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DIFFERENTIAL THERMAL ANALYSIS OF SOME FIBERS CONTAINING CHLORINE

B. C. ENNIS

Department of Defence, Materials Research Laboratories, Maribyrnong, Victoria (Australia)

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ABSTRACT

The differential thermal analysis curves of four fibers containing chlorine (Saran, Cordelan, Teklan and Kanekalon), and their blends, are influenced by experimental conditions, although not to the same extent as those of poly(vinyl chloride) resin in powder form. The curves were determined using two different (Du Pont) cells, and are discussed in terms of sample holder geometry and material composition. The importance of procedural variables in "fingerprint" applications of thermal analysis for routine fiber identification is re-emphasised.

INTRODUCTION

Thermoanalytical methods, particularly differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are being used more frequently to identify and characterise textile fibers[1–3]. In the simplest and most unequivocal applications the melting point of semicrystalline polymers can be used to discriminate between many of the synthetic fibers, and to identify them in the presence of other semicrystalline and amorphous fibers. More subtle differences may be used to distinguish between fibers in the same generic class, and between non-crystalline fibers of natural or synthetic origin. Since these applications, and others aimed at characterising the fiber, involve second order transitions and chemical reactions, they are more sensitive to changes in procedural variables during thermal analysis than are applications which depend only on first order transitions such as melting. For example we[4] have shown that high heating rates facilitate distinguishing between acrylic fibers, and Crighton and Holmes[5] found that the recrystallisation of polyamides could be used for quantitative analysis of wool/nylon blends although the initial melting was unsuitable because of concurrent irreversible reactions of the wool. Although DTA curves of fiber blends are frequently additive[6], first order transitions offer more opportunity for quantitative application and are less likely than chemical reactions to be affected by the presence of other materials.

Thermal methods have been used for preliminary evaluation of high temperature polymers, and also flame resistant and high-temperature resistant fabrics and fibers, but difficulties have been experienced in the interpretation of the results. Michelson[7] has shown that a correlation between the flammability and thermoanalysis of a polyurethane was possible only with a detailed understanding of the reactions involved. Bingham and Hill[8] considered a number of high temperature and non-flammable fibers, including several chlorofibers and blends, and concluded that thermogravimetric curves were more informative than DSC curves which were difficult to interpret.

The DTA curves of poly(vinyl chloride) (PVC) obtained using the standard Du Pont DTA cell were characterised by endothermic dehydrochlorination[9], and slight preliminary exothermic effects have been attributed to pre-melt or crystallisation processes[10] or to stabilizer reactions[9]. The DSC cell of the Du Pont system[11] possesses advantages with respect to both sample presentation and thermoanalytical performance, and it was therefore disappointing to find in routine usage, that halogenated polymers, particularly PVC, could present materially different thermograms under nominally similar conditions in the two cells. The major difference lay in the extent of the exothermic reaction shown in the DSC cell, and was sufficient to lead to misidentification of some materials.

The present work was undertaken to investigate the extent of these anomalies more closely, so that ambiguity and misdirection could be avoided during routine use of DTA for fiber identification and characterisation. The difficulties, which are readily resolved, re-emphasise the need for care and attention to procedural detail[2, 3].

EXPERIMENTAL

Materials

The fibers were obtained from commercial fabrics, and their identities were confirmed by routine methods.

Saran is a vinylidine chloride/vinyl chloride copolymer containing 80% by weight of vinylidine chloride[12].

Cordelan, a flame resistant polychlal, is a matrix fiber comprising poly(vinyl acetal), poly(vinyl chloride), and vinyl chloride grafted poly(vinyl alcohol)[13]. The sample used was the weft of a cordelan/poly(ethylene terephthalate) fabric.

Teklan, a modacrylic fiber, is a copolymer of vinylidine chloride and acrylonitrile[14]. It was available as the warp of a Teklan/Celon (nylon 6) fabric, and as blended yarn in a Teklan/Cotton (40% by weight) fabric.

Kanekalon K, another modacrylic fiber, is a copolymer of vinyl chloride and acrylonitrile[15].

Poly(vinyl chloride). A suitable PVC fiber was not available. An unplasticized, unstabilised PVC resin in powder form, Corvic P65/50 (ICI Australia Ltd.), was used. Although it should be chemically similar to PVC fibers[16], and is a more convenient form for investigation of procedural variables, the powder will not show the effects of fiber orientation in the DTA curves.

