

## Differential Thermal Analysis of Synthetic Fibers

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### Synopsis

The application of differential thermal analysis (DTA) for the characterization and the investigation of the thermal degradation of synthetic textile fibers, to include polyester, nylon 6, propylene, and polytetrafluoroethylene fibers, has been studied. The temperature range was from 50 to 650°C. using laboratory-built DTA apparatus. Experimental considerations and techniques are discussed and such variables as sample preparation, size, cell packing, atmosphere control, and heating rate have been investigated. The conventional technique of grinding or milling DTA samples is shown to cause significant changes in certain samples, particularly in undrawn fibers. The control of sample atmosphere by dynamic gas flow through the sample cell gave peaks that were generally sharper and larger than those found when control was by gas diffusion. Data are given on the various low temperature transitions found in such fibers. Significant differences in low temperature transitions were observed between polypropylene fiber and the bulk polymer as well as between drawn and undrawn nylon 6 fibers. The interpretation of the DTA curves for the decomposition and other reactions at elevated temperatures is discussed. Nylon 6 and polypropylene showed only endothermic reactions indicative of depolymerization processes whereas other fibers showed both endothermic and exothermic reactions in the decomposition range.

Differential thermal analysis (DTA) is a dynamic method whereby the phase transitions and chemical transformations that occur during the heating of a polymeric or other material may be detected. Earlier work<sup>1-4</sup> in these laboratories demonstrated the potential applications of DTA for the identification, characterization, and thermal degradation studies of textile fibers. In the case of synthetic textile materials the detectable thermal changes include the glass transition, crystallization, fusion, moisture desorption, and irreversible reactions and thermal degradation processes.<sup>2,5-9</sup> The application of DTA in studying textile materials is of such recent date that standards for experimental techniques and instrumentation have not yet been established. Therefore, in this paper consideration is given to (1) instrumentation, (2) experimental techniques, (3) changes caused by certain fiber processing steps, and (4) high temperature reactions involving polymer decomposition.

### Experimental

#### *Apparatus*

Two different DTA units, built in the laboratory, were used in the work. One apparatus featured atmosphere control by diffusion into and out of the

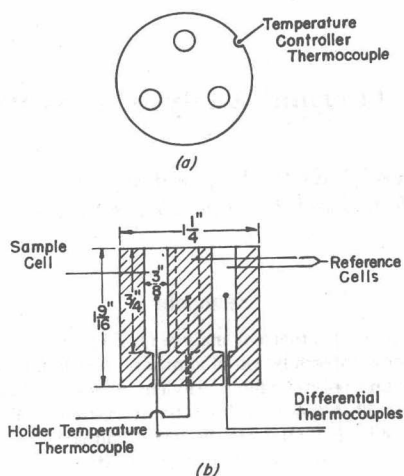


Fig. 1. DTA sample holder: (a) top view; (b) cross section view.

sample holder cells and its design was based on instrumentation described by Gordon and Campbell.<sup>10</sup> A metal sample holder fitted with thermocouples, is suspended in the ceramic core of a standard combustion furnace from a rod attached to a metal plate. With the holder in position the metal plate rests on the top of the vertically positioned furnace completely covering the opening but the furnace tube remains open at the bottom. The sample holder, made of a nickel-chrome alloy (Inconel X), is shown in Figure 1. Chromel-alumel thermocouples of 28 gage wire are introduced through the base of the holder and cemented in a fixed position. The emf representing the temperature difference is amplified by a L & N dc amplifier No. 9835-B. Temperature was measured in the reference substance, calcined alumina ( $\alpha\text{-Al}_2\text{O}_3$ ), in a separate well and the rate control thermocouple was located in the outer wall of the sample holder. The signals for the differential temperature and the reference temperature were recorded on time-base chart recorders using either two 10 in. single pen recorders or a double pen,  $X_1X_2$ , recorder (Leeds and Northrup instruments). The rate of heating was controlled by a cam-operated temperature programmer (West Instrument Co.) or by a solid state temperature programmer (F & M Model 240 Programmer).

The atmosphere is controlled by discharging the desired gas or gases under pressure into the open end of the furnace at flow rates of 3,000 to 6,000 cc./min. via a metal coil gas spreader. Thus, the sample holder is blanketed with the gas and the atmosphere within the sample well is achieved by diffusion of gas into the well. The removal of volatile products arising from the thermal degradation of the sample during a run is apparently accomplished by the driving force accompanying volatilization and is also dependent on diffusion.

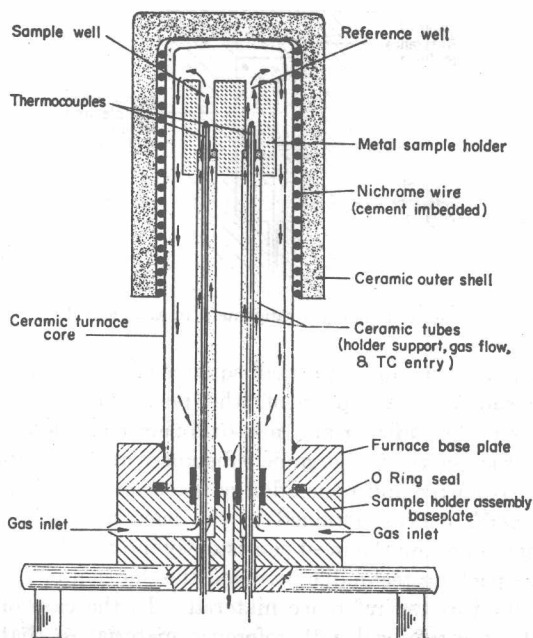


Fig. 2. Dynamic gas flow apparatus: sample holder and furnace assembly.

