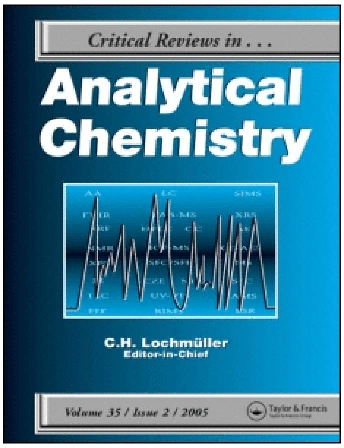

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A REVIEW OF TEXTILE CHARACTERIZATION BY THERMAL ANALYSIS

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I. INTRODUCTION

Thermal analysis has become a widely accepted analytical technique for the characterization of textiles. This paper is a review of techniques and applications of thermal analysis as employed in the study of textile fibers. Frequently, thermal techniques are used in conjunction with other forms of analysis, typically IR and X-ray spectroscopy, as well as mechanical methods. The correlation of data obtained from a variety of methods can yield a more complete picture of fiber properties than any single method. However, it is beyond the scope of this paper to discuss methods other than thermal methods. The fundamental principles of thermal analysis have been discussed at length elsewhere.[1,2]

Thermal analytical methods are very useful for the rapid characterization of many aspects of the responses of fiber structure and properties to treatments for dying, shrinkproofing, texturizing, and other processes. Degradation and decomposition behavior of fibers in flame retardant studies can be monitored conveniently also.

Rangarajan and Francis[3] briefly reviewed principles and applications of common thermal techniques. Slater[4] has reviewed many examples of applications of thermal analysis to fibers. This review discusses applications of these methods to a variety of types of investigation in the field of textiles. The arrangement of articles is according to fiber type. There is a certain overlap involved with investigations of blended fibers such as cotton/polyester fabrics, etc. Also, investigations of additives are placed within the category of the appropriate fiber. For example, acrylic soil release agents are discussed in Section IV as applied to cotton fabric.

II. DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis (DTA) is one of the most widely used thermal analytical techniques for characterizing textiles. It is defined as a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature as the substance and the reference material are subjected to a controlled temperature program. When the sample undergoes some physical change, either a first or second order transition, at a certain temperature, this is recorded as a deviation from the baseline $\Delta T = 0$, either endothermic or exothermic. For instance, the melting of the sample would appear as an endothermic peak.

DTA is an empirical technique with results depending on many variables. Some of the more significant are the cell design between different instruments, the nature and geometry of the sample, how it is packed in the cell, and the heating rate. Consequently, resulting thermograms for the same material often differ among laboratories, particularly on older instrumentation. Modern instrument design has minimized the previously cited effects. However, any continuous investigation must maintain consistent experimental parameters for consistent results.

Amigo and Chanh[5] reported the heats of combustion for seven fibers: polyester, nylon-6, acrylic, polyurethane, rayon, cotton, and wool, computed from DTA thermograms. They differentiate between combustion in air and fusion and decomposition in nitrogen. A calibration curve of enthalpy per peak area with respect to temperature was used to allow for the increase in the heat capacity of the samples with temperature.

Miller[6] describes a DTA cell specifically designed for filamentous materials in controlled environments. Reproducible packing of textile samples in the sample pan for DTA and differential scanning colorimetric (DSC) studies is often difficult. Due to entanglement and the elastic properties of fiber samples, thermal contact and heat transfer are frequently erratic. In Miller's cell (Figure 1) the fiber is wound around an aluminum cylinder instead of being packed in a pan or cap. It is exposed to the flow of gas, and gaseous byproducts are removed as they are formed. The cylinder may easily be removed to determine residue weights.

Maclean[7] emphasizes, with respect to partially oriented polyethylene yarns, that the crystallization temperature as measured by DTA or DSC reflects differences in crystallization rates and is not a true equilibrium thermodynamic quantity. Maclean shows how the position of the endotherm depends on the degree of orientation of the fiber and the scanning rate of the instrument. Again, these effects are very small in well-designed modern instrumentation but their presence must still be recognized.

III. DIFFERENTIAL SCANNING CALORIMETRY

DSC is often used to measure the thermal behavior of fibers. It is defined as a technique in which the difference between energy inputs into a substance and a reference material is measured as a function of temperature as the substance and the reference are subjected to a controlled temperature program.

Philip[8] used differential scanning calorimetry to characterize a variety of semicrystalline polymeric fibers for purposes of identification. The melting points and heats of fusion were tabulated along with the temperatures of any other thermal transitions. The samples were scanned three times. After the first run they were cooled at 20°C/min. After the second run they were rapidly quenched. The shape of the first fusion endotherm was not always reproducible for a given fiber, probably due to the irregular configuration of the fiber in the sample pan. The first fusion ΔH values were always larger than subsequent ones, probably reflecting a high degree of crystallinity resulting from manufacturing spinning and drawing processes. Annealed nylon 66 exhibits a double melting endotherm. Polyester fibers can be recognized by the presence of a solid phase crystallization exotherm in the 120 to 160°C region following quench cooling. Copolymer polyesters can be distinguished from each other and the regular homopolymer polyethylene terephthalates. Triacetates exhibit a solid phase crystallization on the first and third scans.

DSC thermograms are presented for the above polymers and also for polyolefins, polyvinyls, polyacrylonitriles, and modocrylics. The weight percent of components of blended fibers was calculated from the total weight of the specimen, the heats of fusion of single components, and the ΔH measurements from each endotherm.

IV. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is a widely used thermal analytical technique for the study of textiles. This is understandable when the versatility of the method is considered. TGA is an empirical method, the results of which are highly dependent on experimental parameters. Reproducible data can be obtained only with the same instrument under the same conditions. The method is essentially very simple although the analysis of the data in terms of a specific investigation may be complex. The TGA technique measures the mass of a substance as a function of temperature, while the substance is subjected to a controlled temperature program. Any reaction of the sample that results in a weight change is recorded as weight vs. temperature or weight vs. time. This curve can be differentiated with respect to time, yielding a differential thermogravimetric (DTG) curve as a plot of rate of weight loss vs. sample temperature. A DTG curve allows for more sensitive measurement of small changes in the rate of weight loss that are not readily apparent in the original weight loss curve. A related approach to measuring a change in mass with temperature is reported as follows.

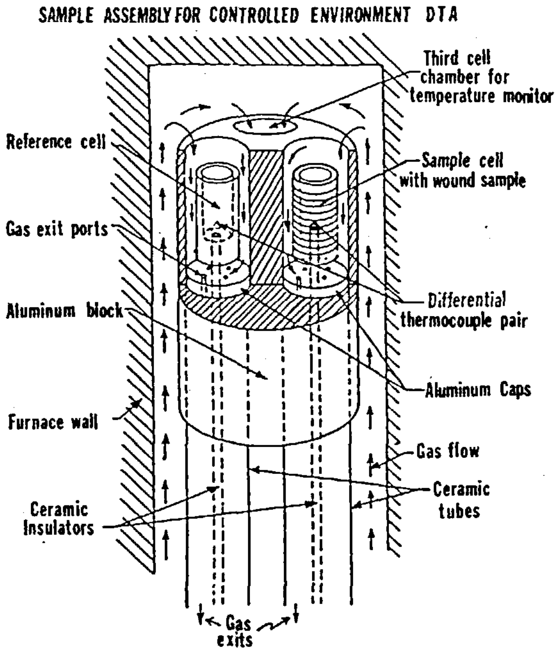

FIGURE 1. Sample holder and furnace assembly for controlled environment DTA. (From Miller, B., *Thermochim. Acta*, 2(3), 225 (1971). With permission.)

McCarter[9] describes an apparatus for measuring the rate at which vapors are evolved during thermal degradation of materials. An inert carrier gas flows across the sample in a furnace through a high temperature zone and into the detector which monitors the mass flow rate of pyrolyzed vapors (see Figure 2). This apparatus yields a measure of reaction velocity. Kinetics of decomposition reactions can be measured from the rate of vapor evolution rather than the weight loss or rate of weight loss as in conventional TGA or DTG. While the differentiation of the TGA curve can be performed manually or electronically, measurement of the rate of vapor evolution is direct and immediate. Detector systems may be designed to be responsive only to specific components of the evolved gases, thus simplifying the resolution of concurrent reactions. Higher rates of pyrolysis may be employed than in conventional methods. The system is simple and flexible in operation and relatively inexpensive.

The relative utility of thermogravimetric analysis as opposed to pyrolysis gas chromatography (PGC) with respect to general textile characterization has been studied and discussed by Crighton.[10] In general, PGC can distinguish between chemically different fiber types more easily than between chemically similar or identical fiber types. Further, operating conditions for PGC are more difficult to reproduce between laboratories than those for TGA, notwithstanding inherent deviations between TGA instruments. With PGC, a pyrolysis temperature must be defined as well as chromatographic conditions suitable for optimum separation of evolved components at that temperature.

With thermogravimetric analysis, the slower heating rate prevents a significant temperature gradient in the sample. The thermogravimetric curve yields the magnitude of a weight loss and the temperature at which it occurs. The broad temperature range scanned allows for the characterization of a broad range of substrates. TGA has been proposed as an easier and more rapid method for determining moisture content in textiles than oven drying or Karl Fisher titrations.[11]

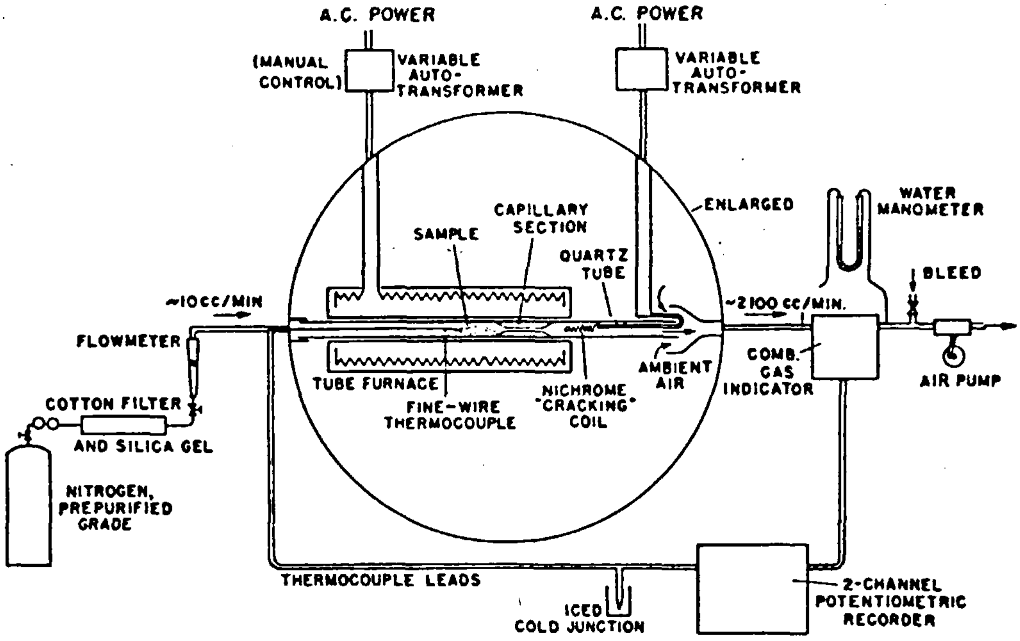

FIGURE 2. Schematic diagram of apparatus for thermal analysis of vapor-producing reactions. (From McCarter, R. J., *J. Appl. Polym. Sci.*, 17(6), 1833 (1973). With permission.)

V. THERMOMECHANICAL ANALYSIS (TMA)

Gill et al. have reported[12] a technique for converting a thermomechanical analyzer from a displacement sensing to a force measuring instrument. First, for measuring fiber tension, a simple load cell with a spring is positioned in parallel with the sample, which can also be considered a spring, such that a given load pushing down is countered by the force of both the sample and the spring. Thus, the thermogram reads tension vs. temperature. Secondly, for measuring stress relaxation, a larger force-constant load cell is placed in parallel with the sample such that the load is greater than that exhibited by the fiber. Stress decay can be monitored directly and the relaxation modulus calculated. This is performed isothermally. This conversion can be carried out rapidly and conveniently.

A dynamic thermoacoustical analytical technique has been reported by Chatterjee[13], and is shown in Figure 3. The time for the propagation of a sonic pulse of constant frequency through a fiber sample is measured with respect to temperature. The fiber sample is held in a temperature programmed device. Molecular transitions which alter the physical or chemical structure of the fiber such that the pulse propagation time is altered show up on the thermogram which records pulse propagation time vs. temperature. Simultaneous DTA and thermoacoustical scans are possible. Thermograms of a variety of synthetic fibers are presented (see Figure 4).