Thermal analysis

The Du Pont Model 900 differential thermal analyzer was used with the standard DTA cell and the DSC cell[11] (this is actually a DTA cell: it has a quantitative potential not available in the standard cell and differs from the latter in that the thermocouple is not in direct contact with the sample). Glass beads were used as reference material in the former, and an empty pan for the latter. Unless otherwise indicated a gas flow of 100 ml min^{-1} was maintained in the DSC cell, a static atmosphere in the DTA cell, and a nominal heating rate of 20°C min^{-1} in both.

The sample yarn or fiber was wound closely and tightly around the chromel: alumel thermocouple, so that when it was inserted in the glass melting point tube in the DTA cell, the sample space was well filled. This was not possible with the coarse Saran monofilament, which was cut into short (2–3 mm) lengths which were tightly packed into the tube to form a bundle into which the thermocouple was forced.

Material for the DSC cell was cut into 3 mm square specimens, or the yarn was cut into short (ca. 2 mm) lengths, and packed in the aluminium pans. The pan lids were inverted to minimise head space and to pack the sample firmly to the base of the pan to obtain good thermal contact. The normal pan lid does not allow significant pressure build-up or pan distortion unless there is rapid gas evolution, since it does not fit tightly unless crimped. However, in some cases perforated lids were used to allow easier efflux of evolved products, and for these four 0.5 mm holes were pierced through the normal lid.

A sample mass of 2–4 mg was used in the DSC cell and about 2 mg in the standard cell, the instrument response was very similar in either cell.

RESULTS AND DISCUSSION

The DTA curves for PVC powder, obtained under various conditions, are shown (Fig. 1) for the range 100–400°C. The dehydrochlorination of PVC is accompanied by a mass loss of the order of 60% of the original weight, and the formation of a carbonaceous foamed char which undergoes further reaction. The factors, particularly thermal resistance, determining the performance of idealised DTA and DSC apparatus have been described[17]. In the standard (Du Pont) DTA cell, the sensing thermocouple is in direct contact with the sample, and foaming decomposition can cause fluctuating thermal contact, and hence an erratic and irreproducible DTA curve. The changing baseline thus compounds the reported difficulty of interpretation of DSC curves of decomposing fibers[8]. As a consequence the curves obtained in the standard cell at temperatures beyond the initial major decomposition have limited utility, and comparison between curves obtained on the standard and DSC cells above the decomposition should be treated with care.

The DTA curve of PVC powder in the standard cell (Fig. 1, f) comprised a small endothermic baseline shift at 250°C prior to a broad endotherm from 250–350°C, peaking at 305°C, and an exothermic trend on further decomposition. The small endothermic shift was not evident in curves obtained on the DSC cell and was

