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Thermomechanical Examination of Fabric Composed of Synthetic Polymers

As the variety of synthetic fibers increases and their use continues to grow the forensic scientist is faced more and more with the problem of identifying them. The work is generally difficult because the available clue samples are usually very small. Fibers found in car headlights after a hit-and-run injury to a pedestrian or under fingernails after a violent crime may consist of only a single filament not more than 1 cm long. Such clues do not provide adequate amounts of material for standard microchemical analysis methods. Moreover, the chemical compositions are very similar within a given class of fibers, such as the nylons, although the fibers within that class frequently differ in mechanical properties as a result of intentional modifications of the fiber-manufacturing processes [1,2]. Consequently, infrared spectrophotometry and pyrolysis gas chromatography produce similar spectra from various nylons, although the nylons differ in mechanical properties.

For several decades the forensic scientist has relied on optical microscopy as the chief tool for identifying fibers [3]. Through microscopic determinations of refractive indexes, birefringences, densities, melting points, solubilities, and various morphological characteristics, considerable differentiation between synthetic fibers is possible. However, microscopic discrimination between fibers of identical chemical compositions generally requires observing differing morphological characteristics. This observation depends to a certain degree on the skill and experience of the investigator. A new technique that could be used to further discriminate between fibers or corroborate the findings of a microscopic examination should be welcomed.

Thermal properties have long been recognized as a useful means of characterizing synthetic fibers [2] but (aside from melting point determinations) were generally too difficult to quantitatively measure to be reliably integrated into a systematic fiber identification scheme.

Thermomechanical analysis (TMA) is a technique by which the contraction or extension of a fiber is measured quantitatively as a function of temperature [4]. Reported herein is the application of TMA to the identification of synthetic fabric fibers.

Experimental Procedure

The thermomechanical behavior of the fibers was measured with a Perkin-Elmer Model TMS-1 thermomechanical analyzer equipped with an extension analysis probe and pro-

grammed by a Perkin-Elmer DSC-1B differential scanning calorimetry unit. The principal components of the TMS-1 analyzer are shown in Fig. 1. Displacement of the probe by expansion or contraction of the heated fiber is converted into an electrical signal by the linear variable differential transformer (LVDT). The force applied by the probe to the sample is the result of the downward force of the load weight and the upward force of the float suspension. Helium is used as a purge gas to prevent condensation and to promote heating and cooling. The temperature of the sample in the furnace is monitored by a Chromel®-Alumel® thermocouple. The fibers are heated at a rate programmed by the DSC-1B unit. Displacement versus temperature is recorded on an x-y recorder.

Details of the fiber-mounting process and the extension analysis probe assembly are shown in Fig. 2. Copper sample clips are crimped to the fiber samples with the mounting tool (Fig. 2a) in order to hold the clips at a reproducible distance (7.6 mm) from one another. For analysis, the fiber samples are mounted on the analyzer in such a way that one sample clip rests on the lip of the sample tube and one is held in the notches at the bottom of the probe (Fig. 2c). Fibers shorter than the 7.6-mm length set by the mounting tool have been analyzed, but the probe design prohibits analysis of fibers less than 4 mm in length (Fig. 2b). With a differently designed probe, one could analyze fibers as short as 1 or 2 mm.

