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THERMAL ANALYSIS OF POLYACRYLONITRILE: IDENTIFICATION OF ACRYLIC FIBRES BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

A fast heating rate DTA technique has been applied to various commercial acrylic fibres (Acrilan, Courtelle, Orlon, Cashmillon, Exlan, Creslan, and Acribel). Their melting points, which may otherwise be obscured by exothermic decomposition, can be reliably determined, and the patterns of thermal events obtained by this method can be used to afford some discrimination between commercial acrylic fibres.

INTRODUCTION

Commercial acrylic fibres contain at least 85% acrylonitrile (AN) copolymerised with a small amount of a functional monomer, to provide specific dye sites, and a larger amount of a third, neutral, monomer, such as methyl acrylate, methyl methacrylate or vinyl acetate, to modify the physical properties of the polymer[1]. Fibres containing less than 85% AN are defined as modacrylics[2]. Identification of individual acrylic fibres, and their differentiation from other classes of fibre, requires a combination of both physical and chemical tests[1,3,4]. Coloured fibres present further complications.

Differential thermal analysis (DTA) is an extremely flexible technique for testing small amounts of single or mixed fibres[5,6,7]. The results are not usually influenced by the presence of dyes and pigments. The very strong and sharp exotherm at about 300°C reported by Schwenker and Beck[8] for Orlon and polyacrylonitrile (PAN) is characteristic for acrylics and may be used to differentiate them from other fibres. The differences between the copolymer and homopolymer were however slight, and no greater than those observed between homopolymers of differing molecular weight[9]. The development of techniques capable of discriminating between homopolymer and various copolymers is thus desirable.

Von Illers[10] studied a series of AN–methyl acrylate copolymers and noted differences in minor thermal effects that were dependent on copolymer content. These small differences would not be detected in routine DTA, and no melting points were found. Slade[11], however, was able to detect the melting point in a series of AN–vinyl acetate copolymers by DTA at 20°C/min, and we[12] have reported the observation of the melting of PAN by DTA at fast heating rates. The failure to observe the melting point of acrylonitrile polymers can be attributed to the rapid decomposition of the polymers at relatively slow heating rates, and the much greater magnitude of the heat of reaction in comparison to the heat of fusion. Thus DTA has not been applied to acrylic fibres in the same way as to other crystalline synthetics such as polyethylene, nylon and poly(ethylene terephthalate). Our previous work[12] has shown that fast heating rate technique may afford a means of overcoming these difficulties.

EXPERIMENTAL

Materials

The homopolymer PAN and the copolymer COPAN (7% vinyl acetate) were obtained from Mitsubishi Rayon Company Limited. The other fibres (Table II) were obtained from commercial textile suppliers and are identified by Trademark. All samples are normal textile fibres and, although the major comonomer and general method of preparation may be known, the exact compositions are subject to commercial secrecy. The samples were of rope or carpet grade fibre, and were used as received.

One sample, COPAN, was extracted with boiling ethanol–benzene mixture (1:2) to remove normal textile finish oils prior to isothermal studies.

Thermal analysis

The DuPont 900 Differential Thermal Analyzer produced by E. I. DuPont de Nemours and Co., Wilmington, Delaware was used in these studies. Both the standard DTA cell and the differential scanning calorimeter (DSC) cell were used[13].

Technique

When using the DSC cell, the sample fibre (2–3 mg) was chopped into short lengths and encapsulated in a lightly crimped aluminium pan so that there was maximum thermal contact between pan and contents. An empty pan was used as reference and the atmosphere (air) was not controlled. The nominal heating rates were between 5 and 100°C/min. For the standard DTA cell an unweighed length of fibre was wound closely round the sample thermocouple, up to the ceramic sleeve, and inserted into the 2 mm glass sample tube. The DTA curves were obtained at a nominal 20°C/min in an atmosphere of air, and glass beads were used as reference. In isothermal studies there was a warm up period of 2–3 min and timing was commenced when the heater voltage fell to within 3 V of the operating isothermal voltage. The isothermal temperature was measured in the glass bead reference and an oxygen free nitrogen atmosphere was maintained by a gas flow of 0.75 l/min.