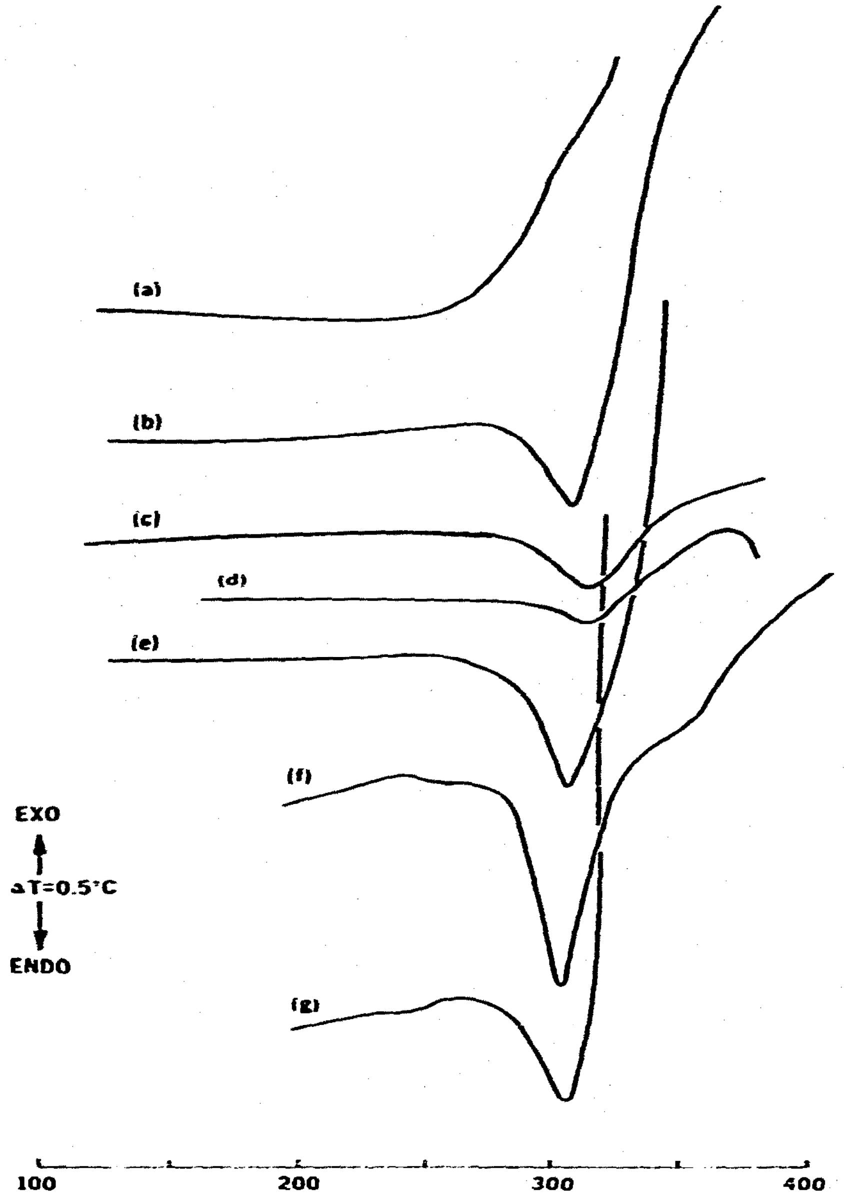

Fig. 1. DTA curves of PVC powder, heating rate 20°C min^{-1}. (a) = DSC cell, open pan, in air; (b) = DSC cell, perforated lid, in air; (c) = DSC cell, perforated lid, in N_2; (d) = DSC cell, open pan, in N_2; (e) = DSC cell, closed lid, in N_2; (f) = DTA cell; (g) = DTA cell, contains sliver of DSC pan.

assumed to result from a sintering of the powder onto the thermocouple. The curve obtained for the DSC cell, using a closed sample pan in nitrogen (Fig. 1, e) showed a relatively small endothermic peak followed by a vigorous exotherm, before deformation of the pan caused an irregular trace. When the product gases were allowed to diffuse from the pan, using either a perforated pan lid or no pan lid (Fig. 1, c and d, respectively) the exothermicity of the reaction was much reduced. In an open pan in air (Fig. 1, a) reaction was apparent at a lower temperature than in nitrogen and was exothermic from the start, while under conditions of limited access of air using a perforated lid (Fig. 1, b) an initial net endotherm was followed by a vigorous exotherm. Finally, when a sliver of DSC pan was included in the DTA sample tube with the PVC, a vigorous exotherm followed the initial endothermic reaction (Fig. 1, g).

Reaction in air in an open pan of either platinum or aluminium gave a DTA curve which was qualitatively the same; under these conditions the DTA curve (Fig. 1, a) obtained in an aluminium pan, therefore, represents a predominantly oxidative decomposition. It seems probable that the corresponding curve in nitrogen (Fig. 1, d) represents predominant thermal decomposition. The standard DTA cell is characterised by an unusually high degree of product retention[18], so that the decomposition takes place in a self-generated atmosphere, and under these conditions is more endothermic. The contrast between DTA curves (Fig. 1, f and g) in the presence and absence of aluminium demonstrates the potential for interaction between sample, or decomposition products, and the container. The initial exotherm in the closed pan (Fig. 1, e) is believed to be due to such an interaction with the pan; although other explanations are possible, for it is known that the evolution of large volumes of gas can cause irreproducible DTA traces[19], and deformation of the sample pan can cause spurious DTA peaks.

The autocatalytic effect of evolved hydrogen chloride, and the modification of the DTA curves of PVC by the presence of additives and plasticizers has been shown[9]. Thus the curves shown in Fig. 1 are not necessarily representative of processed material which may differ in both composition, and particle size (ease of diffusion of product from the material), nonetheless the same factors will be operative and the DTA curve will be determined by procedural variables.