Only single fibers were used, and care was taken to center the fibers held in the probe-sample tube assembly. Because the applied tension can have a strong effect on the observed thermomechanical behavior of a fiber, precautions were taken to ensure reproducible tension distribution in the fiber samples analyzed. Each fiber was analyzed at two different applied tensions; thus, the effect of the different tensions on the observed thermomechanical behavior could be examined as one possible parameter by which to differentiate the fibers. The fibers were analyzed at tensions corresponding to 2- and 3-g weights. Increasing the load weight from 3 to 6 g did not significantly change the TMA results. The zero load weight that counterbalances the buoyancy force from the float suspension was 1.84 g for the TMS-1 apparatus used in these experiments.
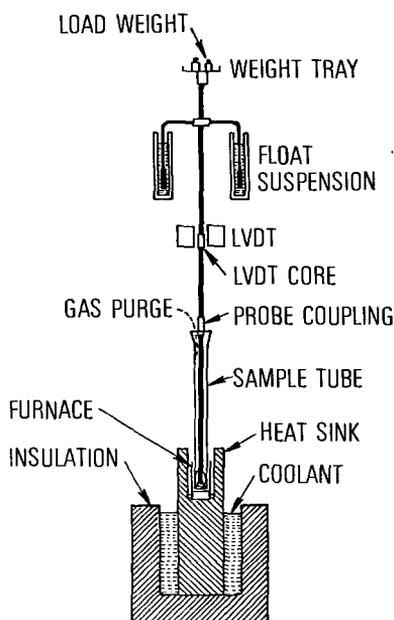

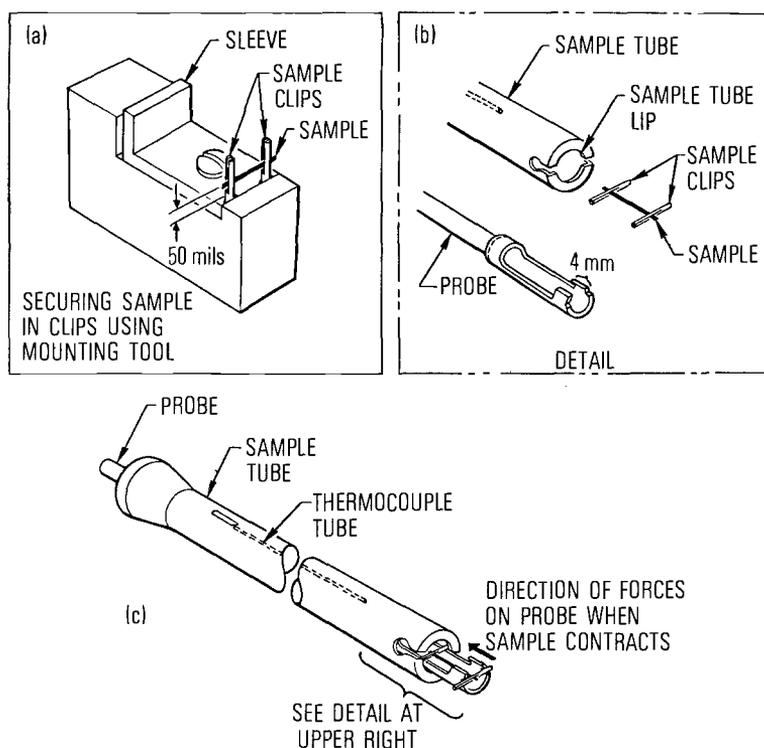FIG. 1—*Perkin-Elmer TMS-1 thermomechanical analyzer.*

FIG. 2—*Sample preparation and mounting for thermomechanical analysis.*

The fibers, obtained from the McCrone Fibre Reference Set [5] and commercial sources, were selected as representative members of major synthetic polymer fiber classes of forensic interest, namely, polyesters, polyamides, acrylics, and polyurethanes.

Results and Discussion

Curves obtained in the thermomechanical studies of synthetic fibers are presented in Figs. 3 through 10. In each plot, the vertical axis represents displacement of the probe such that an upward motion signifies stretching of the fiber and a downward motion signifies contracting; the displacement sensitivity is indicated at the left side of each figure as a percentage of the original fiber length (7.6 mm). The horizontal axis represents the temperature.

The data presented are typical curves obtained for each fiber with the heating rate set at 10°C/min. Increasing the heating rate to 80°C/min produced no major changes in the curves. Using single fibers and carefully mounting the fibers, one can obtain reproducible results with thermomechanical extension analysis, although two curves from the same fiber usually vary slightly from one another. Where reproducibility was a particular problem, two curves for the same fiber are presented. Derivative TMA curves were also obtained, but they did not provide more information than given by those in Figs. 3 through 10.

