

# Evaluation of Thermal History of Polymeric Films and Fibers Using DSC/TMA/DMA Techniques

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## Synopsis

Determining the thermal history of a semicrystalline polymer is an area of extreme importance when it comes to understanding the structure-property relationships. For nylon 6 film and fiber products, we have shown that techniques such as differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA) can reveal the thermal history of the polymer. We believe that the basis of correlation between the heat setting (annealing) conditions and the thermal/mechanical data is the formation of microcrystallites within the amorphous phase upon thermal treatment. Based on a previously published X-ray study, we must mention that a number of changes within the crystalline phase also occur concurrently during the heat setting process of nylon 6. DMA of a highly annealed nylon 6 has helped us identify a broad  $\alpha$ -relaxation in the vicinity of 170°C, tentatively assigned to the mobility of interfacial amorphous domains. We propose that the occurrence of  $\alpha$ -relaxation parallels the crystalline phase changes observed in X-ray studies during the heat setting of nylon 6 products. Although most of the work presented in this manuscript is based on nylon 6, the proposed correlations between the thermal history and DSC/TMA/DMA techniques can be expected for any semicrystalline polymeric film or fiber.

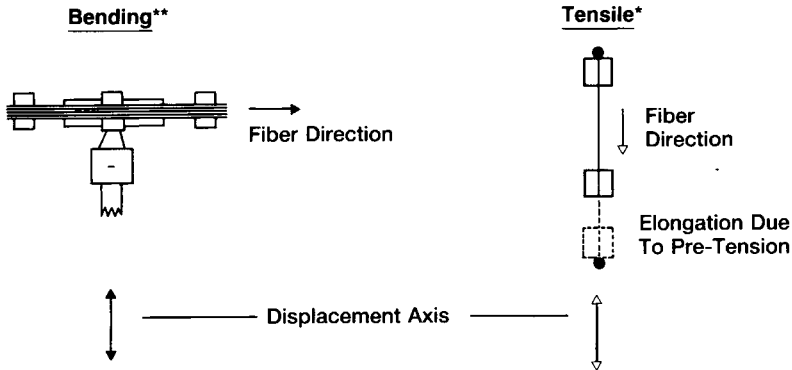
## INTRODUCTION

Nylon 6 is a commonly known polymer and is widely used as films (e.g., packaging) as well as fibers (e.g., carpet yarn). These products often undergo a thermal treatment intended for purposes such as reduction or elimination of residual stresses, enhancing dimensional stability, and improvement of physical properties.<sup>1,2</sup> Such thermal treatments are known to induce morphological changes within the polymer, thereby affecting the product performance. The evaluation of thermal history becomes necessary if one were to attribute the product quality to its morphological characteristics.

The changes induced upon heat setting of nylon 6 fibers have been studied by density, microscopy, and X-ray diffraction (small- and wide-angle) techniques.<sup>3,4</sup> In this manuscript we wish to demonstrate that the conditions of thermal treatment, i.e., time-temperature, are also reflected in the differential scanning calorimetry, thermomechanical analysis, and dynamic mechanical analyses results.

## EXPERIMENTAL

**Sample Preparation.** A commercially available biaxially oriented nylon 6 film and an extruded but unoriented nylon 6 film were heat set under vacuum



\*In the conventional tensile mode, the monofilament fiber (free length  $\approx 5$  mm) is under a pre-tension since small dynamic strains can not be applied to slackened samples.

\*\*In our bending mode, a narrow frame and a medium flat drive clamp (free length = 2 mm) are used. Five single plies of yarn are knotted at one end and pulled and tightened at the other end. The yarns are then alternately clamped and adjusted to obtain a flat, compacted array of about 5 to 7 mm width.

Fig. 1. Schematic of deformation modes used in fiber analysis using DMA.

at temperature between 125 and 200°C for 15 min and subsequently characterized by TMA. Nylon 6 fibers used in this study were heat set by three methods, namely, Suessen method (1 min at 180–210°C in dry heat), autoclave method (30 min at 107–138°C in saturated steam, batch process), and the Superba method (1 min at 107–138°C in saturated steam, continuous process).

In order to avoid the complications in analysis due to absorbed moisture, the samples were first prepared for the DSC and TMA experiments and then dried for at least 3 days at RT under high vacuum. These dried samples were subsequently studied with minimal exposure ( $< 1$  min) to the atmosphere.