Temperatures given are uncorrected for chromel–alumel thermocouples and the initiation temperatures given for decomposition were determined by detection of the initial deviation from the base line. The use of extrapolated onset temperature is precluded because the base line is not reestablished after melting (in some cases) and the catalytic nature of the decomposition does not admit a linearized peak: the combination of these effects gives an extrapolated onset at least as subjective as any estimation of deflection from base line.

RESULTS AND DISCUSSION

In DTA it is generally accepted that,while the differential temperature (ΔT) is increased by increasing the heating rate, this improved sensitivity is obtained at the expense of decreased resolution of successive thermal events[14]. However we have shown[12] that, in the case of PAN subjected to the fast heating, the DTA curve clearly resolves the melting of the polymer (a first order transition which is relatively insensitive to changes of heating rate) from its exothermic decomposition which is shifted to higher temperatures. This shift is the complex result of the autocatalytic nature of the decomposition[12,15], the delayed heat transfer at higher heating rates, and the restricted equilibrium resulting from partial retention of volatile products. The DTA curves of the copolymers COPAN and Courtelle (Table I) are similarly dependent on the heating rate. The melting point is constant and unaffected by changes of heating rate between 5 and 100°C/min; however decomposition of the polymer can supervene before melting can occur. Thus, at a rate of 100°C/min, the decomposition of COPAN does not begin until the melting is complete, but at lower rates it begins during melting, and at a rate of 5°C/min it has proceeded to an extent that precludes detection of melting. The melting of Courtelle can only be observed

TABLE I

EFFECT OF HEATING RATE ON THE MELTING AND DECOMPOSITION OF ACRYLIC FIBRES (DSC CELL)

Fibre	*Heating rate (°C/min)*	*Melting point (°C, Chromel–alumel)*		*Decomposition (°C, Chromel–alumel)*	
		T_0[a]	T_{max}[b]	T_0	T_{max}
PAN	100	334	346	320	386
	80	333	344	290	383
	40	332	338	280	362
	20			265	340
	5			230	310
COPAN	100	250	282	310	392
	80	250	280	[c]	384
	40	245	278	[c]	367
	20	247	278	[c]	335
	5			220	325
Courtelle	100	277	288	230	357
	80	275	287	225	349
	40			220	327
	20			195	306
	5			185	275

[a] Initiation temperature. [b] Temperature of maximum ΔT amplitude. [c] Decomposition begins during melting.

when the rate of heating is greater than 80°C/min. Since the main copolymer in this fibre is methyl acrylate[16] this explains why Von Illers[10] was unable to detect a melting point of AN–methyl acrylate copolymers in DTA studies at 32°C/min.

Typical thermograms of acrylic fibres, obtained from the DSC cell at 100°C/min, are shown in Fig. 1. The DTA curve for Acrilan (curve (d), Fig. 1.) should be contrasted with that obtained from the standard cell at 20°C/min (Fig. 2). Two effects contribute to the more positive identification of thermal events: the configuration of the DSC cell[13] gives an improved baseline which is less subject to drift, and the procedural variables, as indicated above, improve the resolution of the exothermic decomposition. It should be noted that in the standard DTA cell, variation of sample preparation (weight and tightness of packing) can lead to the programmed heating rate being exceeded during the exothermic decomposition. Consequently the temperature of maximum exothermic deflection is not reproducible in the standard cell. However for the DSC cell at high heating rates both the shape of the thermograms and the temperatures of the thermal events were satisfactorily reproducible. In those cases where determination of the melting point was possible at heating rates of 20°C/min, good agreement was found between the value determined in the standard cell and that determined at the higher rate in the DSC cell. There was no difference between bright and semidull grades of the same fibre, due to the presence of any delustrant. It was not possible to distinguish between a low denier Courtelle tow and a much coarser grade of the same fibre.