Polyesters

The 2- and 3-g load weight data for Crimplene®, Terylene®, Kodel®, and Fortrel® polyesters are given in Figs. 3 and 4, respectively.
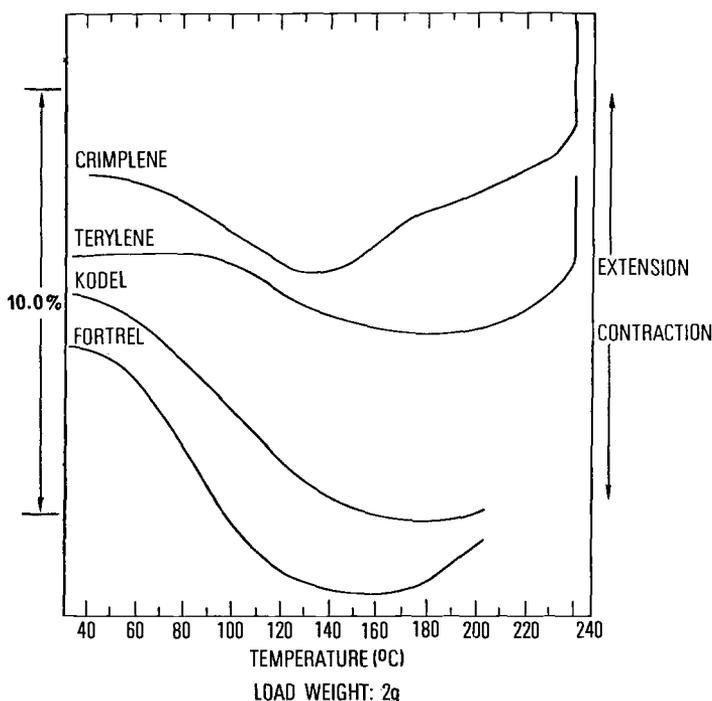
FIG. 3—*TMA curves for polyester fibers with a 2-g load weight.*

The Crimplene polyester from the McCrone Fibre Reference Set is an example of a crimped polyethylene terephthalate polyester likely to be found in double knit fabrics or sweaters. The Terylene is an example of an uncrimped polyester of identical chemical composition likely to be found in tightly woven fabrics. During heating, the crimped fiber undergoes crimp relaxation (an extension). In the 2-g load weight run, crimp relaxation counteracts the normal contraction exhibited by the Terylene and causes the Crimplene to reach the point of maximum contraction at 134°C. Terylene reaches the point of maximum contraction at 180°C. In the 3-g load weight run, the Crimplene exhibits much more extension than the Terylene as a result of the crimp relaxation.

Samples of Fortrel and Kodel polyesters are also shown to be distinguishable. Fortrel fiber displays definite crimped behavior, but its crimp relaxation is not as great as that of Crimplene. In the 2-g load weight run, Fortrel reaches the point of maximum contraction at a higher temperature (160°C) but exhibits less extension in the 3-g load weight run. Kodel (polycyclohexane 1:4 dimethylene terephthalate) appears to be uncrimped, but its greater degree of contraction in the 2-g load weight run makes it distinguishable from the Terylene.

Polyamides

In Figs. 5 and 6, nylon 6, two brands of nylon 6,6, and the high-temperature nylon HT-1 (Nomex®) polyamides are shown to be thermomechanically distinguishable.