The other apparatus used, based on instrumentation described by Whitehead and Breger<sup>11</sup> and Lodding and Hammel,<sup>12</sup> differed primarily in atmosphere control, featuring the "dynamic gas flow" technique as described by Stone,<sup>13</sup> and is shown in Figure 2. In a dynamic gas flow apparatus the atmosphere is provided by passing the desired gas through the sample holder cells. Thus, the sample is continuously swept with fresh atmosphere gas insuring the removal of any degradation products from the sample cavity. Gas flow rates into the sample holder were of the order of 30 cc./min. The auxiliary instrumentation for signal amplification, recording, and heating rate control was the same as that described for the gas diffusion apparatus.

Under optimum conditions with either apparatus a temperature difference  $\Delta T$  of  $0.05^\circ\text{C}$ ., which is equivalent to  $2\text{ }\mu\text{v}$ , could be detected. As previously indicated the reference temperature and not sample temperature was measured so that the temperatures shown on the DTA curves are reference temperatures. Sample temperature is simply determined from the following relationship.

$$T_{\text{sample}} = T_{\text{ref}} + \Delta T$$

#### Procedures

Fiber, fabric, and some bulk polymer samples of 5 to 50 mg. were run at heating rates of  $1^\circ$  to  $10^\circ\text{C}/\text{min}$ . from about  $50$  to  $650^\circ\text{C}$ . Samples were

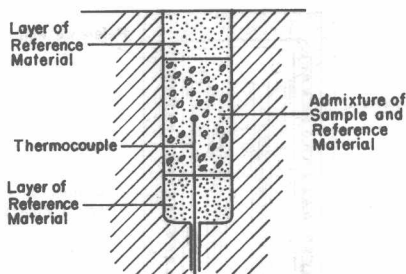


Fig. 3. Packing arrangement in sample cell.

usually prepared by cutting into small squares of  $1/16$  in. or  $1/16$  in. lengths. Samples were run in an atmosphere of either purified nitrogen or compressed air to provide both oxidizing and non-oxidizing conditions. At elevated temperatures the reactions of organic substances are so complex that some separation of oxidative and nonoxidative reactions must be achieved. In general the DTA curves obtained in the inert atmosphere were found to be less ambiguous and the most consistently informative.

The sample packing technique involved the dilution of all samples with the alumina used as the reference material. In the case of organic materials samples are admixed with reference material so that the packing and thermal properties will be determined principally by the reference material regardless of sample shrinkage, melting, decomposition etc.<sup>14-16</sup> A modified "sandwich" packing, developed in previous studies,<sup>1,2</sup> was used in the present work as shown diagrammatically in Figure 3. About one-third of the reference material to be used is deposited in the sample well as a base layer. The cut pieces of sample are then placed around the thermocouple junction together with reference material and the balance of the reference material constitutes a covering layer.

### Results and Discussion

The effects of sample preparation, sample size, cell packing, atmosphere control, and other experimental variables have been studied. The usual method for DTA sample preparation involves grinding or milling to 40-200 mesh.<sup>14</sup> The effects of sample preparation and packing are shown in Figure 4 by representative curves obtained on the samples of undrawn Dacron\* polyester fiber and, using the top curve, the main curve features are identified as (1) the second-order or glass transition  $T_g$  at  $84^\circ\text{C}$ ., which is manifested as a well-defined downward shift in the base line reflecting an increase in the heat capacity of the polymer, (2) polymer crystallization shown by the exotherm with a peak at  $148^\circ\text{C}$ ., (3) polymer fusion shown by the endotherm with a peak at  $266^\circ\text{C}$ ., and (4) polymer decomposition represented by the endothermic process with a peak temperature of  $450^\circ\text{C}$ .

\* Du Pont trademark.

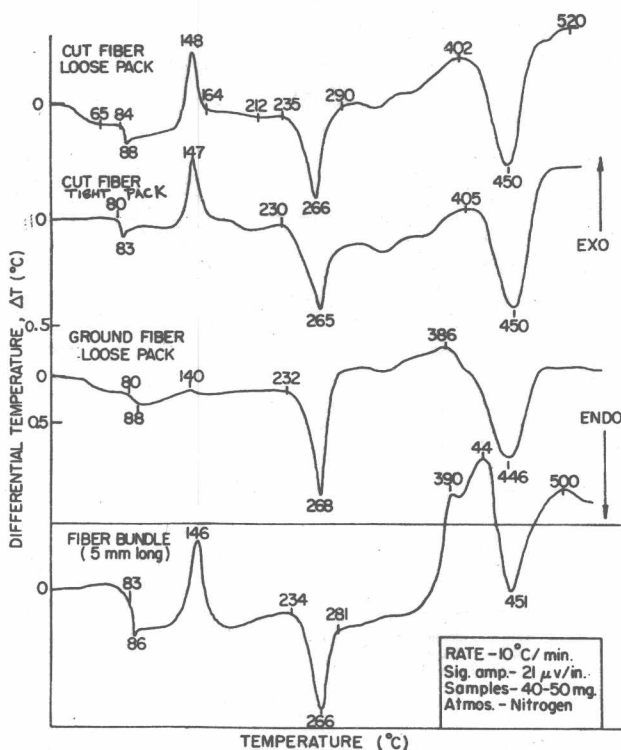


Fig. 4. DTA curves of undrawn Dacron (GD-gas diffusion apparatus): effect of sample preparation and packing.