For Saran the differences between the DTA curves obtained in the two cells were less obvious (Fig. 2). The melting was clearly shown in a broad endotherm peaking at about 170°C, in good agreement with the reported value of 170–175°C for the semi-crystalline vinylidine chloride/vinyl chloride copolymers[16]. Curves obtained in the DTA cell (Fig. 2, c and d) showed an irregularity between 220–270°C, the range over which Saran was observed to decompose with extensive gas evolution. The decomposition was only slightly endothermic and was manifested in the DTA curves by the variable thermal contact causing an irregular trace. In the DSC cell, using a perforated lid in nitrogen, this decomposition was not detected, but vigorous exothermic reaction was evident above 250°C (Fig. 2, b). This could be due to the aluminium pan; although the presence of a sliver of aluminium with the sample in the DTA cell resulted in an increased exotherm, the effect was evident at a higher temperature (Fig. 2, c). In the DSC cell the exothermic decomposition was evident at slightly lower temperatures in air than it was in nitrogen (Fig. 2, a and b).

The DTA curves of the polyblend Cordelan (Fig. 3), showed a broad endotherm at 200–220°C. This endotherm was found to be insensitive to changes of heating rate (5–40°C min^{-1}). As the disorientation of crystallites in poly(vinyl alcohol), and the melting point of formalised poly(vinyl alcohol) fibres[20] commonly occur in this

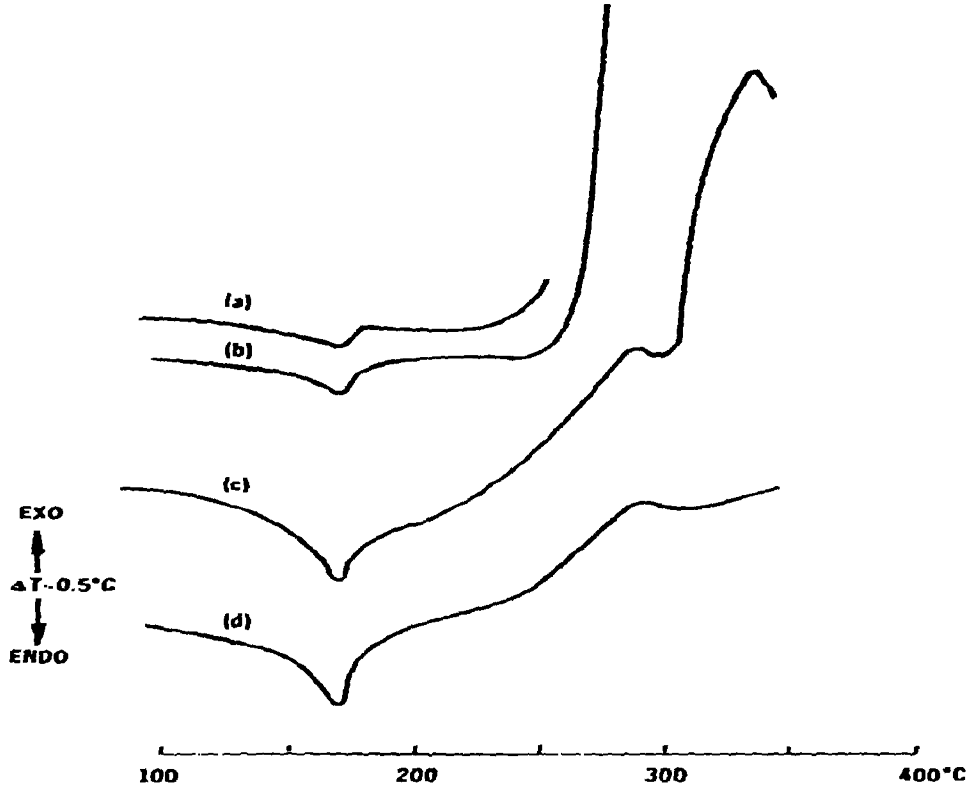

Fig. 2. DTA curves of Saran monofilament, heating rate 20°C min^{-1}. (a) = DSC cell, perforated lid, in air; (b) = DSC cell, closed lid, in N$_2$; (c) = DTA cell, with sliver of DSC pan; (d) = DTA cell.

range[10], this endotherm in the DTA curve of Cordelan can be attributed to the poly(vinyl alcohol) crystallinity. The subsequent decomposition of Cordelan can be interpreted as either a multistage exothermic reaction, or, more probably, concurrent endothermic and exothermic reactions, near 300°C. The DTA curves of the polyblend had little, if any, resemblance to those of the component polymers except for the PVA crystallite disorientation endotherm (Fig. 3, a, b and c). The degree of product restraint affected the DTA curve (Fig. 3, c and d); reaction occurred at a lower temperature in a closed pan than in one with a perforated lid, and the relative balance of the two reactions was changed. The curve obtained in the standard cell (Fig. 3, e) was substantially different and gave clear separation of an endothermic and an exothermic reaction. Under oxidising conditions both reactions were suppressed in favour of a more general exotherm (Fig. 3, f).