In both the 2- and 3-g load weight runs, the nylon 6 exhibits a stronger initial contraction than do the two nylon 6,6 fibers. In the 2-g load weight run, the nylon 6 shows constant extension after the initial contraction, which further distinguishes it from the nylon 6,6 samples. In addition, the 220°C melting point of the nylon 6 (represented in
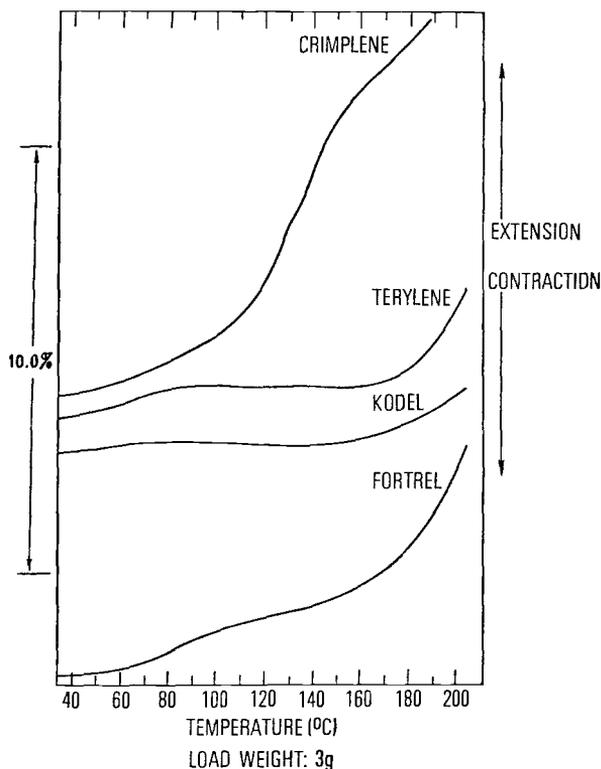
FIG. 4—*TMA curves for polyester fibers with a 3-g load weight.*

Fig. 5 by a vertical line caused by rapid extension after melting) is lower than the melting point of the nylon 6,6 fibers (approximately 250°C).

The high-temperature nylon HT-1 (Nomex) is characteristic in that it shows relatively no thermomechanical behavior for the 2-g load weight and only slight extension for the 3-g load weight. The thermomechanical distinction between the chemically identical delustered nylon 6,6 and the Bri-nylon® 6,6 is probably the result of differences in fiber diameter. The Bri-nylon fibers have a diameter of 19 ± 1 μm, whereas the delustered nylon fibers have an average diameter of 15 ± 1 μm. The difference in diameter is consistent with the observed thermomechanical behavior of the fibers. Bri-nylon, the thicker fiber, shows stronger contraction in the 2-g run and weaker extension in the 3-g run.

Polyacrylonitriles

Thermomechanical analysis curves of Teklan® (modacrylic), Orlon® 42 (acrylic), and Acrilan® 16 (acrylic) are presented in Figs. 7 and 8 for 2- and 3-g loads, respectively. Because the general shapes of the TMA curves for these polyacrylonitriles are quite similar and the reproducibility of the data is poor, it is difficult to distinguish these fibers from one another unless several runs are made. In Fig. 7, two 2-g runs for each fiber are presented in order to indicate the problem in reproducibility for acrylics and to illustrate the kinds of differences one can observe between these fibers.

The typical TMA curve of an acrylic or modacrylic consists of an initial region of slight extension followed by more rapid extension at higher temperatures. At the beginning of
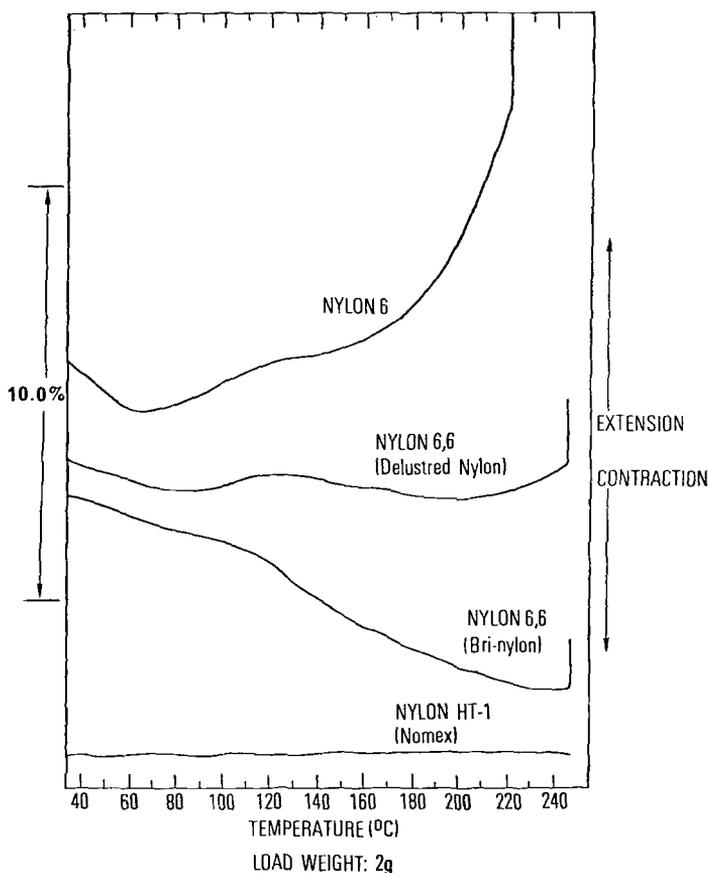
FIG. 5—*TMA curves for polyamide fibers with a 2-g load weight.*