Following polymer fusion there are also indications of one or more exothermic reactions beginning around 350°C. By means of dynamic mechanical measurements  $T_g$  for polyethylene terephthalate fibers has been estimated to be 80°C.<sup>17</sup> and available DTA data from the literature indicates values of 78°C.<sup>9</sup> It should be noted that due to the relatively fast heating rate of 10°C./min. the actual peak temperatures shown can be expected to differ from those from DTA curves obtained at lower heating rates. Some of the effects of heating rate are discussed subsequently.

Tightly packing the fiber sample by tamping the sample mixture in the well does not significantly alter peak temperatures although the base line appears to shift slightly. However, in the cases where the fiber was ground to 40 mesh by a Wiley mill the curve indicates some reduction in the glass transition shift, the crystallization peak has virtually disappeared, and the curve has changed shape somewhat in the region just prior to the decomposition endotherm. In the grinding or milling operation there is apparently sufficient heat generated such that, unless adequate cooling is provided, samples of largely amorphous bulk polymers or undrawn fibers will undergo the low temperature transitions and crystallization process.

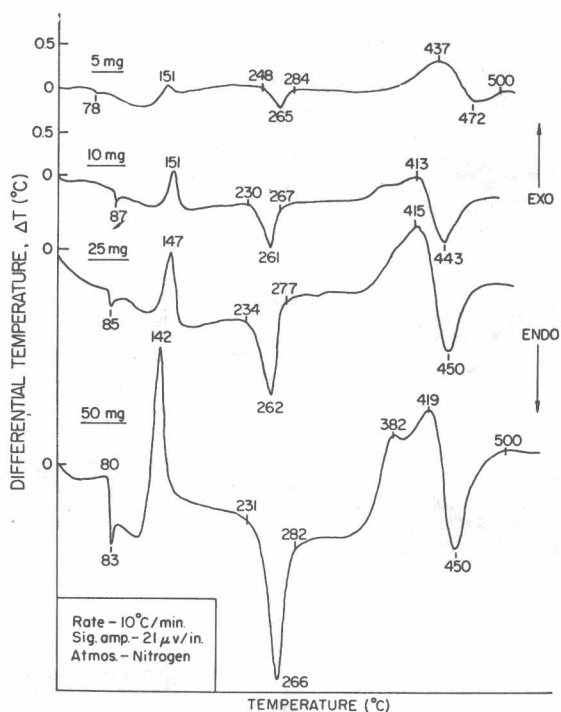


Fig. 5. DTA curves of undrawn Dacron (DGF-dynamic gas flow apparatus): effect of sample size.

It has been shown that milling can cause polymer degradation<sup>18,19</sup> and severe mechanical damage may cause other significant changes in certain fibers<sup>20</sup> that may be reflected in the DTA curve. The curve obtained with the sample in the form of a fiber bundle shows very well defined features with the appearance of two distinct exothermic reactions prior to decomposition. In this case a fiber bundle was slid down over the thermocouple so that the bead was positioned halfway up in the bundle. Samples of fibers cut to a length of about  $1/16$  in. and fabric cut into  $1/16$  in. squares have been found to give highly reproducible results.

Sample size is another extremely important variable to be considered. Intuitively, the smaller the sample the more realistic the results should be. Thus, in the case of a small sample the effect of a thermal gradient will be minimized. The effects of heat capacity differences vis a vis the reference material would also be minimized. Since a finite time is required for a transformation to occur sample size may unduly affect the observed temperature of a given reaction.<sup>15</sup> In Figure 5 the effect of sample concentration is shown for undrawn Dacron fiber in nitrogen atmosphere using the dynamic gas flow apparatus. The DTA curves show that 5 mg. samples give weak reactions with some curve distortion.

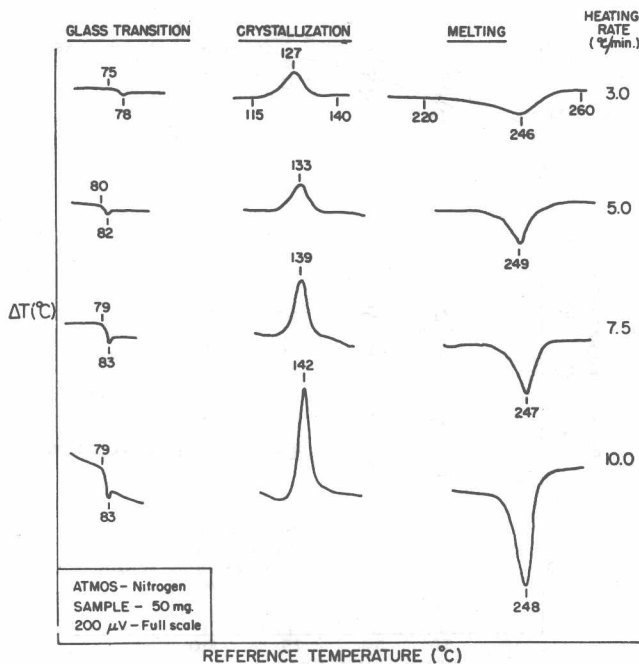


Fig. 6. DTA (GD) curves of undrawn Dacron: effect of heating rate.