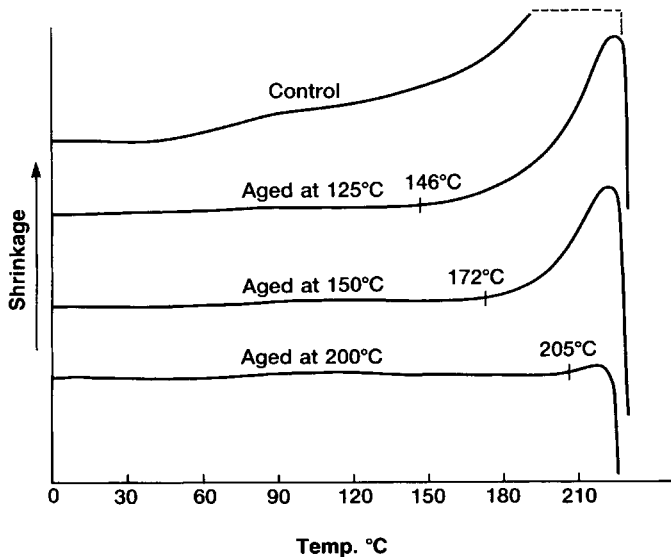


Fig. 2. TMA thermograms showing the dimensional change vs. annealing temperature relationship for a biaxially oriented nylon 6 film analysis along the machine direction.

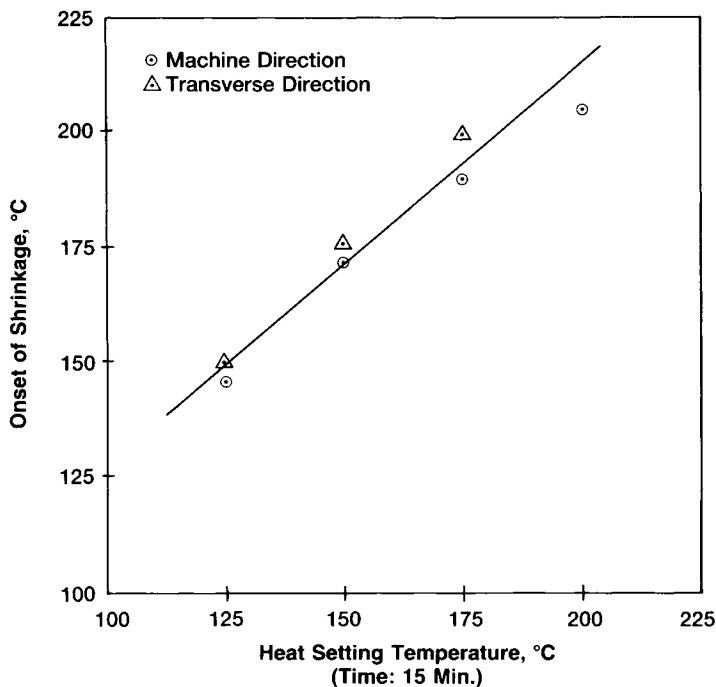


Fig. 3. Shrinkage onset temperature in TMA vs. annealing temperature for a biaxially oriented nylon 6 film.

**DSC.** A DuPont 1090 with a 910 DSC in argon atmosphere was used. A sample of about 11 mg was crimped in an aluminum pan and then heated at 20°C/min rate.

**TMA.** A Perkin Elmer TMS-2 was employed in a helium atmosphere using the extension mode of operation. The sample, 0.31 in. in length, was mounted between two copper clips and heated at 10°C/min rate under “zero load”; the latter includes a minimum weight on the probe such that it is in contact with the sample.

**DMA.** A Polymer Laboratories DMTA unit operating in argon atmosphere was used. A heating rate of 3°C/min, frequency of 1 Hz, and a constant strain (< 1%) were applied. Both bending and tensile deformation modes were used as described in Figure 1.

## RESULTS AND DISCUSSION

We have subdivided this section to separate the analyses of nylon 6 films (oriented and unoriented) and fibers, although the morphological changes upon annealing have a similar origin.

### Thermal History of Films

As shown in Figure 2, the control biaxially oriented film exhibits a continuous shrinkage beginning at the  $T_g$  ( $\sim 40^\circ\text{C}$ ) and ending at the  $T_m$  ( $\sim 220^\circ\text{C}$ ). When the control film is oven aged at 125°C, it undergoes a certain amount of

shrinkage corresponding to the 125°C temperature on the TMA thermogram. Upon subsequent analysis, i.e., TMA of the 125°C aged film, as expected, there is no shrinkage up to at least 125°C. In addition to prior shrinkage, we believe that morphological changes also occur during the oven aging at 125°C which subsequently get reflected in the TMA thermogram. For nylon 6, it is assumed that "microcrystallites" are formed in the boundary layer between larger crystallites and these microcrystallites melt at about 18–25°C above the crystallization temperature at which they are formed.<sup>5</sup> It should be noted that the formation of microcrystallites characterized by their  $T_m = 10\text{--}30^\circ\text{C}$  higher than the annealing temperature is a phenomenon common to almost all semicrystalline polymers.<sup>6</sup> The formation of such microcrystallites might inhibit further shrinkage until these melt, i.e., 10–30°C above the annealing temperature.<sup>6</sup> Our data in Figures 2 and 3 fully supports that the onset of shrinkage in TMA is typically 15–25°C higher than the heat setting or annealing temperature. (Note: discrepancies might occur if the annealing temperature is close to the melting temperature.) Figure 3 also suggests that the same type of correlation exists between the TMA data and the heat setting temperature regardless of the direction of orientation (i.e., machine or transverse) which is to be expected from a biaxially oriented film.