the region of rapid extension, there is often a "knee" in the curves. One means by which to distinguish these fibers is to compare the slopes of the curves in the region of rapid extension. For a 2-g load, the slope of this region is 0.281 ± 0.042%/°C for Teklan, 0.250 ± 0.045%/°C for Orlon 42, and 0.172 ± 0.048%/°C for Acrilan 16. For the 3-g runs, the relative relationship of the slopes for this region is the same, with Teklan > Orlon 42 > Acrilan 16. The temperature that marks the end of the region of slight extension and the beginning of the region of rapid extension is another distinguishing characteristic of these fibers. In the 2-g runs, this temperature is approximately 86°C for Teklan, 90°C for Acrilan 16, and 100°C for Orlon 42. In the 3-g runs, the temperature is approximately 66°C, 84°C, and 92°C for Teklan, Acrilan 16, and Orlon 42, respectively. Finally, Orlon 42 is distinguishable from the other fibers in that it generally has a more pronounced knee in its curves at the beginning of the region of rapid extension. This is shown in Fig. 8, in which Orlon 42 is the only fiber to exhibit an appreciable knee with a 3-g load. With a 2-g load, the knee in the Orlon curve actually manifests itself as a contraction in 50% of its runs. One such run is shown in the lower Orlon curve of Fig. 7.

Although the curves for the polyacrylonitriles sometimes make interclass distinctions difficult, their general shape does differentiate them from the curves of the polyesters, polyamides, and polyurethanes.
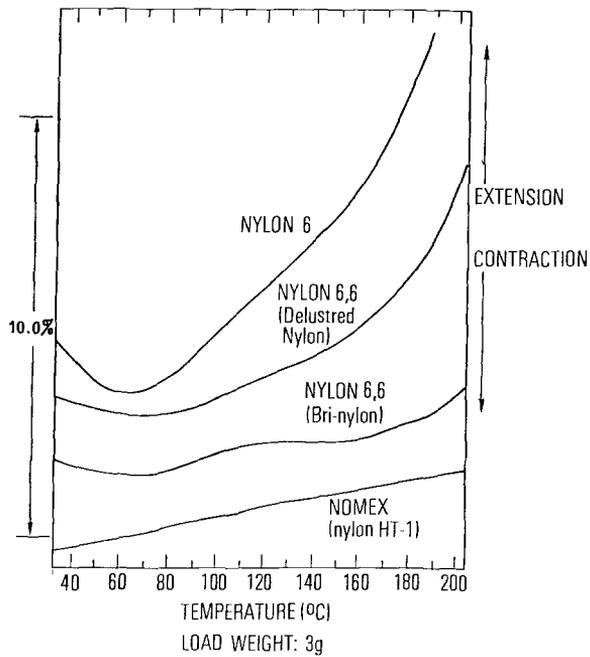
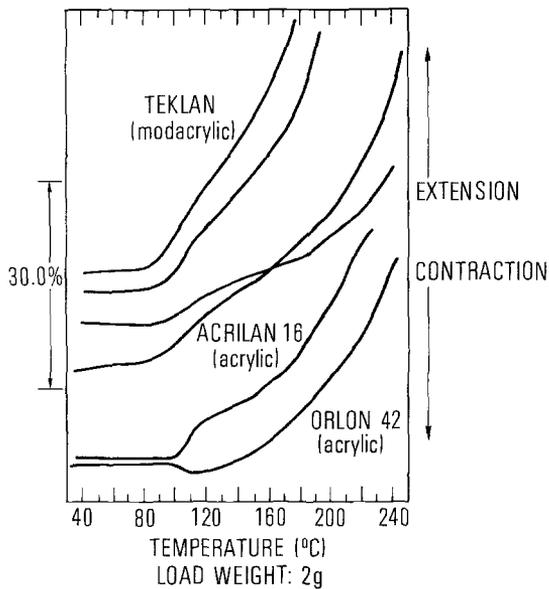FIG. 6—*TMA curves for polyamide fibers with a 3-g load weight.*