Buchanan and Hardegree[14] discuss thermal stress analysis in terms of basic yarn mechanical properties and concepts of fiber fine structure. Whereas thermal mechanical analysis directly measures change in length with temperature, thermal stress analysis holds the sample fiber at constant length and measures the stress directly as a function of temperature with a load cell. Both the thermal and mechanical history of a sample can be determined. The effects of different draw temperatures and ratios, spin-

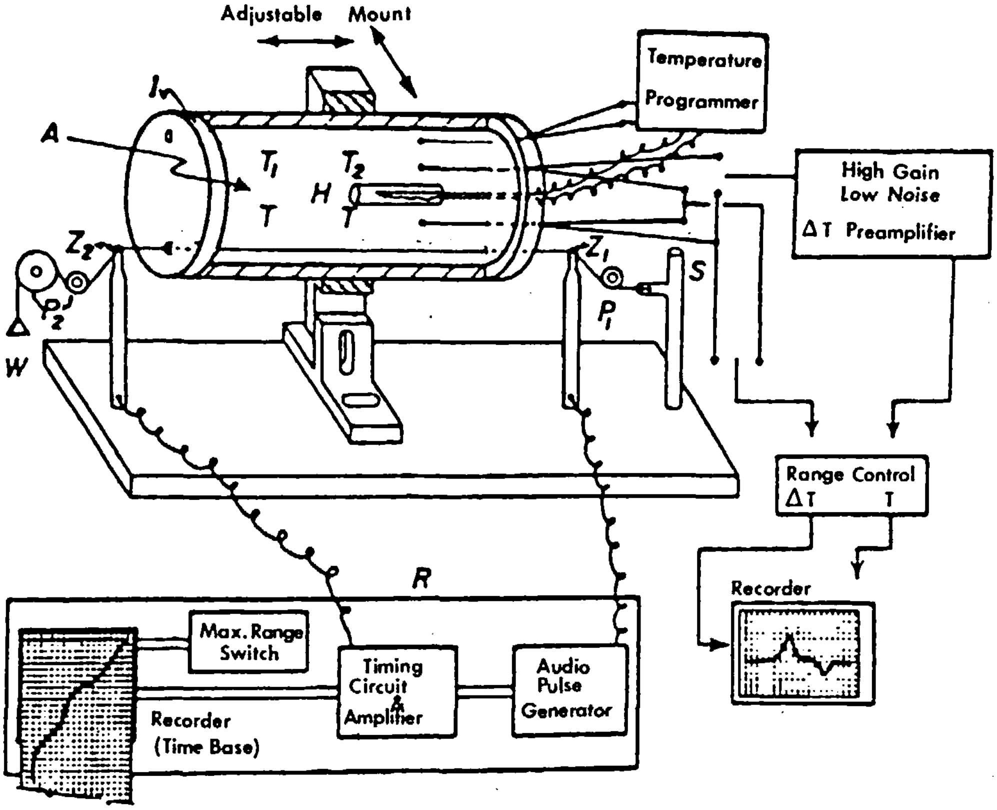

FIGURE 3. A schematic diagram of dynamic thermoacoustical system. (From Chatterjee, P. K., in *Cellulose Chemistry and Technology*, Arthur, J. C., Jr., Ed., ACS Symp. Ser. No. 48, American Chemical Society, Washington, D.C., 1977, 173. With permission.)

ning and texturing conditions, can be observed in the yarn with great sensitivity. In Figure 5, it can be seen that the higher the take-up speed of polyester fiber onto a drum after spinning, the more residual stress remains in the fiber because of more rapid cooling and less time to anneal.

VI. COTTON

A. Cotton and Cellulose

Cotton is a versatile fiber and is frequently blended with synthetic yarns. Many aspects of the thermal behavior of cotton and cotton blends have been studied with thermal analytical techniques. The properties of cotton yarns treated with durable press agents and dyes are commonly studied with these methods.

Sircar and Conrad[15] have investigated the physical and thermal properties of propionylated cotton yarn by DTA, TGA, and mechanical methods. Thermograms indicate that temperature of the onset of significant weight loss decreases, from 235°C for the unsubstituted control, with increasing degree of substitution (see Figure 6). DTA exotherms near 380 and 520°C are probably due to interreactions of cellulose fragments and degradation products.

Miller[16] used DTA and TGA to investigate noncatalytic events occurring during

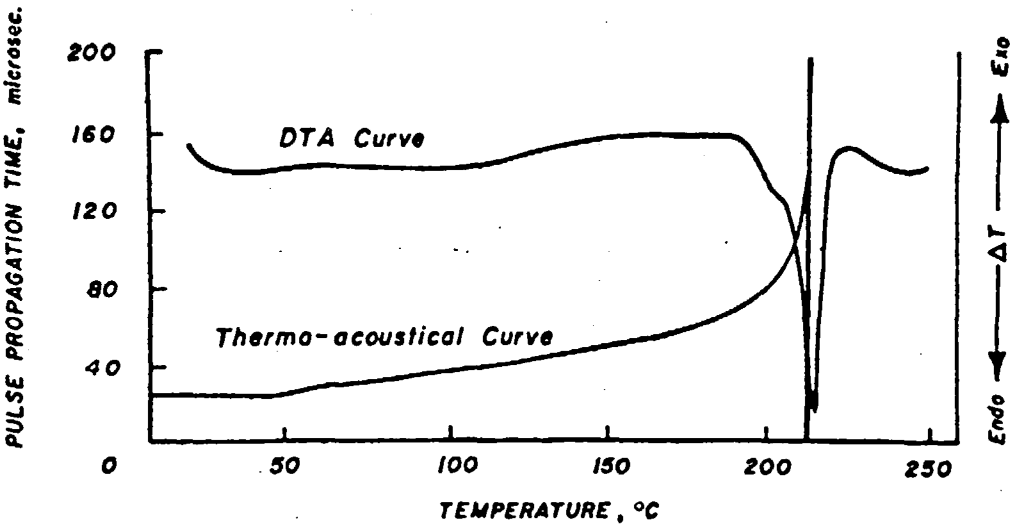

FIGURE 4. Simultaneous DTA and dynamic thermoacoustical analysis of nylon 6,10 in air. (From Chatterjee, P. K., in *Cellulose Chemistry and Technology*, Arthur, J. C., Jr., Ed., ACS Symp. Ser. No. 48, American Cancer Society, Washington, D.C., 1977, 173. With permission.)

heating on cotton treated with acid salts and in particular, zinc nitrate. Acid salts are used as catalysts with various reagents to introduce crosslinks into the cellulose structure of cotton as a durable press treatment. Results vary considerably with the method of packing. However, it is clear that such salts promote exothermic degradation of cellulose at temperatures within the range used in durable press curing. Zinc nitrate alone exhibits endothermic weight loss between 55 and 210°C while decomposing to release $NO_{2(g)}$ and $O_{2(g)}$. $NO_{2(g)}$, a strong oxidizing agent, promotes oxidative exothermic degradation of cotton. An exothermic weight loss is observed near 100°C.

Hobart and Mack[17] have used DSC and DTG to study the reversability of crosslinks in cotton fabric treated with phenyl isocyanate and phenyl carbanilate as durable press agents. DTG was performed in a vacuum both isothermally and dynamically. Kinetic data were obtained from the resulting thermograms. Two decomposition reactions are postulated.

DSC data were analyzed assuming first-order decomposition using the expression $K = Kd/A$ where d is the deviation of the curve from the baseline, A is the amount of peak area remaining between the selected temperature and the higher temperature (where $d = 0$), and K is a constant involving instrumental parameters. From TGA curves, rate constants were calculated using the method of Freeman and Carrol[1] and then the activation energies, enthalpies, and frequency factors as well. Isothermal TGA indicates two concurrent first order dissociation reactions. The first is a rapid *N*-phenylcarbonate decomposition and the second is a slower *N,N'*-diphenylallophonate decomposition beginning near 225°C.

Gilbert and Rhodes[18] have investigated the thermal properties of the reaction products of cellulose and the durable press agents dimethylolurea and dimethylolethyleneurea. Thermograms indicate that the decomposition pattern, an endotherm near 360°C, is not substantially altered by treatment with these agents. Reaction products of these compounds were separately studied. In general, *n*-methylol compounds may crosslink cellulose directly, evolve CH_2O which forms oxymethylene crosslinks, or self-condense to form oligomers that react with cellulose, depending on specific

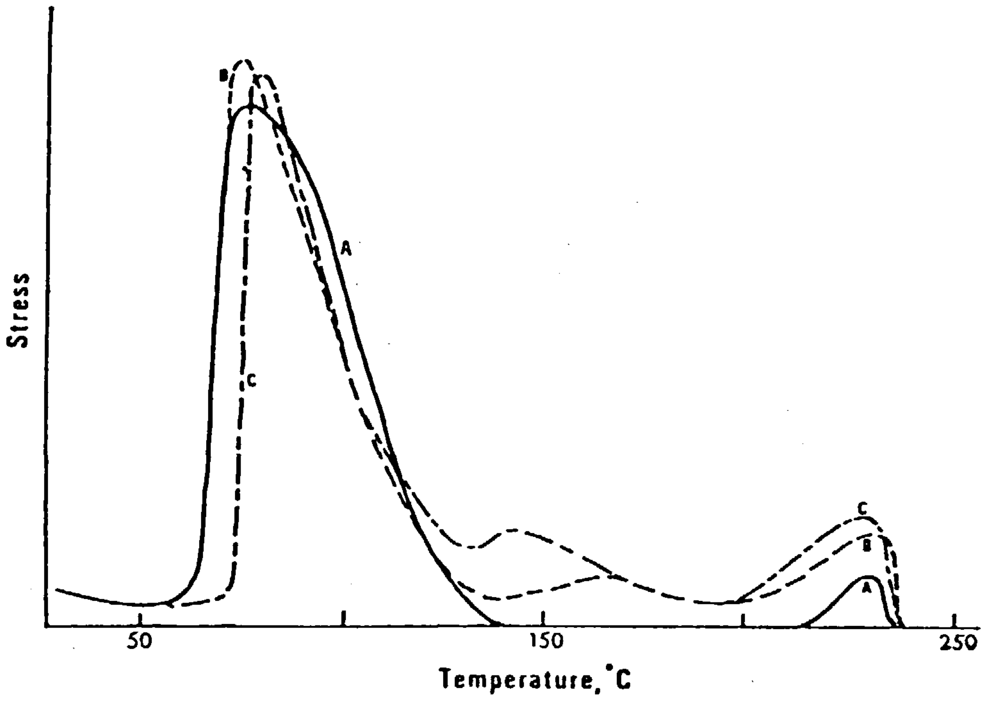

FIGURE 5. Stress-temperature curves for as-spun polyester yarns at spinning take-up speeds of: (A) 45 m/sec; (B) 58.3 m/sec; (C) 61.7 m/sec. (From Buchanan, D. R. and Hardegree, G. L., *Text. Res. J.*, 47(11), 732 (1977). With permission.)

conditions. $MgCl_2$ and $ZnCl_2$ catalyze dimethylolurea polymerization and reaction with cellulose.

Warburton[19] has investigated the reaction of two commonly used durable press reagents, dimethylolethylene urea (DMEU) and dimethyloldihydroxyethylene urea (DMDHEU) with an emulsion copolymer containing 70% methacrylic acid and 30% ethyl acrylate used as a soil release agent. When the two treatments are applied to a fabric in a single step, the soil release characteristics are often inferior to those obtained when a two-step application is used. This apparently occurs when the polymer becomes embedded in a matrix of condensed methylol compound which restricts the swelling necessary for its function as a soil release agent. The soil release properties are longer lasting in the one-step process with respect to laundering. The thermograms of cast films of these compounds were obtained individually and in combination. A discussion is presented on the kinetics and thermodynamics of condensation reactions of *N*-methylol compounds.

At lower temperatures, self-condensation of *N*-methylol reagents to form methylene ether linkages predominates, giving higher temperatures. Above 160°C, esterification reactions can take place with the polymer as well as anhydride formation in the polymer. It is concluded that esterification chemically binds the polymer to the condensed matrix and this is at least partially responsible for the reduced soil-release properties of fabrics cured at higher temperatures.

DeBoer and Borsten[20] observed the extent of hydrogen bonding in stressed and unstressed cotton yarn from DTA thermograms. When cotton yarn is stressed while swollen, there is a subsequent increase in tensile strength.

Varma and Narasimhan[21] obtained the relative thermal stabilities of cotton fiber

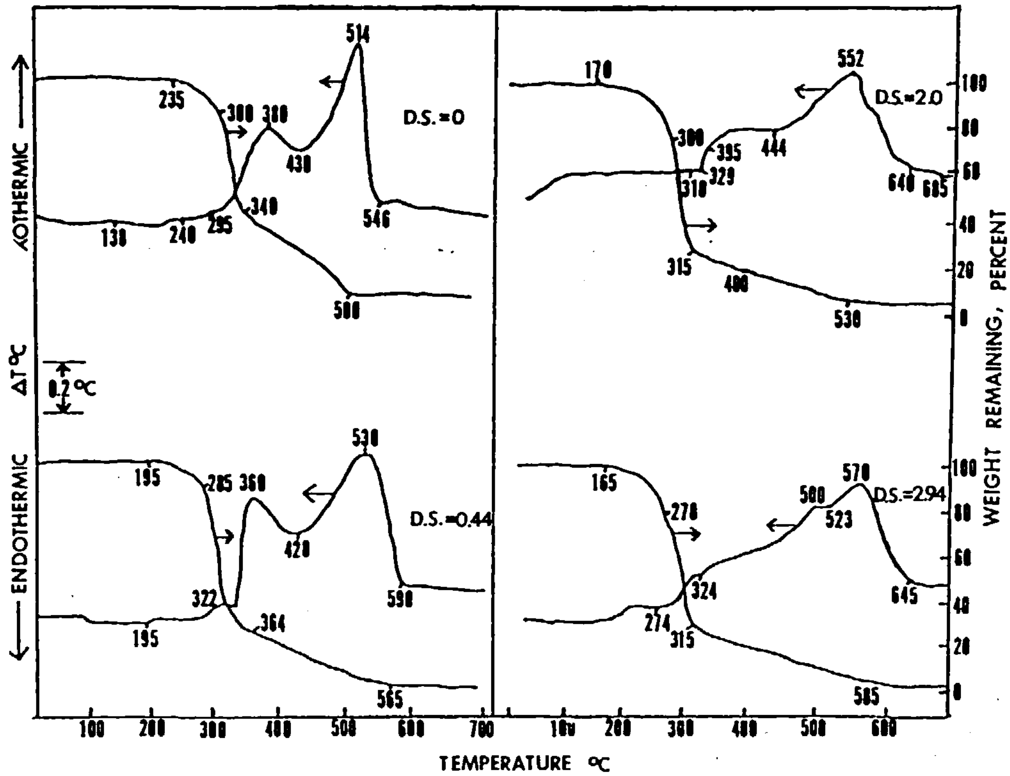

FIGURE 6. Thermographic tracings of propionilated cotton samples. Arrows indicate the ordinate scale to be used with different curves. (From Sirkar, A. K. and Conrad, C. M., *Text. Res. J.*, 38(4), 352 (1968). With permission.)

grafted with various acrylic monomers from thermogravimetric analysis. Their results indicate that thermal stability increases with the extent of grafted polymer and that methyl and ethyl acrylate grafted cellulose is thermally more stable than unmodified cellulose up to about 350°C. Grafts of *n*-butyl acrylate and methyl methacrylate were less stable. Activation energies were calculated for the decomposition reaction in the temperature range 270 to 340°C and shown to correspond to relative thermal stability.