In contrast to the previous materials the modacrylic fibers, Kanekalon and Teklan, gave DTA curves that were not sensitive to the different conditions in the two cells. For Kanekalon (Fig. 4) there was no qualitative difference between curves obtained in air or nitrogen in the DSC cell, or under product restraint in the DTA cell. Teklan (Fig. 5), on the other hand, was slightly more sensitive to oxidation and an

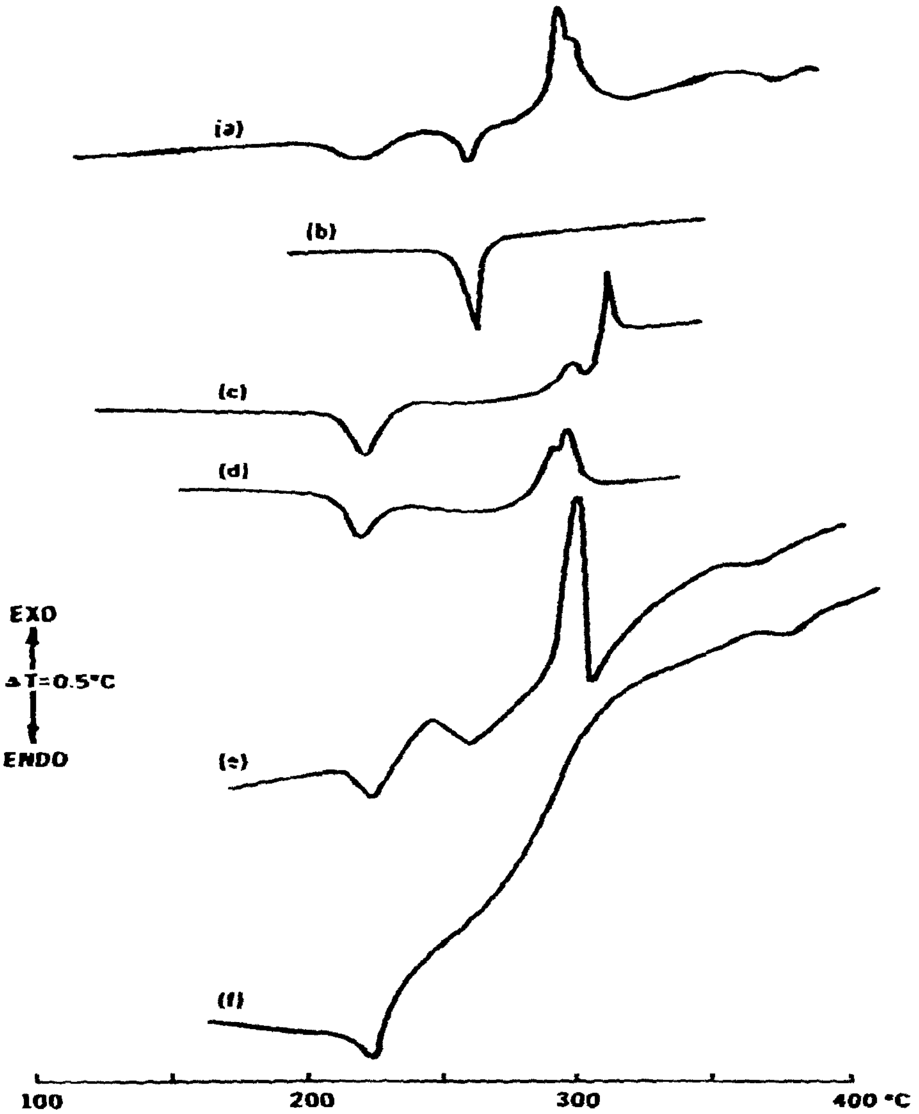

Fig. 3. DTA curves of Cordelan; heating rate 20°C min^{-1}. (a) = Cordelan/polyethylene terephthalate, DSC cell, perforated lid, in N_2; (b) = Polyester, DSC cell, perforated lid, in N_2; (c) = Cordelan, DSC cell, perforated lid, in N_2; (d) = Cordelan, DSC cell, closed lid, in N_2; (e) = Cordelan, DTA cell; (f) = Cordelan, DSC cell, perforated lid, in air.

endotherm was suppressed in the DTA curve under conditions of reasonable air access.