Heating rate has long been recognized as a potent variable in DTA<sup>14</sup> that can cause shifts in peak temperature. Dacron, nylon 6, and polypropylene samples were run in the gas diffusion DTA apparatus at heating rates of 1, 3, 5, 7.5, and 10°C./min. The results obtained on Dacron are shown in Figure 6. All of the results are summarized in Figure 7. The data show that (1)  $T_g$  tends to increase slightly as heating rate increases, (2) crystallization temperature is definitely affected by heating rate, increasing as heating rate increases, (3) melting is not much affected but tends to increase slightly as high rates of heating are reached, and (4) decomposition temperature increases markedly as heating rate increases.

Results have been obtained on some fiber and bulk polymer samples, described in Table I, in air and in purified nitrogen on 50 mg samples of cut fiber.

In Figure 8 the DTA curves of drawn and undrawn Caprolan\* nylon 6 in nitrogen on the gas diffusion apparatus are presented. There is a well-defined endothermic peak for polymer fusion indicating a melting point of 231°C. for drawn fiber versus 231°C. for the undrawn fiber. The fusion peak for the drawn fiber is much larger and sharper than the undrawn indicating a higher degree of crystallinity and/or orientation,

\* Allied Chemical Corporation trademark.

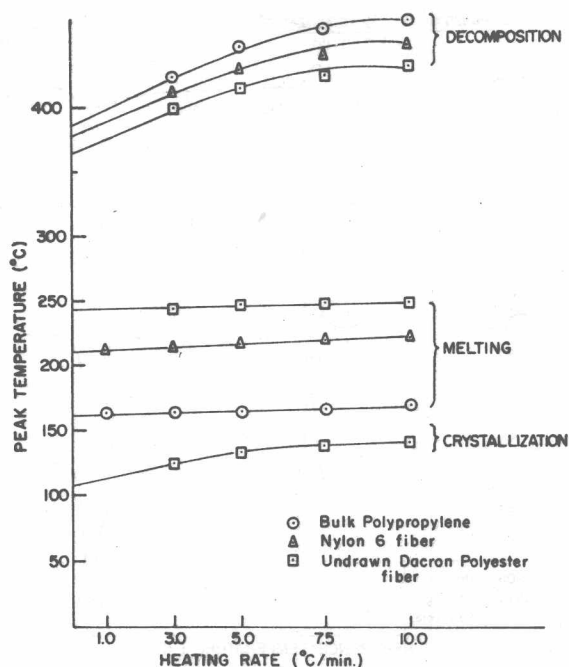


Fig. 7. Variation of DTA peak temperatures with heating rate.

as might be expected. Both melts are observed to start depolymerization, around  $370^{\circ}\text{C}.$  and two reactions are indicated, one much smaller than the other. Strauss and Wall<sup>21</sup> in a study of the pyrolysis of nylon 6 in vacuum concluded that the decomposition involved two competing mechanisms: (1) random hydrolytic scission and (2) free radical depolymerization. The DTA curves for nylon 6 appear to fit this hypothesis leading to the interpretation of the small endotherm around  $400^{\circ}\text{C}.$  as due to random hydrolytic scission followed by the major reaction of depolymerization by a

TABLE I  
Special DTA Samples

Sample	Description
Pure nylon 6	High tenacity, bright, drawn yarn
	High tenacity, bright, undrawn yarn
Polypropylene	Experimental samples of drawn fiber from pure polymer
	pure, bulk polymer



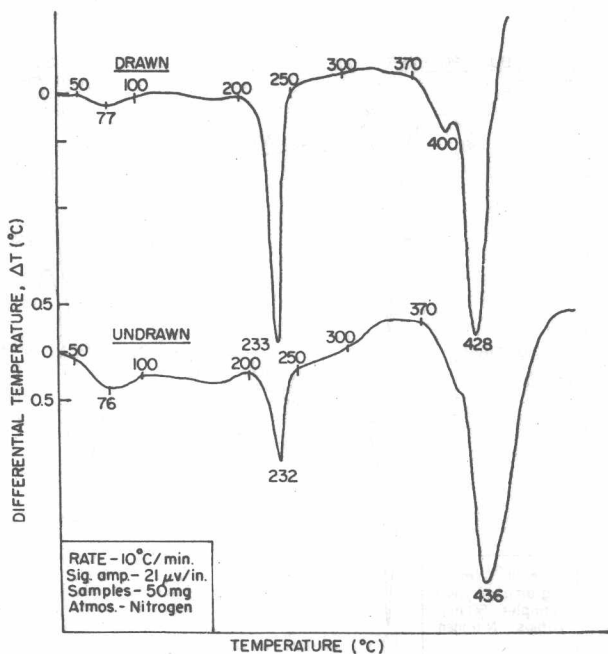


Fig. 8. DTA (GD) curves of nylon 6 fiber.

free radical mechanism. The resolution of the decomposition reactions is better in the case of the drawn fiber.

The air curves for both the drawn and undrawn fibers on the two DTA apparatuses have also been obtained. The gas diffusion DTA curves show a weak endotherm around 90°C. followed by an exothermic rise which is interrupted by the fusion reaction (reference peaks 232–233°C.) with the peak for the drawn fiber being the sharper of the two. The fusion peaks are followed by strong exothermic processes showing a peak at 387°C. for the drawn fiber and 408°C. for the undrawn. These represent oxidative reactions since they are not found in the nitrogen curves. Both samples exhibit strong endotherms with peak temperatures comparable to the main decomposition endotherms found in the nitrogen curves. However, no indication of two reactions is evident probably due to the interference of oxidative reactions. The air curves for dynamic gas flow DTA are generally similar except that the major reactions appear larger as was the case for the nitrogen curves.