Activation energies are calculated according to the method given by Dharwadkar and Karkhanawala:[22]

$$\ln \ln (1-\alpha)^{-1} = \frac{Ea}{Rti^2}\,\frac{100}{Tf - Ti}\,\theta + C$$

where α is the fraction reacted, Ea is the activation energy, Ti is the temperature of inception of reaction, Tf is the temperature of completion of reaction, C is a constant, R is the gas constant, and θ = (T−Ts), where T is the temperature in question. Ts is the temperature of the point of inflection on the thermogram.

Similar work was reported by Sharma and Daruwalla.[23] Thermograms indicate that the thermal stability of cotton grafted with vinyl monomers increases in the order: acrylonitrile > acrylamide > cotton > methylmethacrylate > methyl acrylate. Activation energies are also calculated and are generally consistent with the above rating.

Rodrig et al.[24] have investigated the influence of crosslinking of formaldehyde on the pyrolytic behavior of natural cotton and manmade cellulose. TGA thermograms indicate that small amounts of crosslinking tend to increase the rate of decomposition while higher degrees of crosslinking have the opposite effect. DSC thermograms show that the temperature of the endotherm near 350°C increases with the degree of crosslinking as do the apparent activation energies.

Basch and Lewin[25] have studied stretched rayon samples differing only in degree of stretch. Vacuum TGA experiments were performed isothermally at 251°C. There is an initial rapid, first-order weight loss followed by a slower reaction. The first reaction is due to dehydration and crosslinking in the less ordered regions. The extent decreases with increasing degree of orientation while the rate increases. The second, slower bulk decomposition reaction is due to chain breaking and the rate also increases with degree of orientation. Both reactions result in char. A greater degree of order yields less char.

Wade and Creeley[26] examined the complex formed by the inclusion of chloroform in cotton cellulose swollen with liquid ammonia using dynamic TGA. This chloroform cellulose complex is stable up to 200°C with the chloroform having the effect of breaking up the highly hydrogen-bonded crystal structure as it is included. This would tend to improve the accessability of cotton cellulose to crosslinking and finishing agents in general.

B. Cotton and Blends — Flammability

Thermal analytical techniques are well suited for examining the effects of dyes and flame-retardant additives on the thermal behavior and flammability of textiles. The bulk of research concerning fabric flammability and flame retardants has been focused on cotton- and rayon-containing textiles since these ignite and burn more easily than most other fibers.

Kasem and Richards[27] discuss many aspects of cotton fabric flammability. In particular, they examine the effects of 23 boron-containing compounds on the flammability and decomposition of cotton, vicose rayon, secondary acetate, triacetate, 65 polyester/35 cotton, and polyvinyl alcohol fabrics. Decomposition patterns were observed from DTA and TGA thermograms while other flammability characteristics such as ease of ignition and char length were measured with standard tests. TGA thermograms indicate that, in general, treated cotton and rayon lose more weight at lower temperatures and less at higher temperatures than untreated fabric.

By inducing decomposition at a lower temperature, flame retardant action is achieved by driving off the more volatile decomposition products below their ignition point (about 320°C for cotton). Then at higher temperatures such action is inhibited. Thus the combustion zone does not get enough fuel to propagate combustion. BF_3 catalytically promotes dehydration of the cellulose and then polymerization of the unsaturated products at higher temperatures, resulting in much more residual char.

Sodium tetrafluoroborate appears to be an effective flame retardant for rayon and cotton fibers at levels near 10% although less effective for other fabrics (see Figure 7). A system for rendering such salts stable with respect to repeated laundering has not been developed.

Hobart and Mack[28] have used TGA and DSC to study the thermal stability of ammonia cured, neutralized, tetrakis(hydroxymethyl) phosphonium hydroxide flame retardant ($THPOH\text{-}NH_3$) on cotton. TGA curves for samples run in nitrogen show loss of moisture near 100°C, intermediate weight loss near 225°C, and finally a large weight loss near 300°C due to cotton decomposition (see Figures 9 and 10). In air there is no weight loss near 225°C, indicating that oxidation of material normally volatile in this region produces a nonvolatile product. Also, a DSC exothem observed near 240°C in

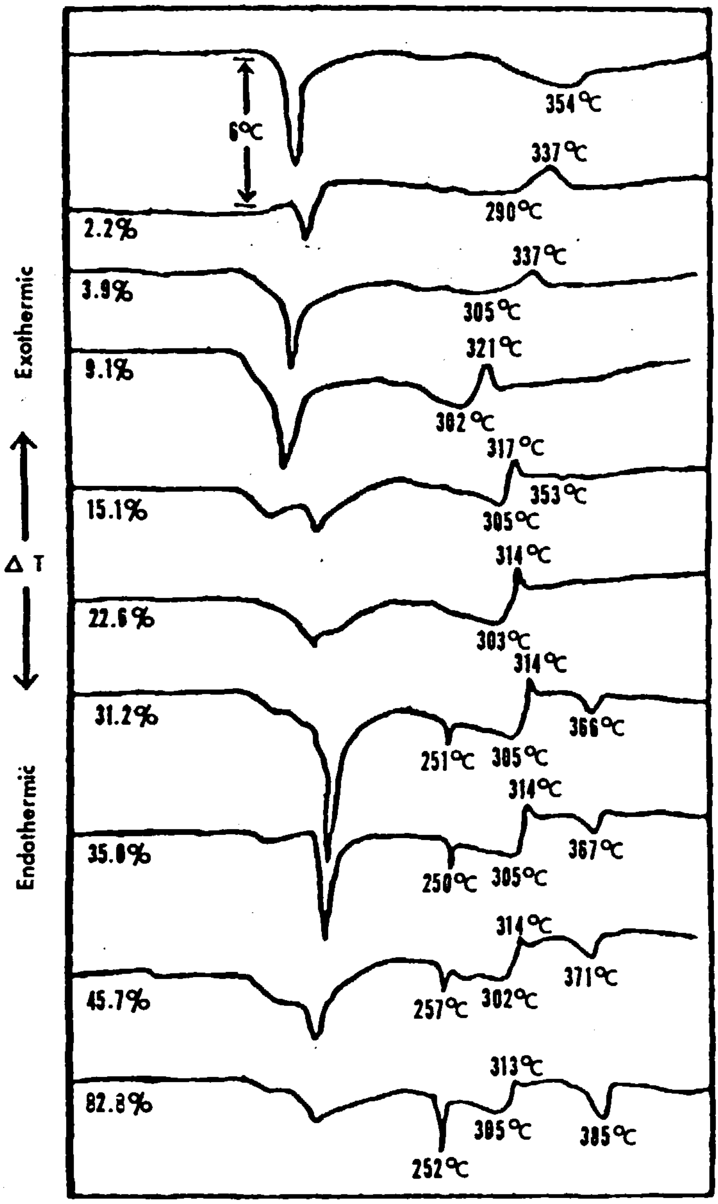

FIGURE 7. DTA thermograms of $NaBF_4$-treated cotton. (From Kasem, M. A. and Richards, H. R., *I & EC Prod. Res.*, 11(2), 14 (1972). With permission.)

nitrogen is absent when the sample is run in air. The decomposition of the treated cotton occurs at a lower temperature than the untreated fibers as with the above-mentioned boron salts.

Bromine is known to be an effective flame retardant for polyester while organophosphorous compounds are effective flame retardants for cellulostic fabrics. Neumeyer et al.[29] undertook a thermogravimetric analysis of polyester/cotton blends treated with tetrakis(hydroxymethyl) phosphonium chloride (ThPc)-urea-poly(vinyl bromide) flame retardant. Samples were heated to 750°C.

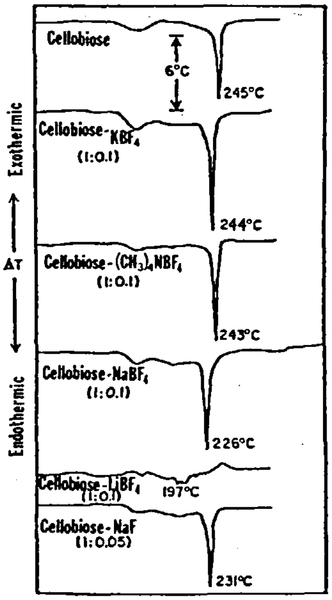

FIGURE 8. DTA thermograms of cellobiosetetrafluoroborate mixtures. (From Kasem, M. A. and Richards, H. R., *I & EC Prod. Res.*, 11(2), 14 (1972). With permission.)

Both the thermal stability and the rate of decomposition for the 100% cotton fabric are lowered when treated with this flame retardant (see Figures 11 and 12). Furthermore, 40% residue remains as char from the treated fabrics as opposed to about 8% from the untreated fabric. The flame retardant has little effect on the temperature or rate of polyester decomposition. In air, the flame retardant again reduces the rate and temperature of cotton decomposition, also eliminating self ignition near 454°C in the untreated fabric. However, the char is almost completely consumed. Polyester decomposition is not greatly affected by the presence of either cotton, flame retardant, or oxygen.

Bingham and Hill[30] also observe that cotton and rayon treated with various flameproofing finishes belonging to the class of *N*-methylolated dialkyl phosphonopropionamides exhibit significant weight loss at lower temperatures than untreated cotton but leave more residual char. From DSC and TG thermograms they observe that both the rate of evolution and the amount of flammable volatites is decreased. Hobart et al.[31] continue with reports on a series of DTA analyses of Thpc-urea-poly(vinyl bromide) treated cotton/polyester blends.

Generally, in nitrogen the fire-retardant treatment alters the 345°C cotton endotherm to a 285°C exotherm, but with little effect on the polyester melting at 250°C and pyrolyzing to a char near 415°C. Both decomposition temperature and rate of decomposition are lowered with addition of the flame retardant. The poly(vinyl bromide) acts on the polyester only in the vapor phase by free radical termination preventing self ignition of char near 490°C (see Figures 13 and 14).

Perkins et al.[32] present a comparison of Thpc-urea-PVBr and THPOH-NH_3 on cotton polyester blends. The latter flame retardant is designed for 100% cotton fabric and is less resistant to repeated laundering.

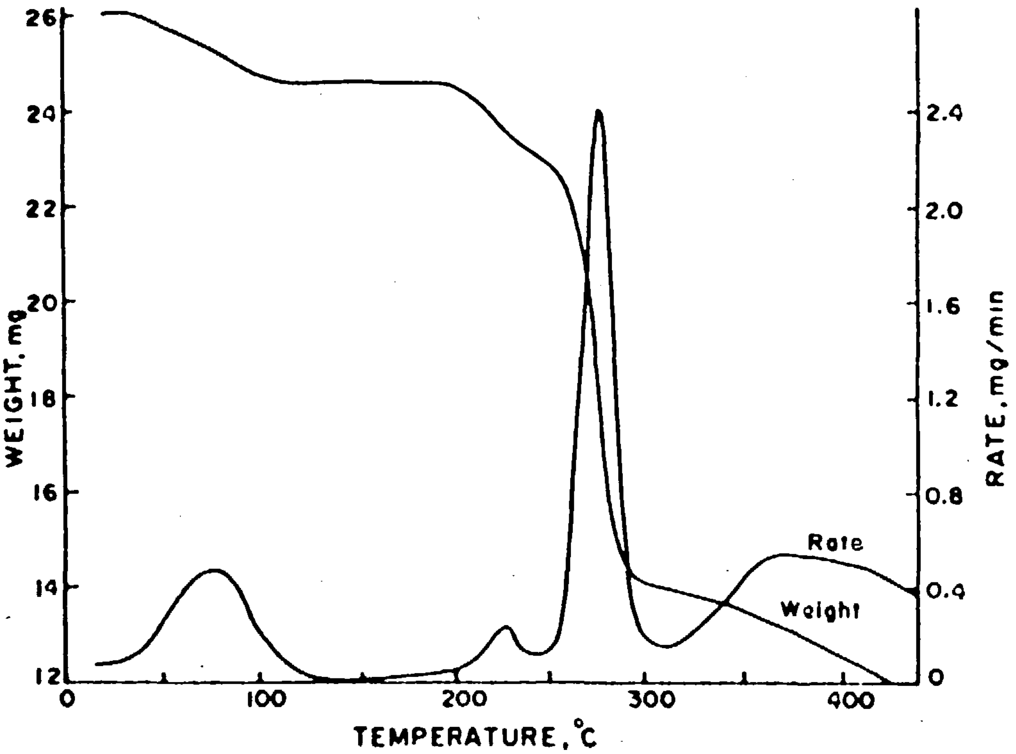

FIGURE 9. TGA curve for THPOH-NH treated cotton sateen in nitrogen. (From Hobart, S. R. and Mack, C. M., *Text. Res. J.*, 45(9), 667 (1975). With permission.)

Miller and Turner[33] discuss a methodology for evaluating the degree of interaction of multipolymer systems undergoing thermal decomposition. The criteria serve as a guide to determine whether or not multicomponent systems are interactive as they decompose at elevated temperatures. For instance, in a noninteracting system, the decomposition temperatures should not change from their respective temperatures when isolated, the kinetics of ignition ought to match those of the faster igniting component, and so on. The components interact to the extent that such parameters change from what they would be in a single component system.