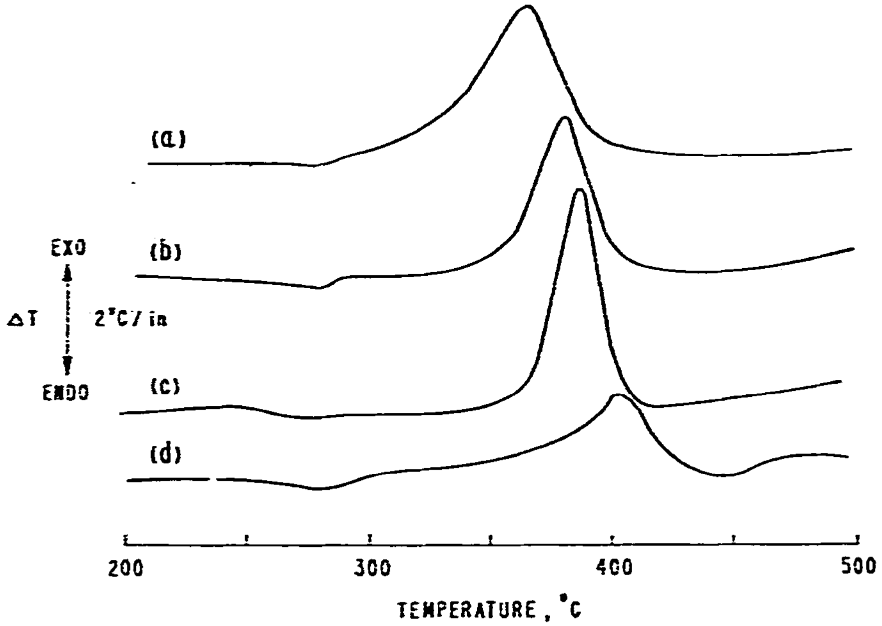

Fig. 1. DTA of acrylic fibres; (a) Orlon, (b) Cashmillon, (c) Creslan-61B, (d) Acrilan-16; encapsulated sample, DSC cell, heating rate, 100°C/min.

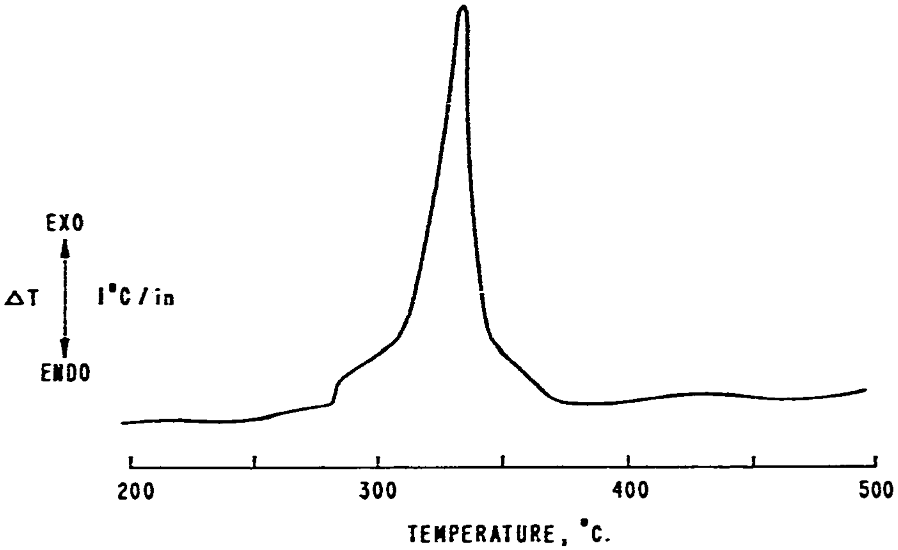

Fig. 2. Thermogram of Acrilan-16 fibre; sample in 2-mm tube, standard cell, heating rate 20°C/min.