The DTA curves of both modacrylics were characterised by small melting endotherms at 190–200°C, which were insensitive to change of heating rate (5–40°C min^{-1}). After melting of the semicrystalline region each fibre underwent endothermic decomposition, peaking near 250°C (Teklan) and 290°C (Kanekalon), and then a

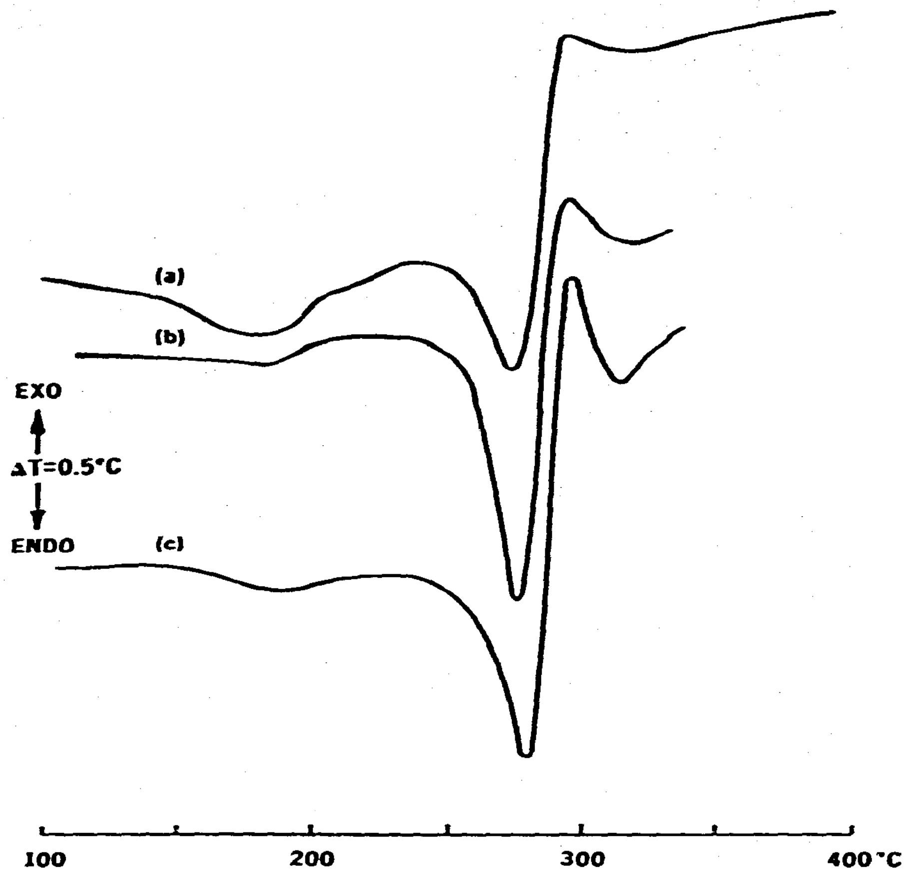

Fig. 4. DTA curves of Kanekalon, heating rate, 20°C min^{-1}. (a) = DTA cell; (b) = DSC cell, perforated lid, in N_2; (c) = DSC cell, perforated lid, in air.

vigorous exotherm, peaking at 280–290°C and 295–300°C, respectively. The endothermic decompositions thus bear a superficial resemblance to the decomposition of Saran and PVC, respectively, while the exotherms are similar to those of acrylonitrile homopolymer[21] and acrylic fibers[4], and, in contrast to a previous report[8], under these conditions the DTA curves of the modacrylics are not dominated by a resemblance to the chlorohomopolymer. The reactions are dependent on heating rate and the balance of exotherm and endotherm can be substantially altered by suitable choice of rate*; this may be utilised in identification.

The DTA curve of the Teklan/Celon fabric obtained at 20°C min^{-1} in the DSC cell (Fig. 6, a) differed from those of the component fibers (Fig. 5, c; Fig. 6, d); the 250°C endotherm was not evident. The curve obtained in the DTA cell (Fig. 6, c) at 20°C min^{-1} was reasonably additive, although some lowering of the Celon melting

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* A fiber identified only as a chlorine containing modacrylic was found (DSC cell closed pan) to have m.p. 210°C, and an exothermic peak at 300°C, at a heating rate of 20°C min^{-1}; at 100°C min^{-1}, there was an additional endotherm peaking at 310°C, and the exothermic peak had shifted to 340°C.