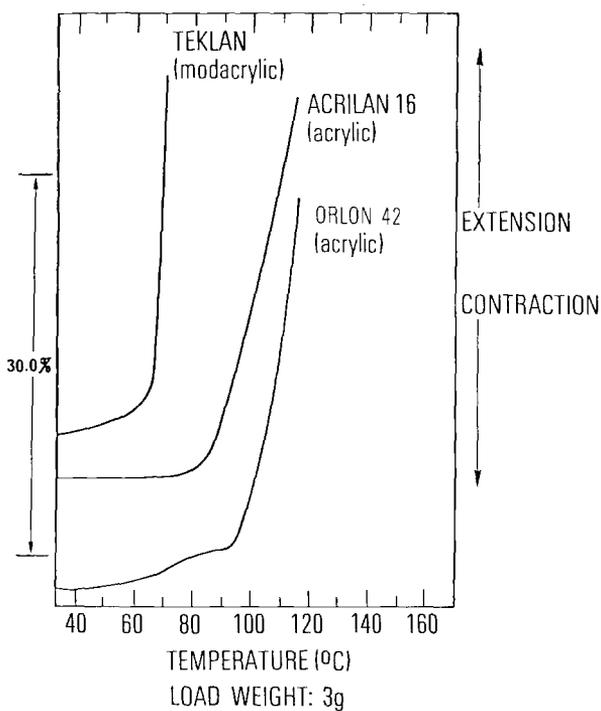FIG. 7—*TMA curves for polyacrylonitrile fibers with a 2-g load weight.*

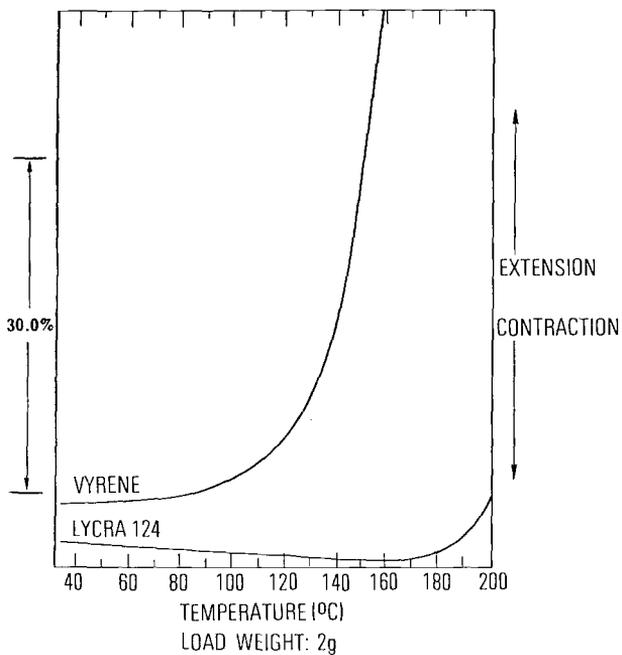FIG. 8—*TMA curves for polyacrylonitrile fibers with a 3-g load weight.*