Fig. 1 shows that the thermogram can be considered as three distinct regions; melting, exothermic decomposition, and post decomposition. The first two of these may overlap. A fourth region, the glass temperature, would be expected between 60 and 100°C. For heating rates above 40°C/min it would be necessary to programme the sample from subambient temperatures to establish an adequate baseline for observation of the glass transition; however lower heating rates are preferable. Table II lists the temperature at the onset of melting and of decomposition, as well as

TABLE II

MELTING AND DECOMPOSITION TEMPERATURE OF ACRYLIC FIBRES (DSC CELL AT 100°C/MIN)

Fibre	*Major comonomer*[16]	*Melting point (°C, Chromel–alumel)*		*Decomposition (°C, Chromel–alumel)*	
		T_0[a]	T_{max}[b]	T_0	T_{max}
PAN		335	346	320	386
Courtelle	6% Methyl acrylate	278	288	235	357
Acrilan-16[c]	7.5% Vinyl acetate	255	284	[d]	400
Vonnel-17[c]		250	284	[d]	394
Orlon			280	260	362
Cashmilon		240	277	310	377
Acribel		230	277	310	377
Crelan-61B[c]	10% Methyl Methacrylate	[e]	275	310	387
Exlan-DK		230	275	[d]	385

[a] Initiation temperature. [b] Temperature of maximum ΔT amplitude. [c] Identical thermograms for bright and semifull grades of the fibre were obtained. [d] Decomposition begins during melting. [e] An exotherm preceeds melting.

the temperature at maximum ΔT amplitude during these processes, for a series of acrylic fibres. No tabulation of the postexothermic effects has been given, since they are associated with terminal degradation of the material and are not sharply defined. However the observed differences are useful in discriminating between the materials (Fig. 1).

The materials listed in Table II are arranged in order of decreasing melting point which has been found to correlate with the amount of the major copolymer present, where this has been reported[16]. The onset of melting of the Orlon sample (curve (a), Fig. 1) cannot be determined accurately because of the coincidental onset of decomposition and the resultant smallness of the endotherm. In contrast the onset of melting of Creslan (curve (c), Fig. 1) is obscured by an exotherm immediately before the melting point. This effect, which is shown only by Creslan could be due to either reaction or to premelting crystallization.

Table II shows that, under conditions of fast heating rate, there are significant variations in the decomposition of these fibres. Thus, compared to the homopolymer, the copolymer containing vinyl acetate (COPAN, Acrilan) begins to decompose at a lower temperature while the maximum ΔT amplitude occurs at a higher temperature. The presence of methyl methacrylate in the copolymer (Creslan) also results in earlier decomposition but the position of maximum ΔT is unchanged, while for a copolymer containing methyl acrylate (Courtelle) both temperatures are much lower. Detailed analysis of the decomposition is precluded by the limited information[16] available on these commercial fibres. Indeed it should be noted that, whereas Von Illers[10] observed an increased stability of methyl acrylate copolymers compared to PAN, Courtelle, with a similar reported copolymer content, showed a different relative stability. This may be attributed to differences in either the physical preparation of the samples, or, more probably, in the chemical composition and history of the materials.

A method for estimating the activation energy for the thermal decomposition of PAN by isothermal DTA has been described[12,15]. A value of 44 kcal·mol^{-1} was obtained. Similar studies on extracted COPAN yielded a value of 31 kcal·mol^{-1}, and show the effect of comonomer. In textile fibres the presence of finish oils effects both the definition and duration of the induction period before the exothermic decomposition and, to ensure comparability, these oils must be extracted from the fibre before determination of the activation energy for the reaction.

This constraint restricts the utility of this parameter in routine evaluation of acrylic fibres; however determination of the activation energy for thermal decomposition, together with the estimation of heat of fusion from the melting endotherm, affords additional discrimination between acrylic fibres beyond that obtained from simple qualitative evaluation of fast scanning rate DTA curves.

CONCLUSIONS

Results have been obtained from commercial materials of complex and undisclosed composition using fast heating rate DTA. Differences in the glass transition point, melting point, and decomposition arise from the varying constitution of the materials, and are disclosed by procedural comparisons based on the pattern of thermal events, relative peak positions, amplitudes and shapes. We believe that the technique may be usefully applied to the study of polyacrylonitriles of known composition and chemical and physical histories.

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