With respect to nylon and cotton blends, the rate of mass transformation is greater than with either single component. DTA thermograms of a 50:50 cotton-nylon blend in nitrogen show an exotherm instead of an endotherm for the cotton decomposition around 350°C when the sample is sealed in a closed pan. In nitrogen, in an open pan, there is the usual endotherm near 350°C. The decomposition of the cellulose is altered by a volatile agent released from the nylon. Evolved gas analysis suggests ammonia. Cotton preheated in a N_2-NH_3 atmosphere yields a very similar thermogram. Evidently cotton forms a compound with ammonia.

VII. WOOL

Wool is a natural material with a complex physical and chemical structure. Consequently, the thermal behavior of wool and wool blends is also complex.

Crighton and Happy[34] and Crighton et al.[35] have characterized several varieties of

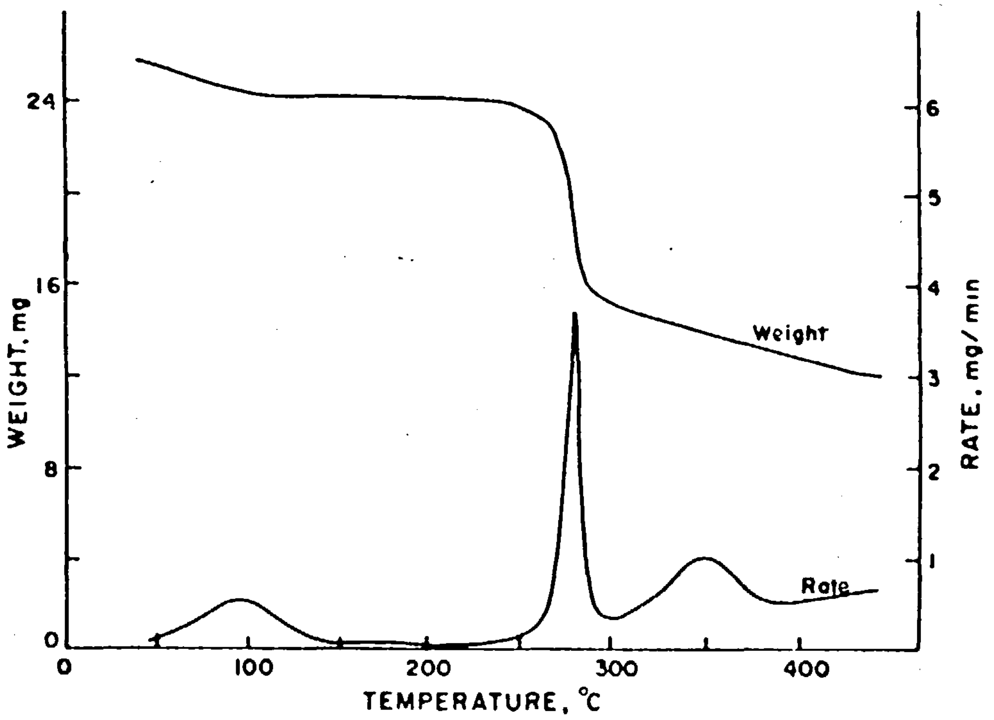

FIGURE 10. TGA curve for THPOH-NH treated cotton sateen in air. (From Hobart, S. R. and Mack, C. M., *Text. Res. J.*, 45(9), 667 (1975). With permission.)

wool by differential thermal analysis. All samples were extracted with ether and alcohol and dried under vacuum. A nitrogen atmosphere was used to differentiate between purely thermal and oxidative reactions. Also, continuous evacuation yielded the most reproducible inert operating conditions by allowing all volatile products to diffuse rapidly from the sample area.

The thermal behavior of wool is sensitive to moisture. Generally, two broad endotherms appear due to water volatilization. A large endotherm appears at around 50°C due to "free" or loosely bound water and a smaller peak appears near 150°C, apparently due to water bound more tightiy at hydrophilic sites with the fiber. These endotherms can be essentially eliminated by holding the samples in the cell isothermally at 150°C for 2 hr before cooling prior to beginning programmed heating at a constant rate. No degradation takes place before 150°C. A second-order transition at 165°C corresponds to the glass transition of amorphous α-keratin.

In the 200 to 250°C region there is an endotherm corresponding to the melting of the α-helical form of wool keratin. This endotherm appears as a doublet with peaks near 220 to 230°C and 230 to 250°C. The low temperature endotherm corresponds to the melting of the paracortical structure of wool while the higher temperature endotherm corresponds to the melting of the orthocortex. The relative sizes of these two endotherms vary with the type of keratin fiber. Human hair, with a relatively high content of paracortex, yields a more prominant low temperature peak while mohair, with a higher orthocortex content yields a more prominant high temperature peak.

Wool previously oxidized with peracetic acid yields much reduced 200 to 250°C endotherms, indicating that these are partly due to disulfide bond cleavage. Further endotherms are observed between 270 and 300°C due to irreversible thermal degradation. Oxidized wool degrades at slightly higher temperatures, indicating an increase in thermal stability.

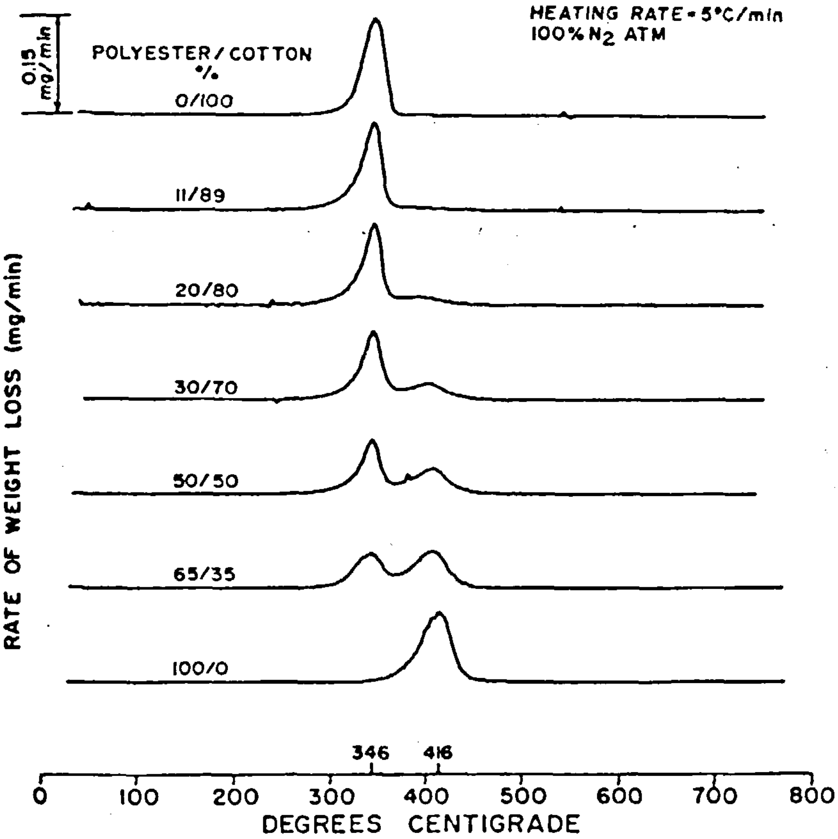

FIGURE 11. DTG of untreated polyester/cotton fabrics. Heating rate 5°C/min in nitrogen. (From Neumeyer, J. P., Wadsworth, J. I., Knoepfler, N. B., and Mack, C. M., *Thermochim. Acta*, 16(2), 133 (1976). With permission.)

Kondo et al.[36] have examined changes in the thermal properties of wool keratin with drawing, using differential scanning calorimetry. The endotherm near 230°C decreases in size when the wool has been drawn. This peak is regenerated when the wool is shrunk after drawing. It appears that these changes may be due to a transition between the α and β chain configuration in wool keratin.

Crighton and Findon[37] oxidized and reduced the cystine crosslinks in merino wool and compared the resulting DTA thermograms with those of untreated wool samples. In both treated and untreated samples there is a general endothermic effect from degradation processes beginning near 200°C. A TG thermogram also shows the degradative weight loss beinning at about 200°C.

Upon reduction with benzyl mercaptan, the α-keratin melting endotherm doublet at 235 and 245°C is reduced to a single smaller peak at about 225°C. Thus, disulfide bridges are implicated in the stabilization of the α-helix configuration in wool keratin. DTA thermograms were also presented of wool keratin after *O*-acetylation, nonspecific acetylation, dinitrophenyletion, and crosslinking with alkali and formaldehyde.

Crighton and Findon[38] have recorded DTA thermograms of treated wool. Also recorded were thermogravimetric curves from the same samples (see Figure 15). Changes in characteristic DTA peaks near 230, 243, 292 and 321°C are tabulated for wool after a variety of oxidative and/or polymeric treatments designed to improve resistance to

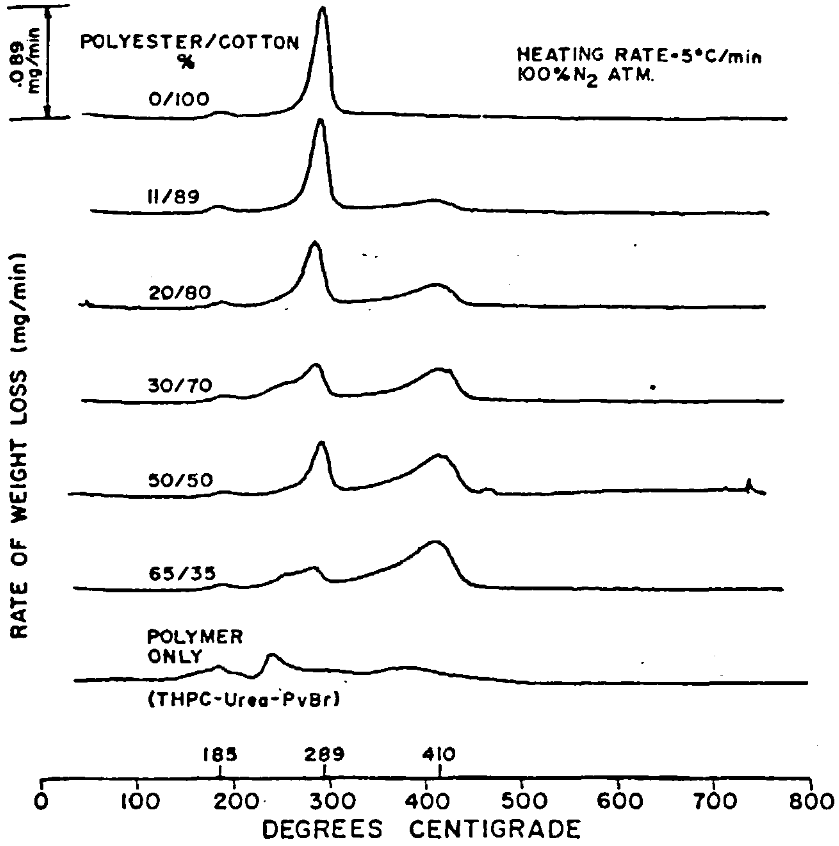

FIGURE 12. DTG curves of polyester/cotton blends treated with THPC-urea-PVBR. Heating rate 5°C/min in nitrogen. (From Neumeyer, J. P., Wadsworth, J. I., Knoepfler, N. B., and Mack, C. M., *Thermochim. Acta*, 16(2), 133 (1976). With permission.)

shrinkage. These authors conclude that DTA is a valuable technique for characterizing wool treatments but that owing to its empirical nature and the complexity of the sample, definitive identification of specific treatments is not possible without supporting information.

Crighton and Holmes[39] have characterized a variety of blends of polyamide fibers with wool, vicose rayon, and cellulose triacetate with DTA. The samples were cut with scissors to 1 2 mm. It was felt that this method of cutting would be less damaging than any kind of grinding or milling. The heating rate was usually 20°C/min until just beyond the last transition, after which was recorded the unprogrammed cooling of the sample in order to observe the polyamide recrystallization exotherm.

Qualitatively, nylon can be observed to be present in blend down to about 10%. Wool can clearly be observed to be present when composing more than 40% of the fiber, depending on the type of blend. Observed transition temperatures are not much affected by blend composition.