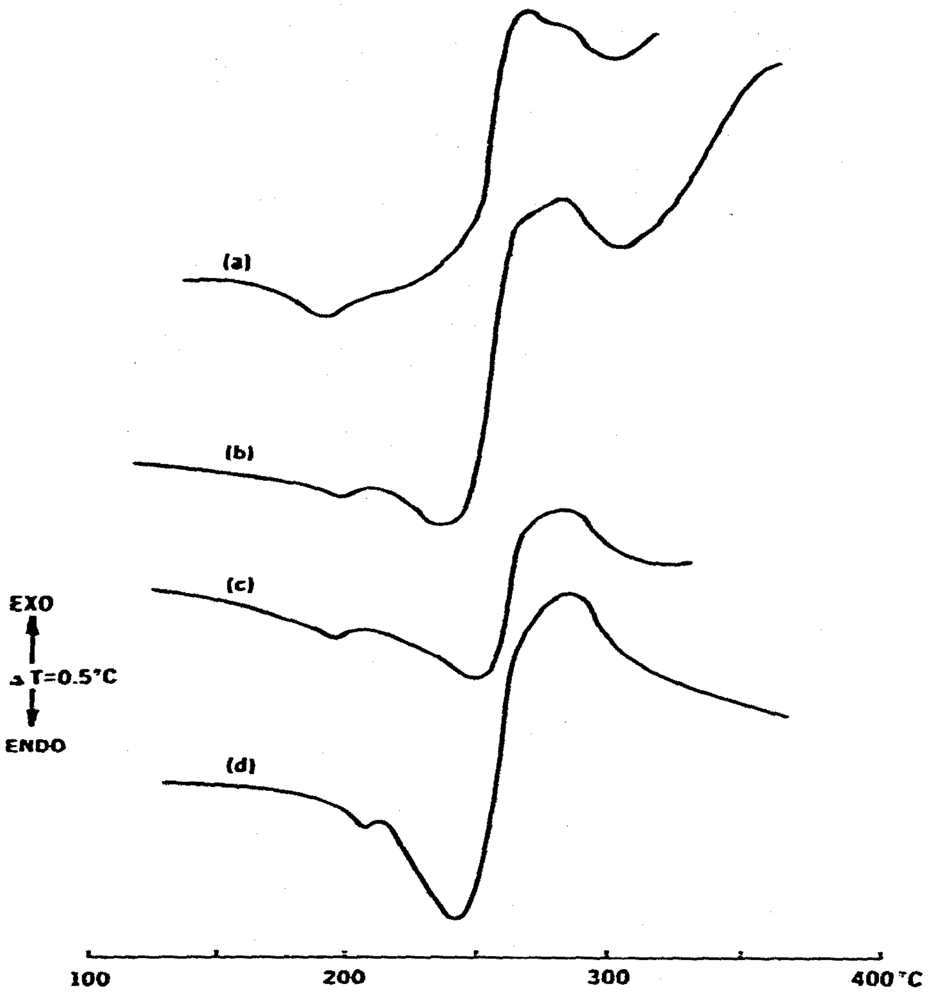

Fig. 5. DTA curves of Teklan; heating rate 20°C min^{-1}. (a) = DSC cell; perforated lid in air; (b) = DSC cell; closed lid, in air; (c) = DSC cell; perforated lid, in N$_2$; (d) = DTA cell.

was evident. At higher heating rates the characteristics of both fibers are again shown in curves obtained in the DSC cell (Fig. 6, b).

In contrast to those of the Teklan/Celon fabric, the DTA curves of the Teklan/cotton blend showed no qualitative difference from those of Teklan alone, except for a dehydration endotherm near 100°C. Cotton presents a relatively uneventful thermogram in this temperature range (150–350°C) on this equipment.

The Cordelan/poly(ethylene terephthalate) (PET) fabric gave a DTA curve in the DSC cell (Fig. 3, a) which showed the melting of the PET (Fig. 3, b) as well as that of Cordelan, and although the reaction exotherm of the Cordelan was slightly modified by the presence of the other fiber, it remained distinctive.