Samples of bulk polypropylene and fiber made therefrom have been run in nitrogen on both DTA apparatuses. The gas diffusion curves in Figure 9 show a possible phase change around 95–100°C which may represent a transition associated with one crystalline modification changing to another followed by the main fusion peak. The reaction at 98°C. in the bulk

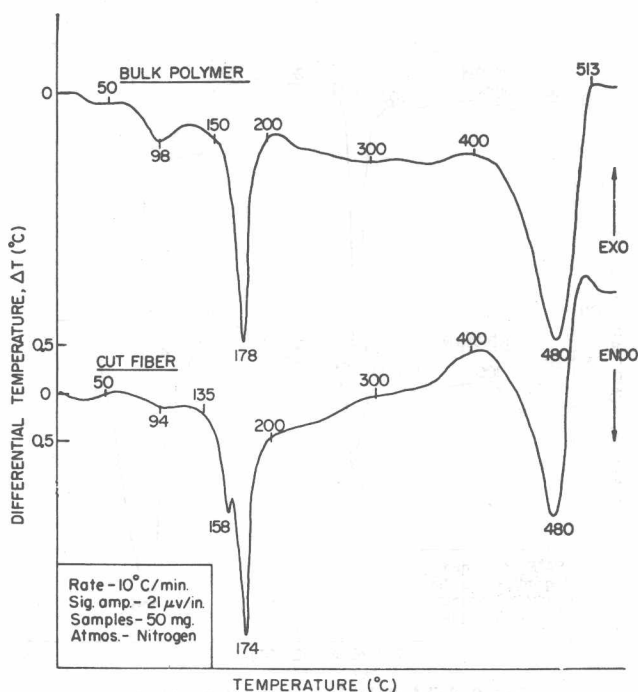


Fig. 9. DTA (GD) curves of polypropylene.

polymer is much reduced in the fiber and the main fusion process in the fiber now shows two peaks. The polymer melt begins to show a decomposition endotherm beginning about 425°C. with a peak at 480°C. The dynamic gas flow DTA curves, shown in Figure 10 follow a similar pattern except that the melting endotherms and decomposition endotherms appear to be larger. The double peaks at 158 and 174°C. observed in the melting region are found only for the drawn fiber and a similar phenomenon has been observed in the case of nylon 66.<sup>2,5</sup> This appearance of two peaks was first reported by White<sup>5</sup> in the DTA curves of nylon 66 yarn and, based on x-ray and birefringence data, he concluded that the first peak involved disorientation prior to crystallite melting. The DTA curve of undrawn polypropylene does not show the early peak at 158°C. and if the melt from the drawn fiber is cooled and rerun the first peak disappears so that this peak at 158°C. is tentatively ascribed to disorientation. The relatively small size of the polypropylene decomposition endotherms has been interpreted as indicating partial degradation to chain fragments rather than to monomer. Madorsky et al.<sup>22</sup> found that vacuum pyrolysis of polyethylene gave products with an average molecular weight of about 700 and Grassie<sup>19</sup> reports the thermal degradation products of polypropylene to be primarily large chain fragments.

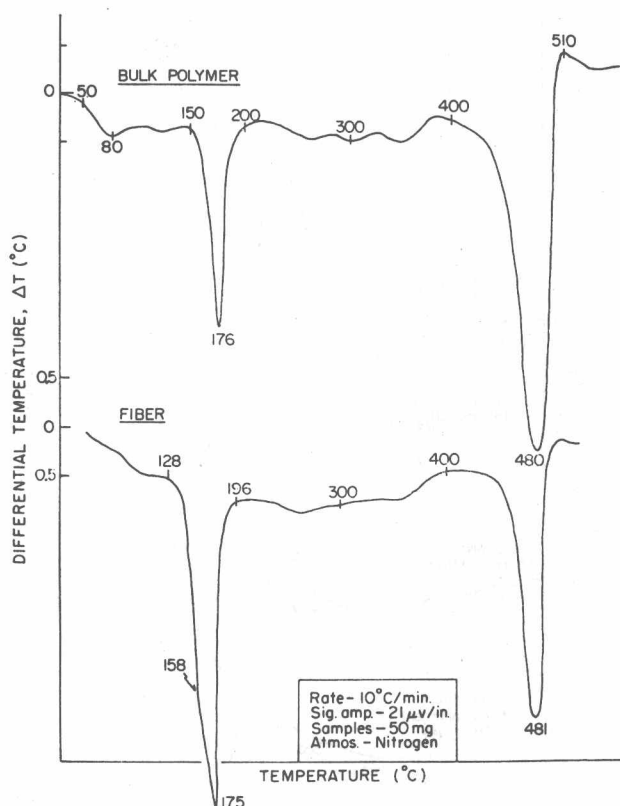


Fig. 10. DTA (DGF) curves of polypropylene.