Quantitative analysis of wool/polyamide blends was undertaken with the use of a high viscosity silicone gum as a diluent for the fibers. With the use of this diluent, the sample thermal conductivities will all be essentially the same. Consequently, peak areas on the DTA thermograms can be quantitatively used to estimate the concentrations of components in a fiber blend after appropriate calibration with known blends. Semi-

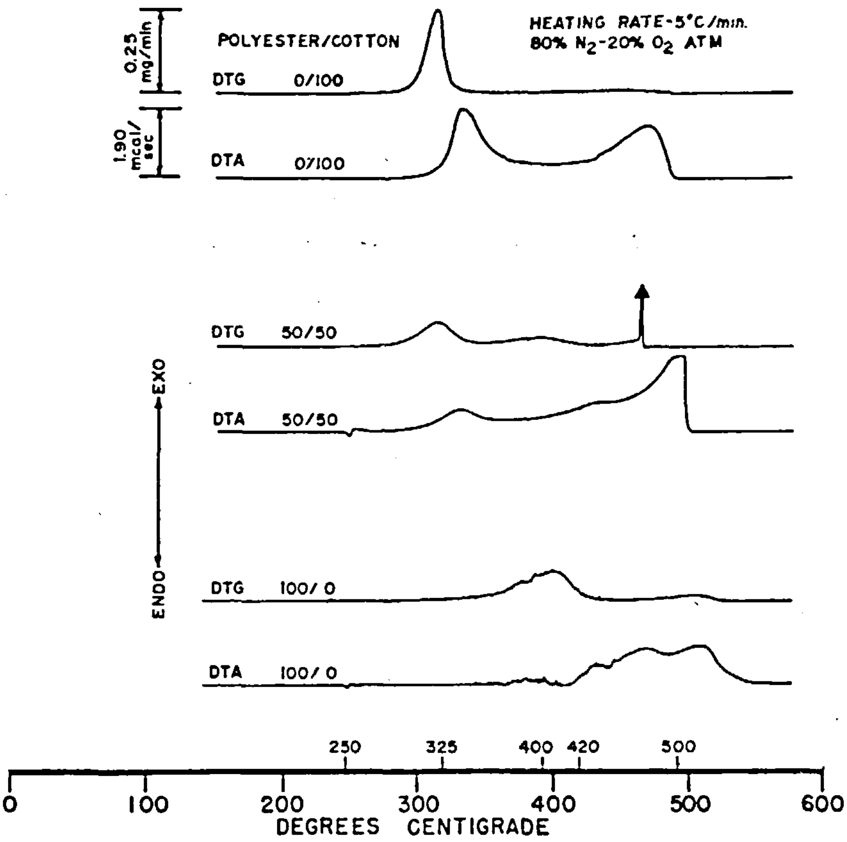

FIGURE 13. Comparison of DTG and DTA curves for untreated polyester/cotton blends in air. (From Hobart, S. R., Mack, C. H., Donaldson, D. J., and Neumeyer, J. P., *Thermochim. Acta*, 16(2), 149 (1976). With permission.)

quantitative assessment of a wool/polyamide blend, suitable for many purposes, can be achieved very rapidly. The technique is applicable to tertiary blend systems.

Haley[40] used a DTA instrument in a specific heat measurement mode to compare wool treated with a shrink-resistant polyurethane coating to untreated wool. Haley notes that above 270°C untreated wool melts to form a foam which inhibits combustion and is partially responsible for the good flame-resistant properties of untreated wool.

Coating of the wool with a shrink-resistant polyurethane material induced an exotherm between 110 and 190°C due to polymer oxidation and reduced the formation of foam. In general, Haley notes that thermalanalysis alone is limited for studies of flame resistance in wool textiles.

Burrell and Crighton[41] have developed a high pressure differential thermal analysis system for the study of aqueous α-keratin systems. Previous DTA studies of wool in the presence of water, where most samples are sealed in ampules, have omitted the measurement of pressure as a variable.

These authors describe a DTA appartus with a cell designed to measure aqueous wool systems to 200°C and 450 lb/in.^{2} (see Figure 16). A variety of wools was studied at different heating rates and pressures. Several endotherms in the normal region of the major water evaporation endotherm can be observed and resolved into doublets

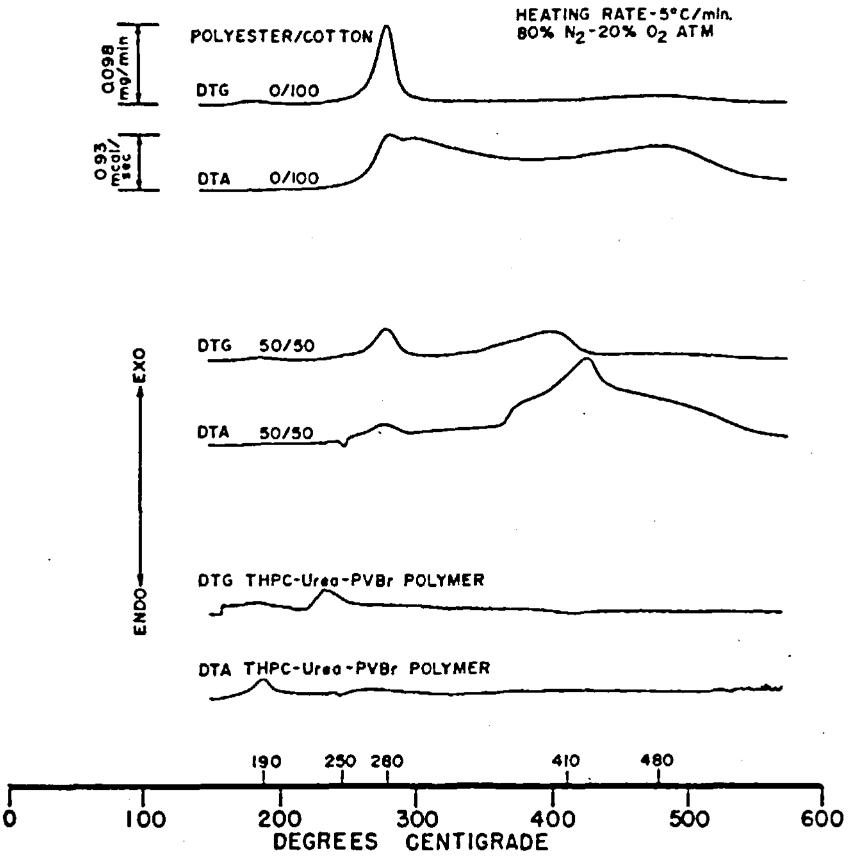

FIGURE 14. Comparison of DTG and DTA curves for flame-retardent treated polyester/cotton blends in air. (From Hobart, S. R., Mack, C. H., Donaldson, D. J., and Neumeyer, J. R., *Thermochim. Acta*, 16(2), 149 (1976). With permission.)

at higher pressure. Also, the temperature of some transitions is quite pressure sensitive. For instance, the 230 and 260°C endotherm doublet observed at one atmosphere can be shifted down to the 140 and 150°C region under 450 lb/in.[2] This versatility allows for better discrimination between overlapping events if one is more pressure sensitive than another.

VIII. SILK

Magoshi et al. reported a series of measurements on the physical properties and structure of silk.[42,43] DSC curves of cast fibers of silk fibroin show the glass transition temperature of amorphous fibroin to be near 175°C. X-ray data indicate that an exotherm near 212°C corresponds to the conformational change from random coil to the β-form crystalline phase. A large endotherm near 280°C involves degradation of the sample.

Further work[44] by these authors and others yielded more detail. Conformational change from the random coil to the β-form occurs in both solid and liquid phase upon treatment with hydrophobic solvents and also with drawing on heat treatment of the solid phase above 190°C.

Figure 17 shows the variations of DSC peak temperatures with scanning speed. Data

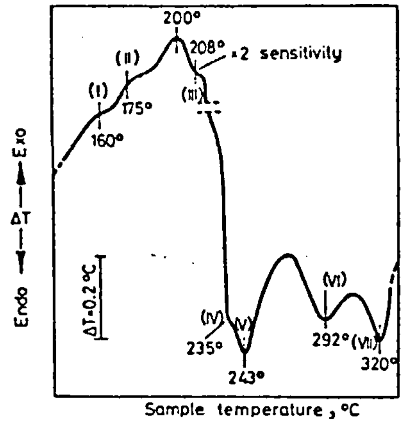

FIGURE 15. DTA of "Standard" Merion wool fiber (continuous evacuation heating rate 20°C/min). (From Crighton, J. S. and Findon, W. M., *J. Therm. Anal.*, 11(2), 305 (1977). With permission.)

from dynamic mechanical measurements, X-ray diffraction, and infrared measurements are also presented.

IX. POLYAMIDES

Hampson and Manley[45] obtained DTA thermograms of latex-treated nylon fabrics. They were able to differentiate among styrene-butadiene, polychoroprene, and natural rubber and quantitatively assess the amount of material deposited.

Anton[46] investigated the thermal response of nylon 6,6 and nylon 6,6/6 (90/10) by DSC as well as by IR and NMR spectroscopy. He discusses a variety of thermal transitions observed from all three techniques. Changes in heat capacity and the glass transition temperature can be observed in DSC traces. Infrared can be used to measure the effect of temperature on specific structural bonds. NMR spectra of drawn nylon 66 show a major relaxational mode from the rupture of interamide hydrogen bonds in the 120 to 160°C range on the general structural mobility of chain segments, a parameter which influences the rate of dye uptake. A good picture of fiber response to temperature may be generated by using thermal techniques in conjunction with others.

Stowe et al.[47] have studied nylon 6,6 yarn exposed to UV radiation. On a DSC thermogram they observed a shoulder at 258°C near the major melting peak at 261°C for irradiated samples. They suggest that chain cleavage has allowed molecules in the amorphous regions to relax into a more ordered configuration.

Buchanan and Walters[48] have determined the glass-transition temperatures, (TG), of 31 polyamide homopolymers and copolymers. The TG temperature is sensitive to relative humidity since water will act as a plasticizer. Saturated rings increase the value of TG in contrast to aliphatic chains which lower it. The crystalline morphology and molecular orientation have a variable effect. Usually greater degrees of crystallinity and order result in a higher value of TG.

Dynamic tensile properties provide perhaps the most sensitive measure of TG but are sensitive to deformation frequency. The TG temperature may be calculated from

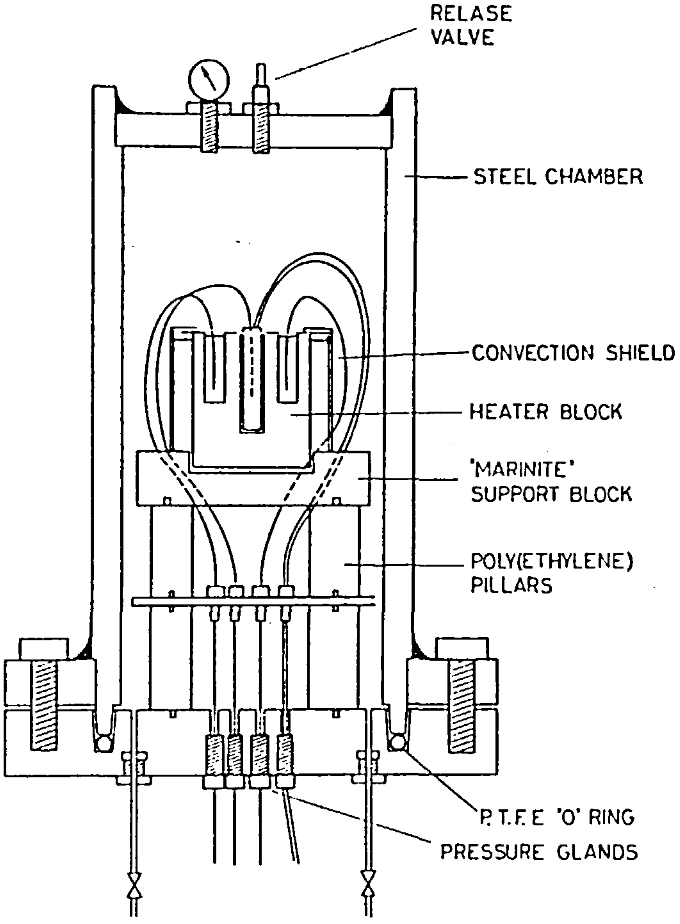

FIGURE 16. High pressure DTA cell. (From Burrell, E. R. and Crighton, J. S., *Therm. Anal. Proc. 4th Int. Conf.*, Hayden, London, 1975, 195. With permission.)

a knowledge of molecular structure, principally the mean spacing between amide groups, and the authors have done so for several polyamide copolymer systems with good results. Many parameters affect the value of TG which should be reported together with the experimental technique and measurement conditions.

Arakawa et al.[49,50] used differential scanning calorimetry to measure the melting points of crystallites in nylon 6 samples with a draw ratio of 3.2:1. The filaments were methoxymethylated for various periods of time in order to prevent reorganization and thickening of the lamellar crystals during heating. The methoxymethylation of the amorphous segments of the nylon prevents further crystallization. Figure 18 indicates that after a sufficient period of methoxymethylation, the actual melting point of the original crystallites in these samples converges on 195°C.

Todoki and Kawaguchi[51] discuss the origin of the double melting peaks in drawn nylon 6 yarns. They also use a technique for inhibiting the reorganization of crystals during DSC measurements.

The samples are irradiated with γ-rays in acetylene gas prior to thermal analysis. The irradiation introduces crosslinks into the amorphous region of the yarn thus preventing its crystallization. The melting curve obtained was similar, in general, to that obtained for methoxymethylated nylon 6 by Arakawa et al.

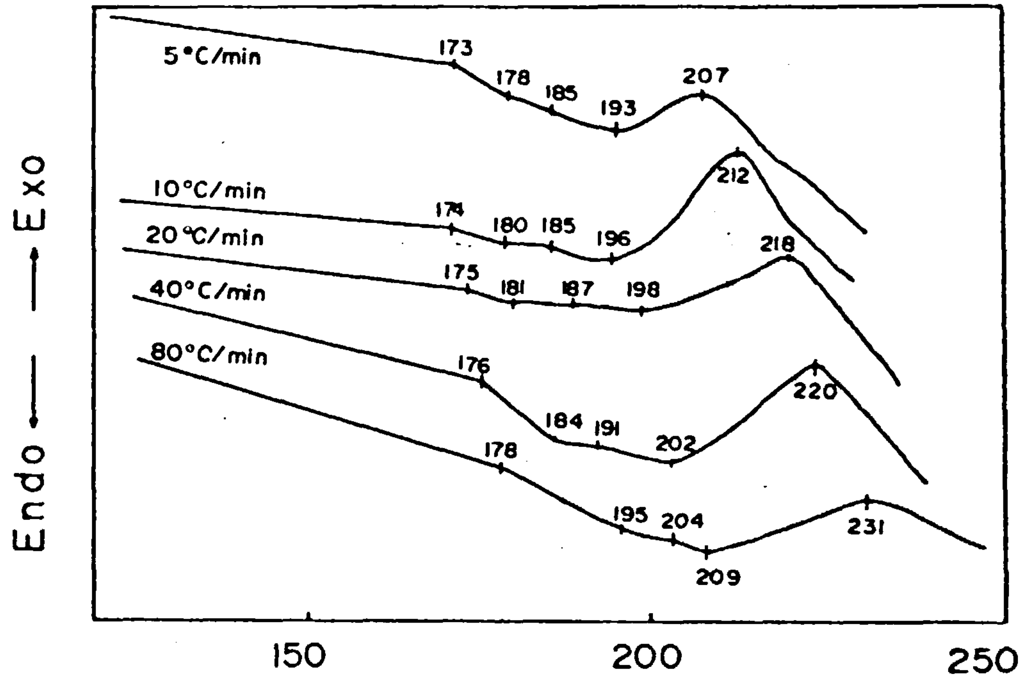

FIGURE 17. DSC curves of silk fibroin in the random coil configuration recorded at heating rates of between 5 and 80°C/min in nitrogen. (From Magoshi, J., Magoshi, Y., and Nakamura, S., *J. Appl. Polym. Sci.*, 21(9), 2405 (1977). With permission.)