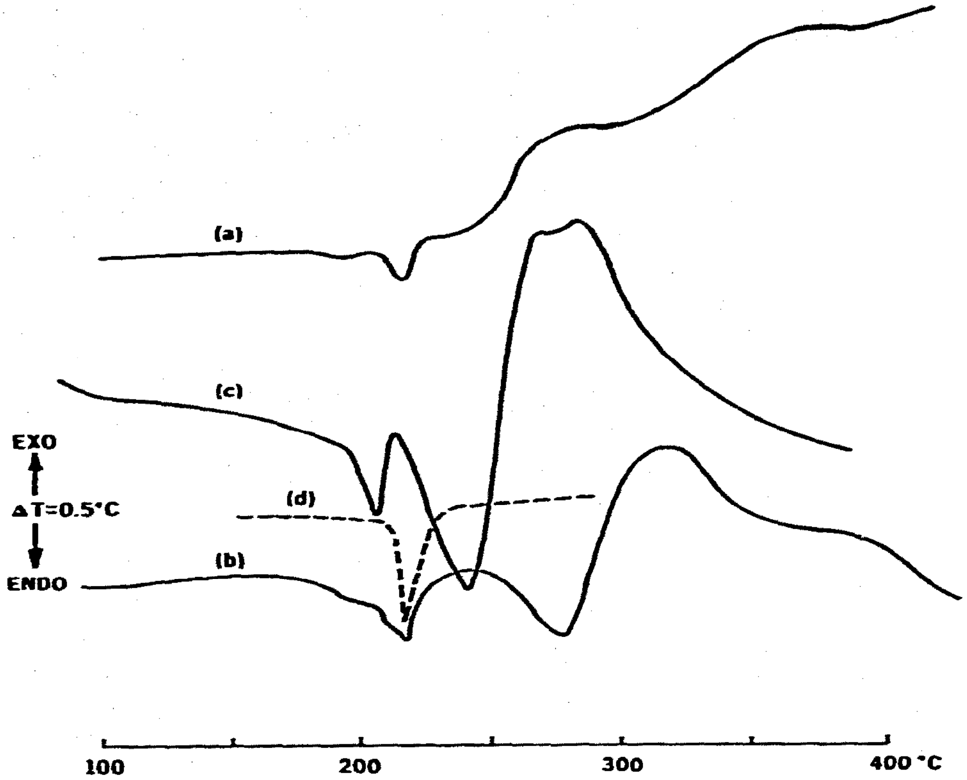

Fig. 6. DTA curves of Teklan/Celon. (a) = DSC cell, perforated lid, in N_2, 20°C min^{-1}; (b) = DSC cell, perforated lid, in N_2, 100°C min^{-1}; (c) = DTA cell, 20°C min^{-1}; (d) = *Celon*, DSC cell, perforated lid, in N_2, 20°C min^{-1}.

CONCLUSIONS

There is a continual need for an awareness of the procedural nature of DTA and DSC results. The foregoing can be explained in terms of cell geometry and construction affecting the interaction of sample, product and container.

During decomposition reactions there are major changes in the mass, size, shape, heat capacity and thermal transfer properties of the sample, which result in changes in the baseline of DTA and DSC curves[17]. This complicates interpretation of the curves over extended decomposition and temperature ranges and between different instruments. The present work has shown differences between the Du Pont DSC and DTA cells. Bingham and Hill[8], in studies which included some chlorofibers and modacrylics under somewhat similar conditions (the extent of diffusion through their perforated sample pan lids cannot be assessed, since no detail is given, but it seems probable that there is an effective self-generated atmosphere) obtained curves which show significant differences to the present results, in terms of apparent general exothermicity.

In the present case, it has not proved practical to investigate the interactions of chlorofibers and the procedural variables pertaining to the DSC cell in greater detail since even the presence of a purge gas (100 ml min^{-1}) was insufficient to protect the cell from corrosion by gaseous products*. For this reason, even though the DSC cell is more convenient to use for fiber and fabric samples and gives improved thermoanalytical performance, the standard DTA cell (in the Du Pont system) is preferred for routine identification of unknown fibers by "fingerprint" thermograms.

In either case, it should be recognised that the cell itself can contribute substantially to the shape of the DTA curve obtained; in the case of the standard cell by retention of volatile products in the proximity of the sample, and in the case of the DSC cell by further interaction of the sample or products with the aluminium pan. Great caution is therefore required when measures of thermal/chemical stability are compared to other properties of interest such as strength retention or flame resistance.

The various fibers containing chlorine have characteristic DTA curves, which are in some cases sensitive to procedural variables. There can be no confidence that the DTA curves of any particular blend, mixture or alloy of two or more components will be additive in respect of decomposition, although greater reliance can be placed on first order transitions.

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* Contamination and corrosion of the cell can lead to baseline drift, excessive noise, reduced sensitivity, and spurious peaks. Reversible phenomena have been observed at times, for example an endothermic peak at 260°C, reversible at the *same temperature* on cooling. The constantan "Thermo-Electric Disc" in the DSC cell has a limited life, which is shortened if corrosive products are liberated from the sample.

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