TABLE II  
Comparison of DTA Peak Data

Sample	Gas diffusion		Dynamic gas flow	
	$T(^{\circ}\text{C.})$	Hgt. (in.)	$T(^{\circ}\text{C.})$	Hgt. (in.)
Fusion Peak Data				
Dacron	266	1.7	266	3.0
Nylon 6	233	4.9	236	7.0
Polypropylene-fiber	174	4.4	175	6.2
Polypropylene-bulk	178	4.1	176	4.0
Decomposition Peak Data				
Dacron	450	2.1	450	3.0
Nylon 6	428	5.2	434	7.0
Polypropylene-fiber	480	3.3	481	5.0
Polypropylene-bulk	480	3.5	480	6.7

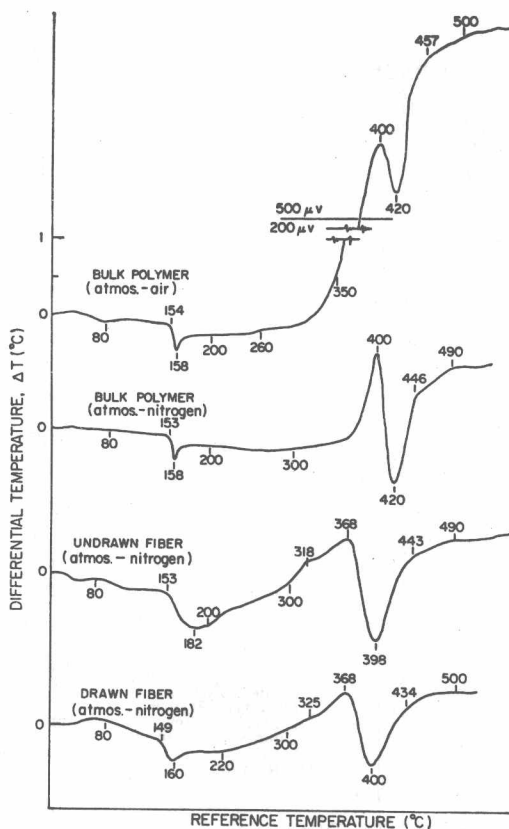


Fig. 11. DTA curves of polycarbonate bulk polymer and fiber.

In order to facilitate the comparison of gas diffusion DTA with dynamic gas flow DTA, data on the temperatures and heights of fusion peaks and decomposition peaks are presented in Table II. The results show that in every instance save one the peak heights obtained under dynamic gas flow conditions are increased about 45% over the gas diffusion peak heights. However, peak temperatures are quite comparable. It is also apparent by inspection of the various DTA curves shown herein that in the case of dynamic gas flow generally sharper major peaks are obtained but that the resolution of small peaks is not very different from those obtained under gas diffusion conditions.

The curves for polycarbonate bulk polymer (Lexan-General Electric Corp.<sup>23</sup>) and experimental fibers made therefrom are shown in Figure 11. The glass transition  $T_g$  is reported to be 145 to 150° C. and it is difficult to induce crystallization in the polymer.<sup>24,25</sup> In the case of partially crystalline samples the melting point has been reported as 267°C.<sup>24</sup> DTA

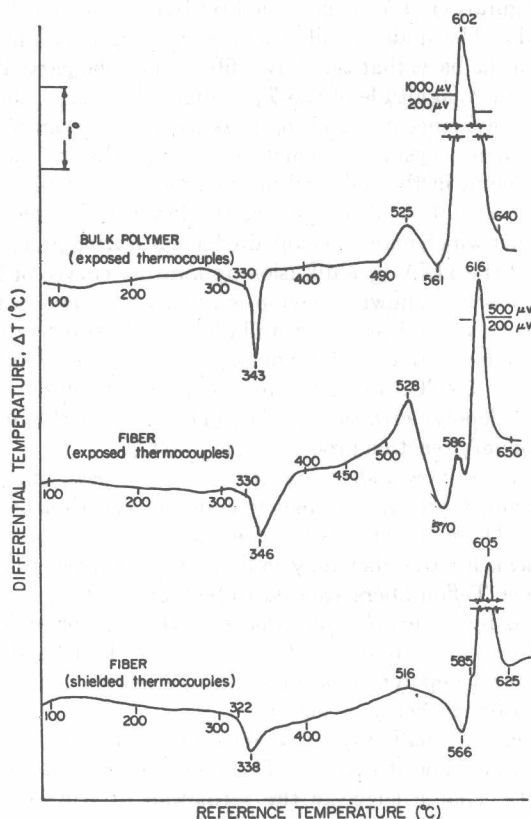


Fig. 12. DTA curves of Teflon bulk polymer and fiber ( $10^{\circ}\text{C./min.}$ -nitrogen atmospheres).

curves of the bulk polymer in air and nitrogen show a  $T_g$  of about  $153^{\circ}\text{C.}$  but there is no evidence of subsequent crystallization or melting. The effect of oxidation can be seen in the air curve with a strong exothermic process beginning around  $300^{\circ}\text{C.}$  which is interrupted by an endothermic decomposition process with a peak at  $420^{\circ}\text{C.}$  followed by further oxidation of the decomposition products. In nitrogen the same pattern is found except for the lack of any significant exothermic process after decomposition. The occurrence of the same endothermic decomposition process suggests thermal depolymerization.

The DTA curves of fiber samples indicate significant changes from the bulk polymer which may involve the effects of the spinning process. The shape of the  $T_g$  is different in that no endothermal peak is present and the change in the base line is more gradual. The shape of the  $T_g$  in the DTA curve has been discussed by Wunderlich and Bodily<sup>26</sup> who have proposed

that the configuration of  $T_g$  is governed by the rate at which the polymer melt is cooled. The undrawn fiber shows the larger  $T_g$  change as might be expected on the basis that the drawn fiber should be partially crystalline thus reducing the magnitude of the  $T_g$  change. However, the drawn fiber curve shows no evidence of a melting peak so that this sample is indicated to have little or no crystalline structure. An exothermic process around 320°C is not found in the bulk polymer curve. The decomposition peak temperature (400°C.) is also significantly lower than that of (420°C.) the bulk polymer which may reflect chain damage during processing.