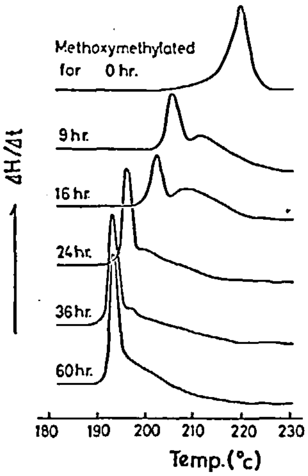

FIGURE 18. Change of the thermogram of drawn nylon 6 heat treated at 170°C with methoxymethylation time. (From Arakara, T., Nagatoshi, F., and Arai, N., *J. Polym. Sci. Part B.*, 6(7), 513 (1968). With permission.)

The authors distinguish between two types of crystalline components and attribute the double melting peak to three successive processes occurring during heating. In the region up to about 210°C, exothermic reorganization or perfection of the crystal I component takes place. Between 210 and 230°C the melting of the crystal I component coincides with the recrystallization into the crystal II component of higher melting point. Above 230°C, the final melting of the recrystallized crystals or the crystal II component occurs.

This study was continued[52] by obtaining DSC thermograms of nylon 6 yarns of different draw ratios constrained to prevent shrinking during heating. A piece of fine wire was attached to each end of a weighed sample and then the sample was wound around a small aluminum plate with the wires secured to prevent shrinking. The sample was then encapsulated in a standard DSC sample pan. Thermograms were also obtained of unconstrained samples of different draw ratios both irradiated and unirradiated.

Constrained yarn only exhibits a single melting peak, apparently due to perfection of the original crystals and subsequent monotomic melting of them with no opportunity for recrystallization. For unconstrained samples, the melting temperature is almost independent of draw ratio, i.e., crystal orientation. The melting temperature of constrained samples increases linearly with draw ratio. Also, constant length annealing causes no change in degree of crystal orientation, whereas tensionless annealing causes a decrease in degree of crystal orientation with increasing annealing temperature.

The melting temperature of constrained samples is strongly affected by the degree of orientation of the sample and almost independent of the degree of perfection of the crystals. Irradiated samples annealed at 230°C and then constrained for DSC analysis show two peaks at 220 and 231°C due to recrystallized randomly oriented crystals and the surviving oriented crystals, respectively. Thus this technique may be useful for detecting inhomogeneous orientation of crystals.

The authors explain that the crystals in nylon 6 act as crosslinks in the oriented polymer and allow for a temporary decrease in entropy with increasing temperature under constraint, as with an elongated crosslinked rubber. As the last segments melt, these crosslinks disappear, resulting in a sudden entropy increase. The overall result is a kind of superheating effect allowing crystal segments to exist even above the equilibrium melting point.

X. FIRE-RESISTANT AND HIGH-STRENGTH FIBERS

Bingham and Hill[53] surveyed three main groups of flame-resistant fibers. They present DSC and TG thermograms for treated cellulostic materials, chlorine-containing materials, and high-temperature-resistant materials, generally polyamides.

The chlorine-containing fibers examined are Leavil® and Clevyl®, both 100% polyvinyl chloride; Teklan®, a copolymer of polyacrylonitrile and polyvinylidene chloride; Acrilan®, a polyacrylonitrile fiber; a modified Acrilan® with flame retardent, and polychlal, a polyvinyl chloride/polyvinyl alcohol fiber. These all exhibit thermogravimetric traces that indicate a two-step degradation process. The first rapid weight loss corresponds to the elimination of hydrogen chloride gas, generally near 280°C. At 310°C Acrilan® releases hydrogen cyanide gas. The release of these gases inhibits combustion. The second degradation step at higher temperature corresponds to decomposition of the fiber structure. Combining Leavil® with wool or flax increases the temperature of the second degradation step, probably because of endothermic reactions occurring in these natural fibers opposing the exothermic degradation of the Leavil® fiber. The following third category fibers all stand out in terms of exceptional thermal stability.

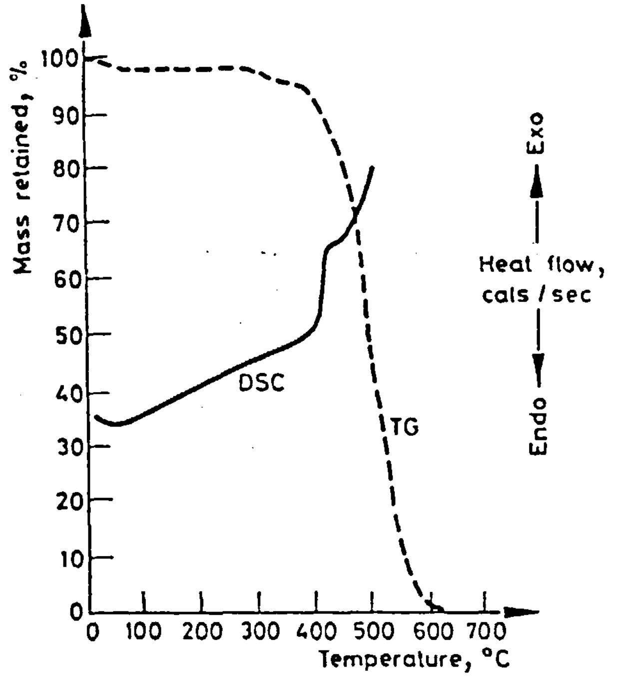

FIGURE 19. DSC and TG traces of Durette® in air. (From Bingham, M. A. and Hill, B. J., *J. Therm. Anal.*, 7(2), 347 (1975). With permission.)

DSC and TGA thermograms of the polyamidimide Kermel® and the crosslinked and chlorinated aromatic polyamide Durette® show no significant degradation below 400°C (see Figures 19 and 20). The aromatic polyamide Nomex® and the phenol-formaldehyde Kynol® also exhibit excellent thermal stability starting to degrade at 410 and 370°C, respectively. (See Figures 21 and 22.) Polybenzimidazole (PBI) begins to degrade near 500°C and is the most thermally stable fiber examined by these authors.[53]

In a subsequent paper[54] the same authors rank several of these high-temperature-resistant fibers using a manikin fitted out with temperature sensors, dressed in the appropriate material and exposed to flame. The fabrics are rated in terms of the number of seconds of such exposure required to raise the skin temperature above 45°C.

Using a thermobalance, the same fabrics were rated according to thermal stability at heating rates of 5°C/min, 100°C/min, and also heated rapidly to a temperature between 400 and 1000°C and held there isothermally. A good degree of correlation was observed between the relative thermal stabilities in the isothermal thermogravimetric tests with the former flame tests. This allows for greater confidence in correlating flammability tests with thermogravimetric behavior of fabrics.

The thermal behavior of Nomex® Kevlar® 29, and Kevlar® 49 high-performance fibers was studied in detail by Brown and Ennis.[55] Nomex® is poly(1,3-phenylene isophthalamide). Kevlar® 29 is poly(*p*-benzamide), and Kevlar® 49 contains structural poly(1,4-phenylene terephthalamide).

TA curves show Kevlar® 49 melting at 560°C and decomposing at 590°C. There appears to be a glass transition near 300°C observed as a exothermic shift in baseline (see Figures 23 and 24). Rapid contraction of Kevlar® 49 occurs above 400°C in air but not in nitrogen as seen from isothermal TMA experiments at 400°C. Thus, this contraction is associated with oxidation. Rupture was brittle with no signs of softening.

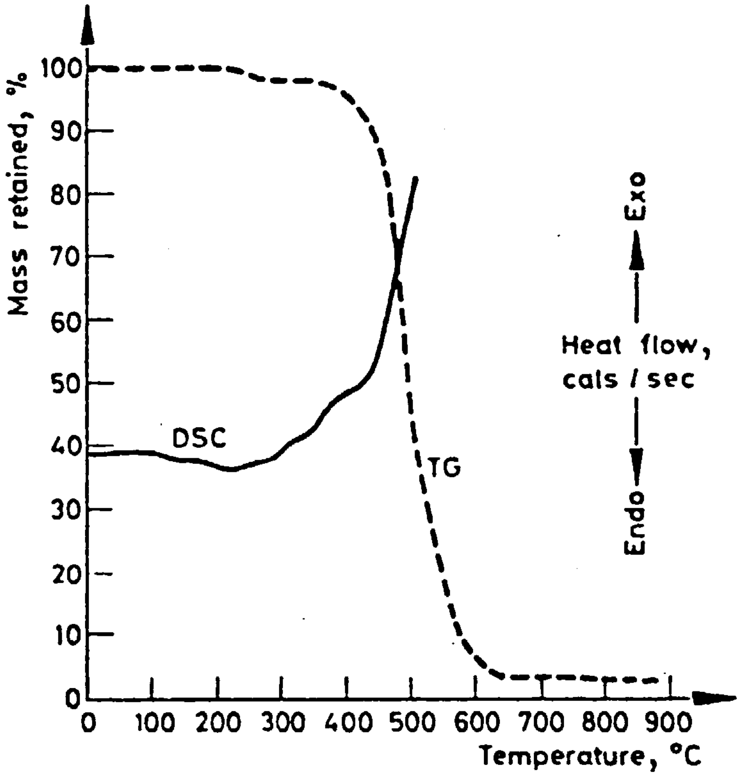

FIGURE 20. DSC and TG traces of Kermel® in air. (From Bingham, M. A. and Hill, B. J., *J. Therm. Anal.*, 7(2), 347 (1975). With permission.)

DTA curves of Nomex® show a change in baseline near 320°C and a decomposition endotherm near 440°C but no evidence of melting. TMA curves for Nomex® (Figure 25) show a positive coefficient of expansion below the TG value in contrast to the negative coefficient of expansion below the TG value for Kevlar® 49.

Chatfield et al.[56] discussed the thermal behavior of Durette®, a chlorinated aromatic polyamide. From TGA thermograms, decomposition of Durette® appears bimodal (see Figure 26). The first degradation step beginning near 370°C is a thermal one, independent of environment while the second is oxidative. In oxygen, flaming was observed near 450°C. Evolved gas analysis was also undertaken with a summary of volatile products presented. Significant amonts of hydrogen cyanide, acrylonitrile, benzene, and other toxic gases are released.

A qualitative and quantitative analysis of all degradation products was undertaken as a basis for further mechanistic studies pertaining to polymer thermal decomposition as well as for animal bioassay experiments for estimating toxicological hazards to humans during fire exposure. The authors repeated this study[57] for Nomex®, a nonhalogenated aromatic polyamide. The thermal behavior is very similar with thermal degradation beginning near 375°C and oxidative degradation beginning near 475°C, consuming the fabric and leaving no char. DTA thermograms are very similar for Nomex® and Durette® with the exotherm for Durette® about 30°C higher (see Figure 27).

XI. POLYESTERS

Berndt and Bossmann[58] have analyzed heat-set poly(ethylene terephthalate) (PET)

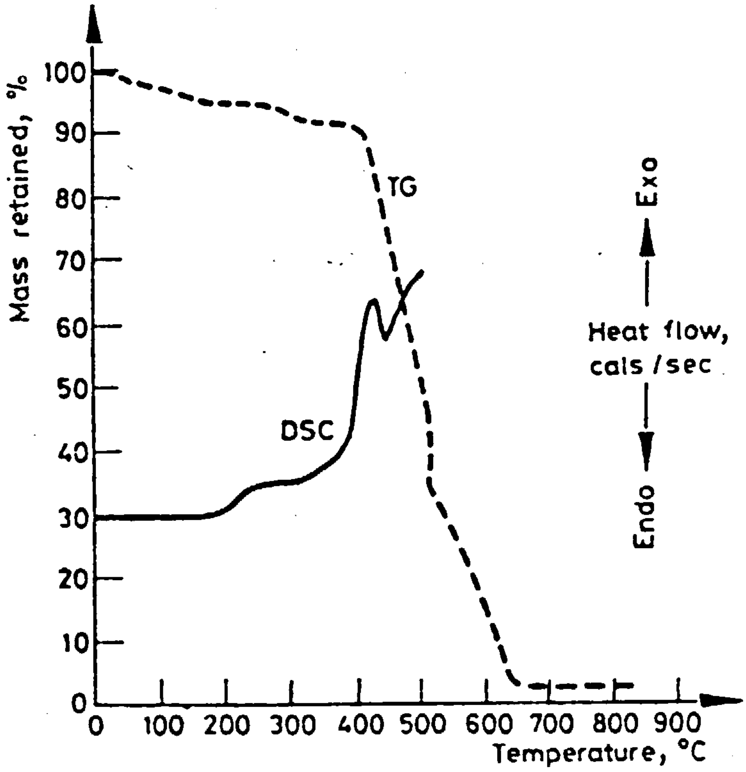

FIGURE 21. DSC and TG traces of Nomex® in air. (From Todoki, M. and Kawaguchi, T., *J. Polym. Sci. Phys. Ed.*, 15(9), 1507 (1977). With permission.)

fibers using DTA. PET samples were heat treated for times varying from 0.2 sec (e.g., analogous to false twisting) to 4 hr (e.g., analogous to heat setting of heavy technical fabrics) and the feasibility of DTA for defining the thermal history of the fabrics, as produced under ordinary commercial thermal processing, was studied.