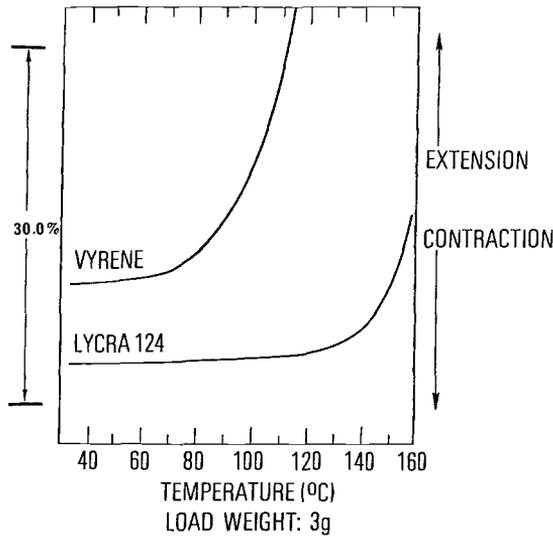FIG. 9—*TMA curves for polyurethane fibers with a 2-g load weight.*

FIG. 10—*TMA curves for polyurethane fibers with a 3-g load weight.*

Polyurethanes

The results for Vyrene® and Lycra® 124 polyurethane fibers are presented in Figs. 9 and 10. Again, the differences in the observed thermomechanical behavior of the two fibers are probably the result of a difference in fiber diameter. In the 2-g run, Lycra 124, the thicker fiber, shows contraction, whereas Vyrene shows extension. In the 3-g run, the Lycra exhibits less extension than the Vyrene. Although it is not difficult to distinguish the large, opaque, elastic polyurethane fibers from the other fibers discussed, it is of interest that the thermomechanical behavior of the polyurethanes is also characteristic.

Conclusions and Summary

In a systematic series of studies, thermomechanical examination was used to identify very small single filaments of fabric fibers. A wide assortment of synthetic polymer fibers was examined, and the thermomechanical curves were recorded to show the characteristic changes in fiber extension or contraction as the temperature was raised and lowered. Successful identification was achieved for fiber filaments less than 1 cm in length and weighing less than 1 μg. Thermomechanical curves were obtained at two different values of the applied tension, because the change in the curves as a function of tension was effective in achieving reliable identification of the fibers. Fibers that cannot be distinguished from one another by means of chemical analysis were shown to be distinguishable by thermomechanical analysis, because the thermomechanical curves show the effects of previous differences in mechanical processing of the fibers.

The studies present three general areas of comparison for differentiating fibers on the basis of the thermomechanical data obtained: (1) the shape of the TMA curves, where extensions and contractions occur as a function of temperature; (2) the degree of extension and contraction that takes place; and (3) the effect of different applied tensions on the observed thermomechanical behavior of the fiber. In most cases, the shape of the curves for a particular tension is sufficient for differentiating most of the fibers studied here. In fact, in a blind test, seven out of seven samples from the fibers studied (including repeats) were successfully identified on the basis of their 2-g load weight runs alone.

While TMA can clearly be employed as a tool for comparing fibers, the similarities between curves of certain of the fiber classes suggest that it could also be used as a more specific method of identification. For example, one could conceivably identify a fiber as a polyacrylonitrile on the basis of its TMA curve. However, TMA data on more fibers would have to be collected before this could be done reliably.

Experiments were also performed which showed that washing and drying fibers had little effect on their TMA curves and dyed fibers also showed TMA behavior typical of their fiber class. Therefore when a fiber is so heavily dyed that optical microscopic identification techniques become difficult TMA could be used.

In view of its potential for providing a wide range of useful data for distinguishing synthetic fibers, TMA could become a valuable technique for forensic scientists.

References

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