In Figure 12 the DTA (gas diffusion apparatus) curves of Teflon\* bulk polymer and fiber are shown. Teflon is reported to have a transition at 327°C. that involves a loss in crystallinity.<sup>27</sup> Grassie<sup>19</sup> reports thermal degradation around 600°C and Madorsky and Strauss<sup>28</sup> found only 17% volatilization at 500°C. for 30 min. Various pyrolysis studies<sup>19, 28-30</sup> have indicated depolymerization to monomer,  $C_2F_4$ , with subsequent formation of secondary reaction products  $C_3F_6$  and  $C_4F_8$ .

The DTA curves show a sharp endotherm with a peak at 343°C. for the bulk polymer and a broad, asymmetric endotherm with a peak at 346°C. for the fiber. These transitions involve the loss of crystallinity and the asymmetric peak for the fiber may indicate a second reaction due to disorientation since Teflon fibers are said to be highly oriented. This transition is followed by an exothermic process with a major endothermic decomposition beginning about 530°C. with a peak around 560-570°C. due to free radical depolymerization of the polymer. This endotherm is followed by major exothermic reactions.

In the fiber case a small exothermic reaction is found at 585°C. with the main exotherm peaking at 616°C. The presence of exothermic reactions in an inert atmosphere suggests the formation of covalent bonds, e.g. the formation of new products. Thus, the DTA curves show exothermic peaks following depolymerization reflecting the formation of secondary reaction products described by Lewis and Naylor<sup>29</sup> and others.<sup>19, 28</sup>

### Conclusions

The results show that DTA is a highly useful method for the unambiguous characterization of synthetic fibers from low temperature transitions through decomposition. It is shown that DTA can detect changes resulting from the conversion of bulk polymers into fibers as well as reveal certain changes in fiber fine structure due to further processing.

A good correlation was found between DTA results and data on the thermal degradation behavior of fiber-forming polymers from more conventional methods. Thus, DTA can provide "thermal spectra" that not only serve as fiber "fingerprints" but are also interpretable in terms of molecular rearrangements, depolymerization, new product formation, and other chemical changes that occur during the thermal degradation of synthetic textile materials.

\* Du Pont trademark.

It has also been shown that increasing the rate of heating from 1 to 10°C./min. causes the peak temperatures for polymer crystallization and decomposition to increase significantly whereas the glass transition and melting temperatures are not greatly affected although a tendency to increase somewhat at high rates of heating was observed.

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### References

1. Schwenker, R. F., Jr., L. R. Beck, Jr., and W. J. Kauzmann, Navy Contract N140-(132)57442B, Final Report, February 1960.
2. Schwenker, R. F., Jr., and L. R. Beck, Jr., *Textile Res. J.*, **30**, 624 (1960).
3. Schwenker, R. F., Jr., and J. H. Dusenbury, *Textile Res. J.*, **30**, 800 (1960).
4. Schwenker, R. F., Jr., L. R. Beck, Jr., and E. Pacsu, Div. of Cell. Chem., paper No. 42, abstracts of 138th ACS Mtg., New York, September 1960.
5. White, T. R., *Nature*, **175**, 895 (1955).
6. Keavney, J. J., and E. C. Eberlin, *J. Appl. Polymer Sci.*, **3**, 47 (1960).
7. Ke, B., in *Organic Analysis, Volume 4*, J. Mitchell, Jr., eds., Interscience, New York, 1960, p. 361.
8. Ke, B., *J. Appl. Polymer Sci.*, **6**, 624 (1962).
9. Hay, A., paper presented at the Eleventh Canadian High Polymer Forum, September 1962.
10. Gordon, S., and C. Campbell, *Anal. Chem.*, **27**, 1102 (1955).
11. Whitehead, W. L., and I. A. Breger, *Sci.*, **111**, 279 (1959).
12. Lodding, W., and L. Hammel, *Rev. Sci. Instr.*, **30**, 885 (1959).
13. Stone, R. L., *Anal. Chem.*, **32**, 1583 (1960).
14. Smothers, W. J., and Y. Chiang, *Differential Thermal Analysis*, Chemical Publishing Co., New York, 1958.
15. Vassallo, D. A., and J. C. Harden, *Anal. Chem.*, **34**, 132 (1962).
16. Mackenzie, R. C., and B. D. Mitchell, *Analyst*, **87**, 420 (1962).
17. Ward, I. M., *Textile Res. J.*, **31**, 650 (1962).
18. Hess, K., and E. Steurer, *Z. Physik Chem.*, **A193**, 234 (1944).
19. Grassie, N., *Chemistry of High Polymer Degradation Processes*, Interscience, New York, 1956, p. 110.
20. Schwenker, R. F., Jr., and J. C. Whitwell, *Textile Res. J.*, **23**, 804 (1953).
21. Strauss, S., and L. A. Wall, *J. Res. Natl. Bur. Std.*, **60**, 39 (1958).
22. Madorsky, S. L., S. Strauss, D. Thompson, and L. Williamson, *J. Polymer Sci.*, **4**, 639 (1949).
23. Christopher, W. F., *Plastics Engr. J.*, **14**, 31 (1958).
24. Freeman, H. I., and M. J. Coplan, *Some Properties of Polycarbonate Fibers*, paper presented at 33d Annual Meeting, Textile Research Institute, New York, March 1963.
25. Krum, F., and F. H. Müller, *Kolloid Z.*, **164**, 81 (1959).
26. Wunderlich, B., and D. M. Bodily, *J. Polymer Sci.*, **C6**, 137 (1964).
27. Roff, W. J., *Fibers, Plastic and Rubbers*, Butterworths, London, 1956.
28. Madorsky, S. L., and S. Strauss, *J. Res. Natl. Bur. Std.*, **66A**, 401 (1962).
29. Lewis, E. E., and M. A. Naylor, *J. Am. Chem. Soc.*, **69**, 1968 (1947).
30. Goldfarb, I., R. J. McHenry, and E. C. Penski, *J. Polymer Sci.*, **58**, 1283 (1962).