The change in the shape of the endotherm and peak the temperature with heating rate (Figure 28) is indicative of a reorganization taking place during scanning which is a rapid process relative to the rate of heating. An explanation can be found in the theory of Zackman and Stuart[50] who found that less perfect crystals that are formed at lower temperatures partially melt and recrystallize upon heating. At higher heating rates, the rate of melting exceeds the rate of recrystallization which increases the temperature of the partial melting endotherm with the crystals melting at a higher temperature.

The maximum of the small partial melting endotherm observed prior to the major melting endotherm, as in Figure 29, is directly related to the setting temperature and is defined as the effective temperature, Teff. The endotherm of a thermal process is replaced by that of a subsequent process with a higher effective temperature. A hydrothermal treatment for a given time interval causes a higher heat setting effect on PET than hot air does because of the greater thermal conductivity. In addition, the effective temperature increases with the dwell time of the thermal treatment. Consequently, the overall intensity of a thermal treatment should be characterized by the effective temperature indicating changes in the state of order in the polymer rather than the machine temperature of the treatment.

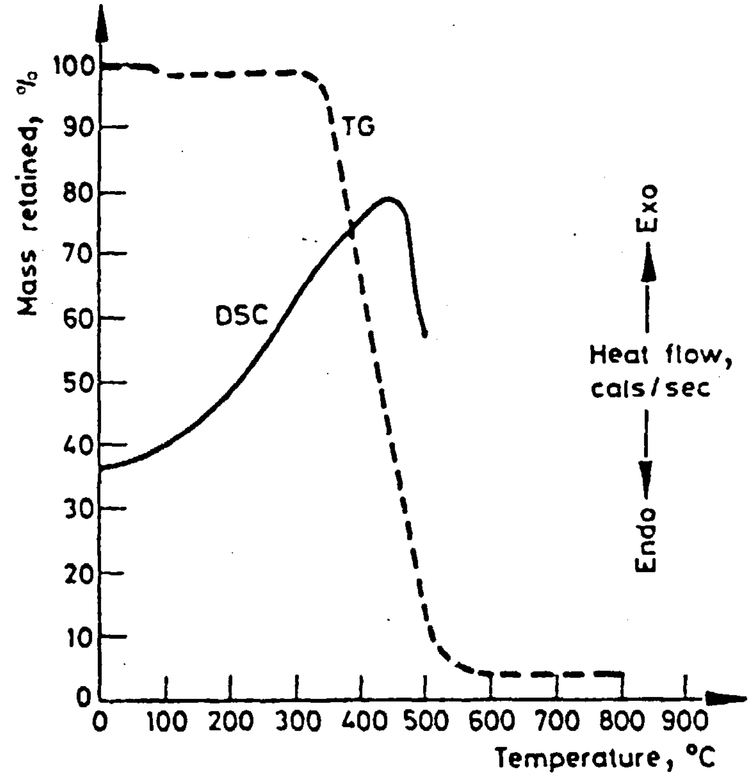

FIGURE 22. DSC and TG traces of Kynol® in air. (From Bingham, M. A. and Hill, B. J., *J. Therm. Anal.*, 7(2), 347 (1975). With permission.)

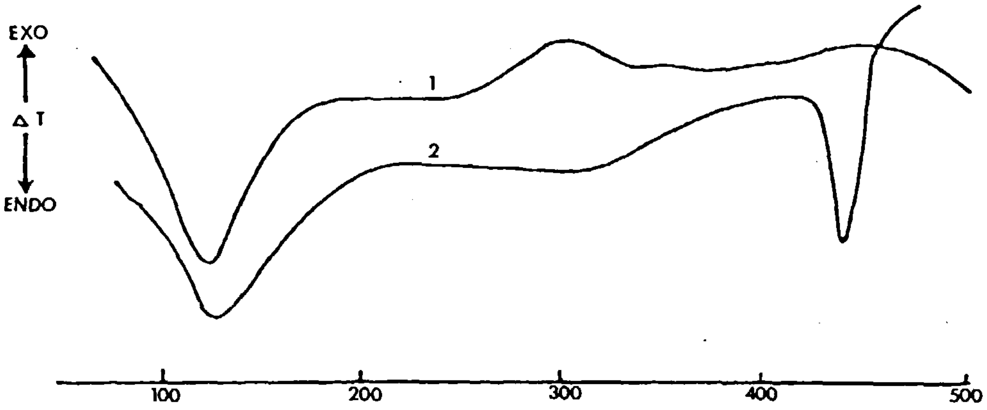

FIGURE 23. DTA curves for Nomex® and Kevlar® 49 in air, standard cell. (1) Kevlar®, 20°C/min; (2) Nomex®, 20°C/min. (From Brown, J. R. and Ennis, B. C., *Text. Res. J.*, 41(1), 62 (1977). With permission.)

Oswald et al.[60] have contributed to the investigation of the middle endotherm of thermally treated, drawn PET yarns. From thermal, mechanical, and X-ray data, the authors discuss a mechanism for this phenomena. In general, tensile properties of fi-

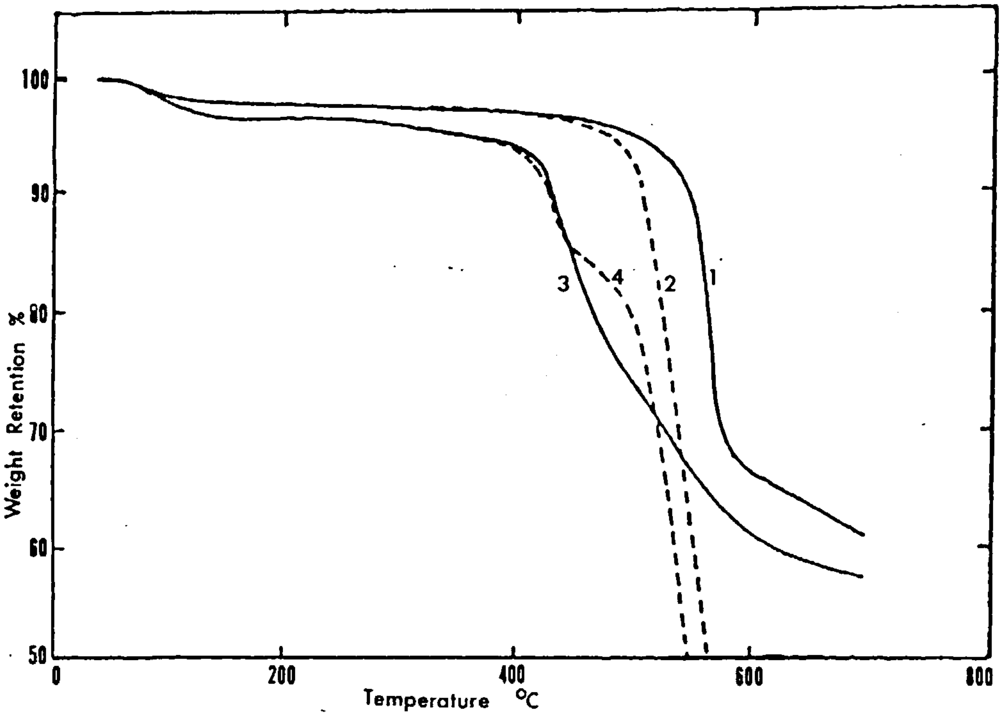

FIGURE 24. TG curves for Kevlar® 49 and Nomex® in air and nitrogen. (1) Kevlar® 49 in nitrogen; (2) Kevlar® 49 in air; (3) Nomex® in nitrogen; (4) Nomex® in air. (From Brown, J. R. and Ennis, B. C., *Text. Res. J.*, 41(1), 62 (1977). With permission.)

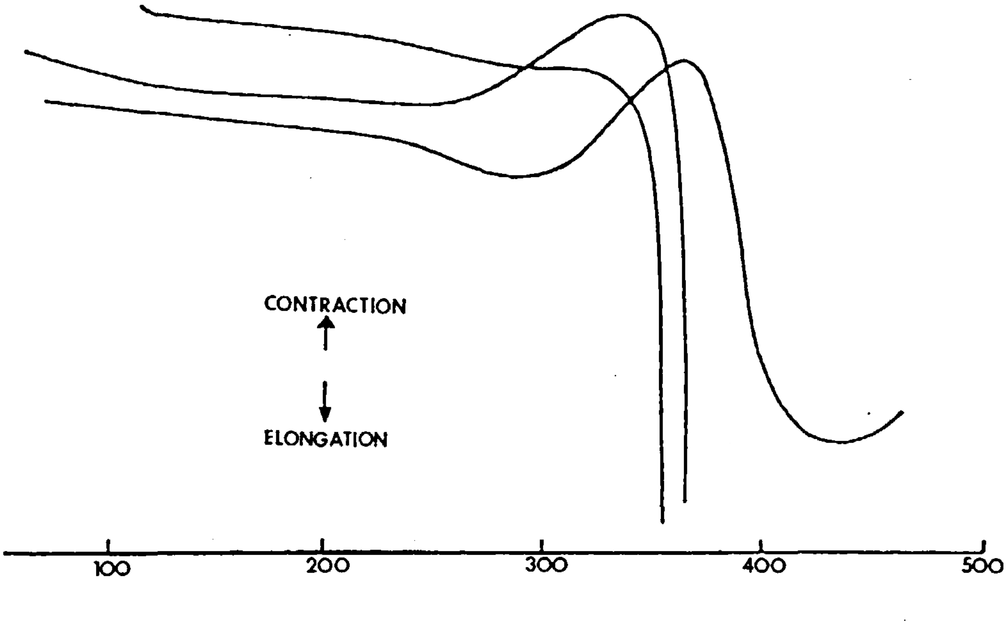

FIGURE 25. TMA curves for Nomex® in air. (From Brown, J. R. and Ennis, B. C., *Text. Res. J.*, 41(1), 62 (1977). With permission.)

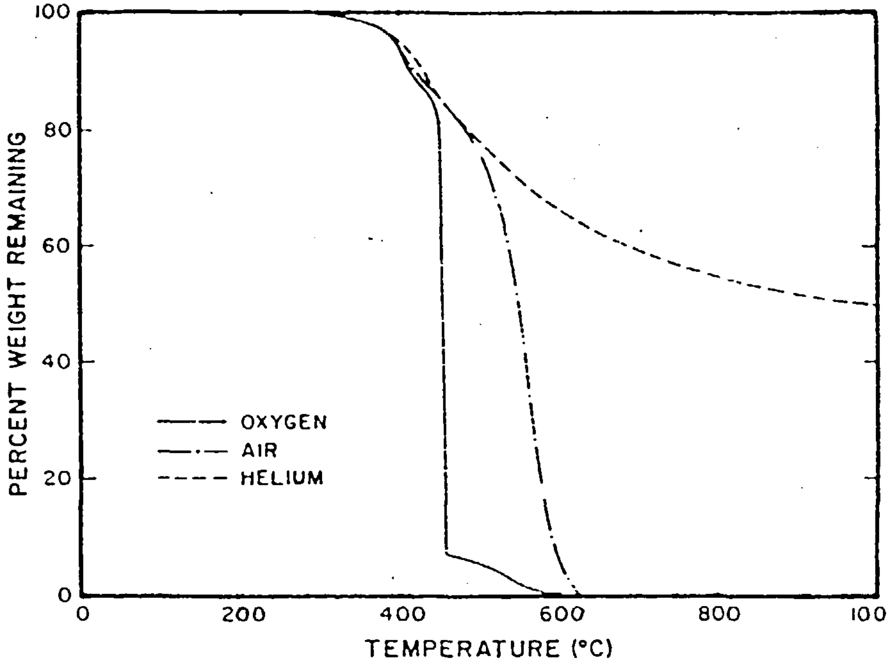

FIGURE 26. The effect of environment on sample weight loss for the chlorinated polyamide, Durette®, at a heating rate of 10°C/min. (From Chatfield, D. A., Einhorn, I. N., and Mickelson, R. W., *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Pap.*, 36(2), 604 (1976). With permission.)

bers heat treated at any given temperature below 220°C reach final equilibrium values within 1 sec of exposure, while DSC thermograms show a gradual alternation of the middle endotherm over much larger time intervals. Apparently, two opposing processes are occurring.

With the initial release of strain just beyond the glass transition temperature, the densely packed, highly oriented amorphous regions tend toward disorientation and higher entropy resulting in shrinkage of the fiber. However, the increased segmental mobility also allows for the formation and growth of crystalline nuclei in this same region, thus decreasing the enthalpy of the system.

Both the onset of shrinkage and the formation of nuclei occur rapidly at temperatures just above the TG temperature, and the nuclei would, in effect, crosslink the extended amorphous chains before complete disorientation can occur. Subsequent exposure time to thermal treatment promotes an increase in the size and/or perfection of the small crystallites, thus increasing the peak temperature of the middle endotherm. Thus there is an equilibrium between internal strain and the tendency to form more perfect crystallites. The behavior of the fiber is largely determined by the degree of order in these highly oriented amorphous regions.

Weigmann and Lamb[61] have exmined the effects of various rubber-curing systems involving amines, as are encountered in the manufacture of automobile tires, on polyester yarns at elevated temperatures. DTA thermograms demonstrate the formation of complexes of ZnO, stearic acid, and several accelerators at different temperatures. These complexes have lower thermal stability than the accelerators themselves and release amines at lower temperatures.

