i> <sup>*</sup> (%)	<i>Ratio h(2)/h(1)</i>
Redon	3	0.34
Velicren	5	0.38
Cashmilon	8	0.51
Toraylon	10	0.53

\* Data from Sanders<sup>11</sup>.

TABLE 2

THERMAL ANALYSIS DATA, CROSS-SECTIONAL SHAPE AND COMPOSITION OF 28 ACRYLIC FIBRES

<i>Fibre</i>	<i>DTG Curve</i>	<i>T<sub>max</sub></i> (°C)	<i>Wt. loss</i> (to 700°C) (%)	<i>Ratio</i> <i>h(2)/h(1)</i> <i>in DTG trace</i>	<i>Cross sectional shape</i> *	<i>Composition</i> **
Courtelle	Fig. 1A	362, 396	46	—	1	2
Courtelle Latent Crimp		360, 395	47	—	1	2
*** Tacryl	Fig. 1B	386	49	0.27	1	2
AF500	Fig. 1C	370	58	—	1	1
Zefkrome		373	59	—	1	1
AF 100	Fig. 1C	384	61	—	1	7
Orlon 23	Fig. 1C	393	51	—	5	2
Leacril 16	Fig. 1C	406	70	—	2	4
Acrilan 16		408	71	—	2	4
Vonnell 17		408	72	—	2	4
Orlon 21	Fig. 1C	416	61	—	5	8
Exlan	Fig. 1C	417	71	—	1	5
Nymcrylon	Fig. 1D	389	50	0.19	3	2
Orlon 42		388	50	0.24	3	2
Orlon 75		388	49	0.24	3	2
Orlon 72		387	51	0.25	3	2
*** Tacryl		386	49	0.27	1	2
Dolan 25		390	50	0.28	6	2
Redon		385	50	0.34	3	2
Crilenka		397	48	0.35	1	6
Dralon		382	50	0.35	3	2
Acribel		374	45	0.37	2	6
Velicren		388	47	0.38	2	2
Euroacril		387	48	0.44	1	2
Exlan L		384	49	0.47	1	2
Cashmilon		390	49	0.51	1	2
Orlon 28		375	50	0.53	3	3
Toraylon		390	46	0.53	2	2
Orlon 44		372	52	0.63	3	3

\* 1 Round, 2 Bean, 3 Peanut, 4 Lobed, 5 Acorn, 6 Mixed peanut and bean.

\*\* 1 Acrylonitrile, 2 Acrylonitrile/methyl acrylate, 3 Acrylonitrile/methyl acrylate/methyl vinyl pyridine, 4 Acrylonitrile/vinyl acetate, 5 Acrylonitrile/vinyl acetate/methyl vinyl pyridine, 6 Acrylonitrile/methyl methacrylate, 7 Acrylonitrile/vinylpyrrolidone, 8 Acrylonitrile/unknown, (taken from ref. 2).

\*\*\* Tacryl classified with and without residual solvent peak.

— indicates negligible second peak.

### *Classification of 28 commercial acrylic fibres*

The thermal analysis data and cross-sectional shapes for the 28 commercial acrylic fibres studies are detailed in Table 2. The copolymer compositions, where known, are also indicated from previous infrared studies<sup>2</sup>.

Fibres giving DTG traces of the types shown in Figs. 1A–1C are easily characterised using the thermal analysis data and no further discrimination is obtained by considering cross-sectional shape. The acrylic fibre Tacryl is classified twice (DTG types 1B and 1D) to take account of the possibility that all the residual solvent (kerosene, peak at 310°C in type 1B DTG trace) has been lost prior to examination. Fibres which could not be discriminated either originate from the same manufacturer, such as Courtelle and Courtelle Latent Crimp (Courtaulds), AF500 and Zefkrome (Dow Chemical), or they are essentially the same fibre manufactured under licence at different sites, such as Leacril 16, Acrilan 16 and Vonnell 17<sup>11</sup>.

Most of the fibres examined gave DTG traces of the type shown in Fig. 1D and are reported to contain methyl acrylate or methyl methacrylate<sup>2, 11</sup>. The most significant parameters for this group of fibres are the DTG ratio and the cross-sectional shape. Thus in Table 2, fibres within the group have been tabulated in terms of increasing DTG peak ratios rather than in terms of increasing  $T_{\max}$  values, as used for the other groups. Although some of the fibres in this group can be uniquely characterised (Dolan 25, Crilenka, Acribel, Velicren and Toraylon) each of the remaining fibres is similar to at least one other fibre from a different manufacturer. The one exception is provided by the terpolymer fibres (acrylonitrile/methyl acrylate/methyl vinyl pyridine) Orlon 28 and Orlon 44 (both Du Pont) which have low  $T_{\max}$  values and although similar to one another they can be discriminated from all the other fibres.

### *General discussion*

This study has shown that thermal analysis data (from TG and DTG) can readily be used for the characterisation of commercial acrylic fibres. When the cross-sectional shapes of the fibres are considered in addition to the data from thermal analysis the 28 different fibres studied can be classified into about 17 groups, some fibres overlapping with more than one group.

Samples of fibres weighing at least 100  $\mu\text{g}$  are required for analysis and in many applications more than sufficient sample will be available. However in forensic science, crime investigation being the particular concern of the authors, samples requiring analysis often weigh a few micrograms or even less. An organic mass spectrometer is a suitably selective and sensitive detector for the thermogravimetric analysis of such microsamples<sup>1, 2</sup>.

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