### Résumé

On a étudié l'application de l'analyse différentielle thermique (DTA) à la caractérisation et à l'étude de la dégradation thermique de fibres synthétiques, y compris les fibres de polyester, nylon-6, le polypropylène et le polytétrafluoroéthylène. On a employé des appareils DTA, construits au laboratoire, dans le domaine de température de 50°C à 650°C. On discute les considérations et techniques expérimentales, et les variables comme la préparation et la grandeur de l'échantillon, le contrôle de l'atmosphère et la vitesse de chauffage ont été étudiés. On a trouvé que la technique conventionnelle d'écraser ou de mouler les échantillons DTA donne lieu à des changements significatifs pour certains échantillons, plus spécialement dans le cas de films non-étirés. Le contrôle de l'atmosphère de l'échantillon par un courant gazeux dynamique à travers de la cellule de l'échantillon, donne des pics qui sont, en général, plus nets et plus étroits que ceux trouvés lors du contrôle par diffusion gazeuse. On donne des résultats pour différentes transitions à basse température trouvées dans ces films. On a trouvé des différences significatives entre des transitions à basse température entre le polypropylène fibreux et le polymère en bloc et également pour les fibres de nylon-6 étirées et non-étirées. On discute l'interprétation des courbes DTA pour la décomposition et d'autres réactions à des températures élevées. Par le nylon-6 et le polypropylène, on ne constate que des réactions endothermiques, ce qui indique un processus de dépolymérisation, tandis que les autres fibres montrent dans le domaine de décomposition des réactions endothermiques et exothermiques.

### Zusammenfassung

Die Anwendung der Differentialthermoanalyse (DTA) zur Charakterisierung des thermischen Abbaus von synthetischen Textilfasern, nämlich Polyester-, Nylon-6-, Polypropylen- und Polytetrafluoräthylenfasern, wurde untersucht. Der Temperaturbereich des im Laboratorium gebauten Apparates erstreckte sich von 50°C bis 650°C. Die experimentellen Grössen und Verfahren werden diskutiert und Probenbereitung, Grösse, Zellpackung, kontrollierte Atmosphäre und Erhitzungsgeschwindigkeit als Variable untersucht. Das übliche Verfahren des Zerreibens oder Mahlens von DTA-Proben ruft bei gewissen Proben, besonders bei nicht gereckten Fasern, wichtige Veränderungen hervor. Die Kontrolle der Probenatmosphäre durch dynamische Gasströmung durch die Probenzelle lieferte im allgemeinen schärfere und grössere Maxima als bei Kontrolle durch Gasdiffusion. Die Daten der verschiedenen in den Fasern festgestellten Tieftemperaturumwandlungen werden angegeben. Wichtige Unterschiede bei den Tieftemperaturumwandlungen ergaben sich zwischen der Polypropylenfaser und dem unverarbeiteten Polymeren sowie zwischen gereckten und ungereckten Nylon-6-Fasern. Die Interpretation der DTA-Kurven bei der Zersetzung und anderen Reaktionen bei erhöhter Temperatur wird diskutiert. Nylon-6 und Polypropylen zeigten lediglich endotherme, für Depolymerisationsprozesse charakteristische Reaktionen, während andere Fasern im Zersetzungsgebiet endotherme und exotherme Reaktionen aufwiesen.



## Differential Thermal Analysis of Linear Polyesters

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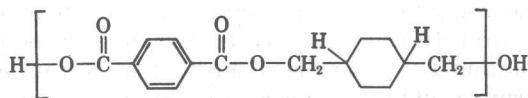
### Synopsis

Differential thermal analysis (DTA) was used to measure crystallization, melting, and glass transition temperatures of poly(ethylene terephthalate), poly-1,4-cyclohexylenedimethylene terephthalate, and some copolyesters. These values are affected in different ways by systematic changes in such factors as copolymerization, molecular block formation, crystal perfection, nucleation, thermal history, and orientation. At least two types of abnormally high melting structures were formed and identified. The stability of these polymers to thermal and oxidative degradation was studied by DTA.

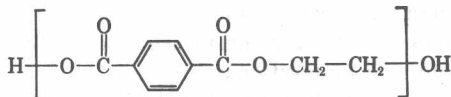
### Introduction

Differential thermal analysis (DTA) may be used to measure melting, crystallization, and glass transition temperatures of polyesters. Oxidative and thermal breakdown also may be measured. These thermal properties are affected by systematic variations in the molecular or crystalline structure of the polyester, which may be brought about by copolymerization, heat treatments, nucleation (by orientation or other means), or by rate of heating in the DTA measurement.

Polyethylene terephthalate (T2) and poly-1,4-cyclohexylenedimethylene terephthalate (T16) and a variety of copolyesters were studied by DTA to determine the effects of the above factors on these systems.\* The basic repeating units are as follows:



Poly 1,4-cyclohexylenedimethylene terephthalate (T16)



Polyethylene terephthalate (T2)

\* We are indebted to C. J. Kibler and J. G. Smith, of these Laboratories, for the T2, T16, and copolyesters used in this work. The compositions of these resins were verified by NMR and infrared spectroscopy.