McGregor et al.[62] have studied thermomechanical measurements on conventional

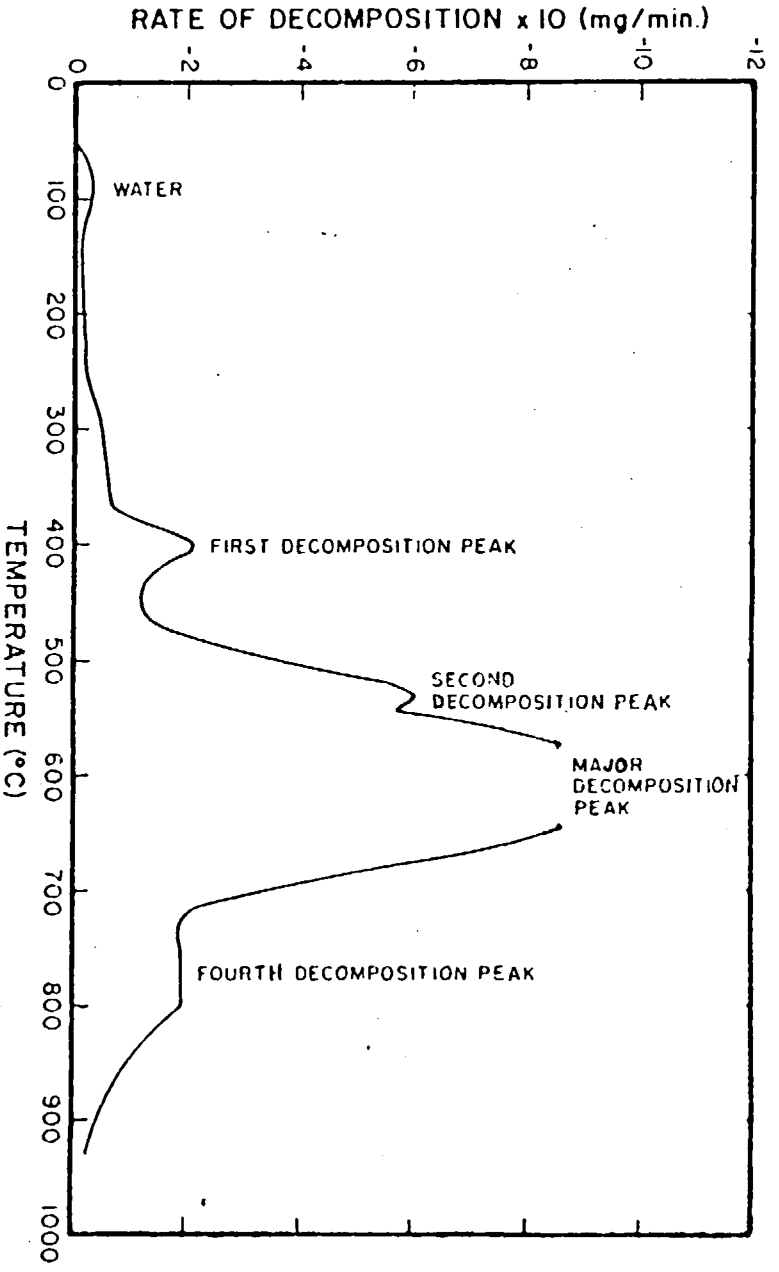

FIGURE 27. Differential thermogram of the decomposition of the aromatic polymer Durette® at a heating rate of 5°C/min. (From Einhorn, I. N., Chatfield, D. A., and Mickelson, R. W., *Am. Chem. Soc. Div. Org. Plast. Chem. Pap.*, 36(2), 588 (1976). With permission.)

false-twist, pin-textured polyester yarns. Each thermomechanical response curve was analyzed in terms of eight parameters, which were expressed in eight normalized regression equations in terms of seven experimental and instrumental parameters. The eight TMA parameters are correlated with a variety of other textured yarn properties includ-

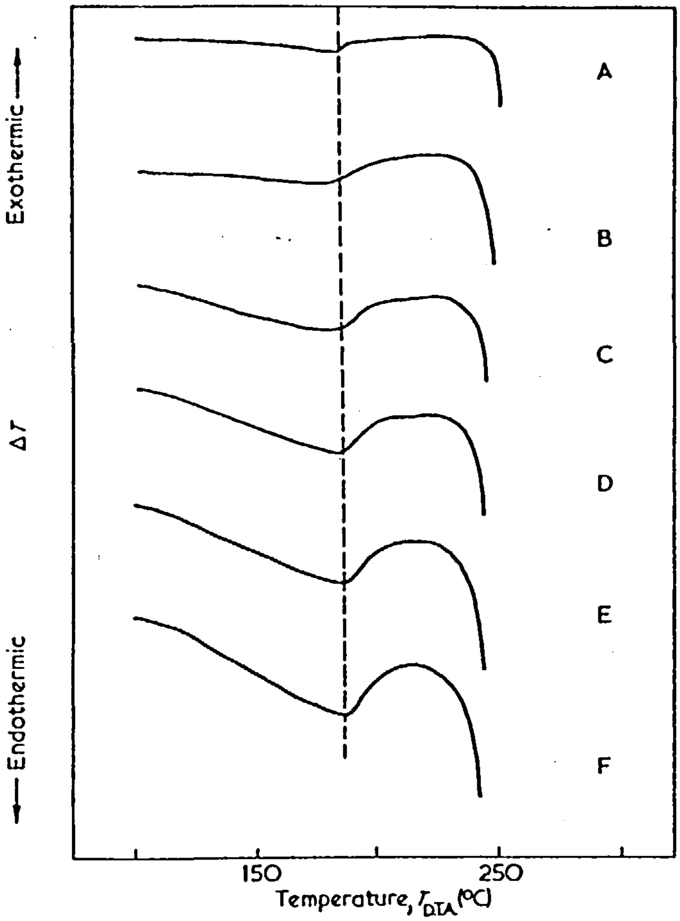

FIGURE 28. DTA traces of PET fibers heat set at 180°C for 20 sec; DTA heating rates (°C/min). (A) 5, (B) 10, (C) 15, (D) 20, (E) 25, (F) 30. (From Berndt, H. J. and Bossmann, A., *Polymer,* 17(3), 241 (1976). With permission.)

ing response to dyes. The possibility is suggested of using specific patterns of TMA parameter responses to detect textured yarn faults, to aid in textured yarn quality control, and possibly to predict textured yarn dyeability.

Quyun[63] has reported a table of birefringence vs. crystallization exotherm temperature for PET homopolymer yarn. As the yarn is oriented in the spinning process thus increasing the birefringence, the temperature of the crystallization exotherm decreases. This latter is indicative of the adhesive behavior of one filament to another on a solid surface. The adhesive tendency of the yarn decreases with the decrease in the crystallization exotherm.

XII. ACRYLIC FIBERS

Layden[64] has reported the melting points for methyl methacrylate-polyacrylonitrile copolymers. He observed an endotherm just below the major decomposition exotherm near 340°C. The onset of melting occurs near 320°C for fibers containing 2.8% MMA

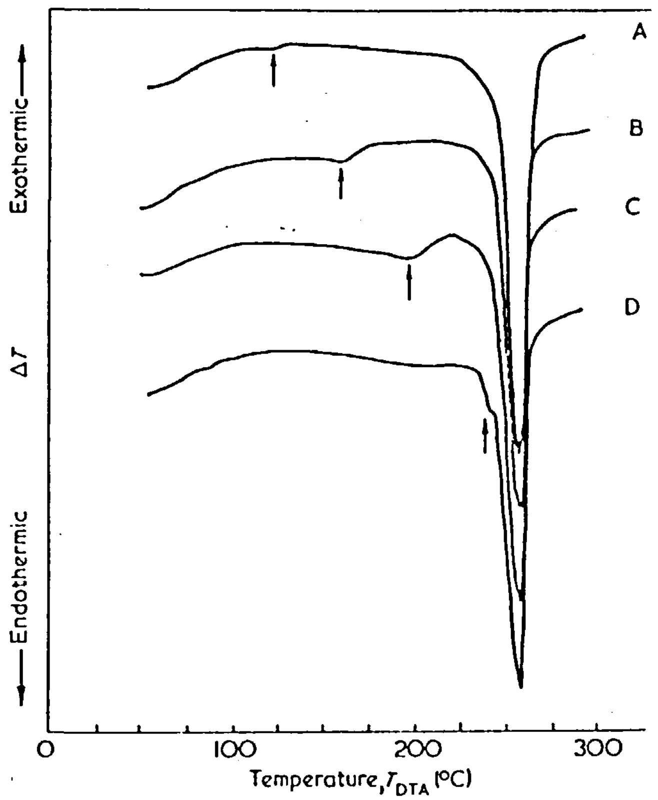

FIGURE 29. DTA traces of PET fibers heat set for 20 sec at the various temperatures (°C). (A) 110, (B) 150, (C) 190, (D) 230. (From Berndt, H. J. and Bossmann, A., *Polymer*, 17(3), 241 (1976). With permission.)

and near 245°C for fibers containing 10.6% MMA (see Figure 30). The extrapolated melting point for the polyacrylonitrile (PAN) homopolymer is about 330°C. Fibers heated to a temperature just below this endotherm were discolored but had not flowed; fibers heated to a temperature between the endotherm and exotherm near 340°C had flowed. As usual the reported temperatures are sensitive to the heating rates.

Dunn and Ennis[65] discussed the identification of acrylic fibers by DTA and DSC. Commercial acrylic fibers contain at least 85% acrylonitrile polymerized with other monomers such as methyl acrylate, methyl methacrylate, or vinyl acetate to modify the physical properties of the polymer. Modacrylic fibers contain less than 85% polyacrylonitrile. In general, a strong sharp exotherm near 300°C distinguishes acrylics from other fibers. Melting points are hard to observe at low heating rates due to the near coincidence of melting and decomposition. Melting, a first-order process, is relatively insensitive to heating rate, while the more complex decomposition process is quite sensitive to the heating rate. Thus at higher heating rates it is possible to move the decomposition exotherm to a higher temperature and observe the smaller melting endotherm.

The melting and decomposition temperatures of ten commercial acrylic fibers were tabulated. In addition to a qualitative evaluation of the DTA thermograms, improved discrimination between yarns can be achieved by determining the heat of fusion from the melting endotherm and the apparent activation energy for thermal decomposition.

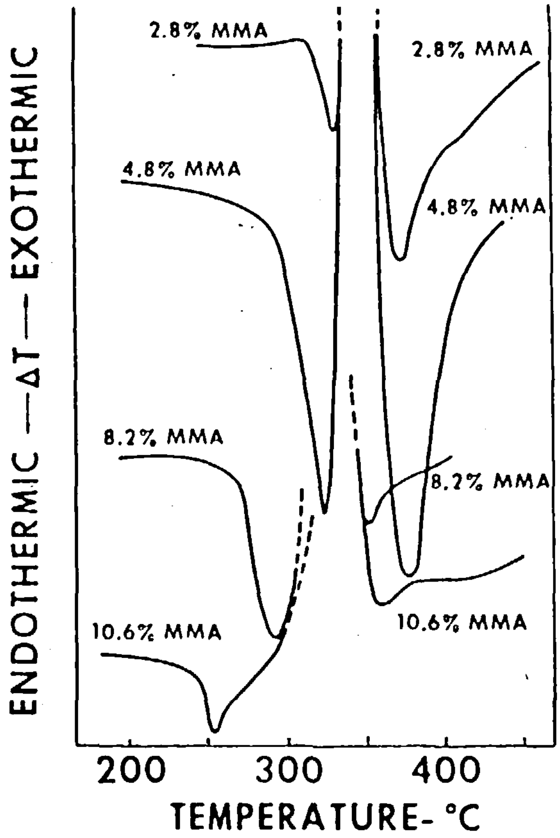

FIGURE 30. DTA traces obtained from acrylic fibers having various concentrations of methyl methacrylate. The endotherms preceeding the strong exotherms are attributed to melting. (From Layden, G. K., *J. Appl. Polym. Sci.*, 15(5), 1283 (1971). With permission.)

Manocha and Bahl[66] studied the thermal decomposition of fibers of a copolymer of acrylonitrile with 6% methyl methacrylate. While the peak temperature of the exotherm at 264 ± 2°C is unaffected by changes in the atmosphere, the temperature of the initiation of the exotherm decreases and the height of the exotherm increases as the atmosphere is changed in the order nitrogen to air to oxygen. Apparently, an oxidation exotherm is superimposed on the cyclization exotherm at the same temperature (see Figure 31).

Thermal stabilization of PAN fibers preparatory to carbonization should be carried out at low heating rates in an oxidizing atmosphere instead of nitrogen. A lower heating rate results in less damage to the fiber and preoxidation suppresses subsequent exothermic behavior and consequent fragmentation when carbonizing the fibers.

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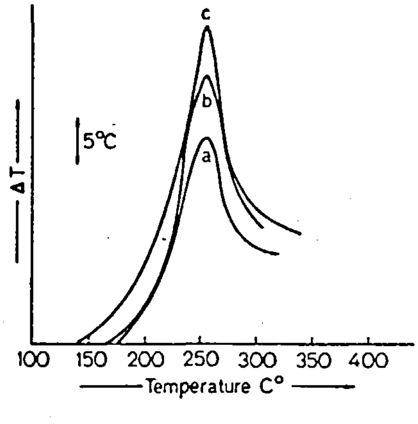

FIGURE 31. DTA curves of polyacrylonitrile fibers under different atmospheres. Heating rate 5°C/min. (a) Nitrogen, (b) air, (c) oxygen. (From Manocha, L. M. and Bahl, O. P., *Agnew. Makromol. Chem.*, 64(1), 115 (1977). With permission.)

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