TMA thermogram of the unoriented film exhibits no major change until the melting temperature approaches where an accelerated extension takes place (Fig. 4). As shown in Figure 5, the onset temperature of accelerated extension in TMA matches with the heat setting or annealing temperature of the unoriented nylon 6 film. This correlation is again believed to be related to the microcrystallite formation. We note that the onset of shrinkage is 15–25°C higher while the onset of extension matches closely with the annealing temperature (Figures 3 and 5). A possible explanation is that the shrinkage process having to compete with the thermal expansion (extension) of the polymeric film is

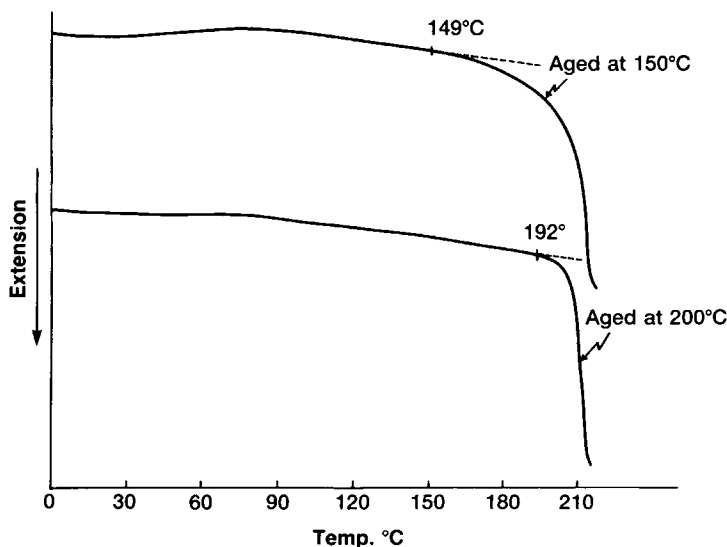


Fig. 4. TMA thermograms showing the dimensional change vs. annealing temperature relationship for an unoriented nylon 6 film.

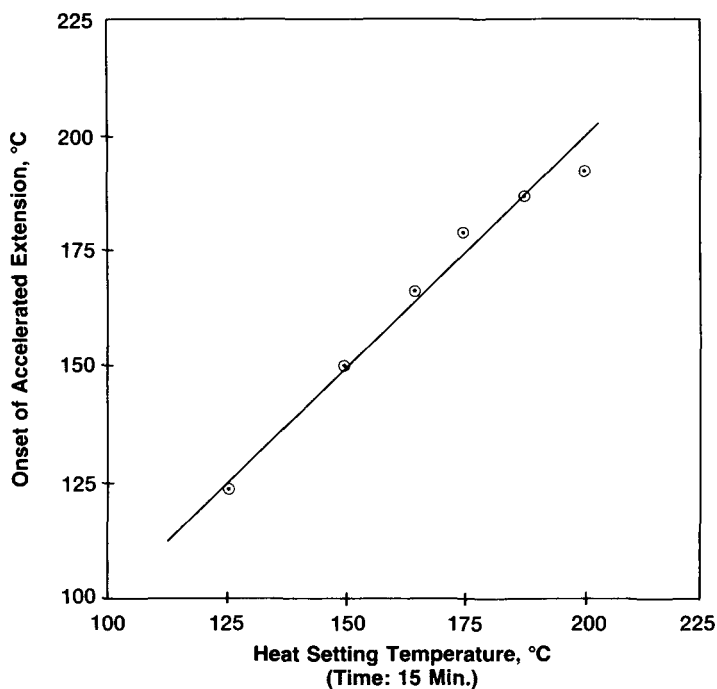


Fig. 5. Accelerated extension onset temperature in TMA vs. annealing temperature for an unoriented nylon 6 film.

detected with a delay. Nevertheless, a correlation between the TMA data and the heat setting temperature exists for the nylon 6 films (oriented or unoriented) and these correlations can, in turn, be used to reveal the thermal history of unknown films, especially when no other variables prevail.

### Thermal History of Fibers

In general, the DSC thermogram of a moisture containing nylon 6 yarn reveals two endotherms: The first represents the loss of moisture and the second

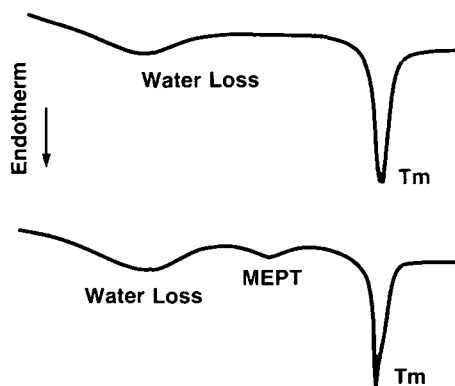


Fig. 6. Schematic representation of MEPT in the DSC thermograms.

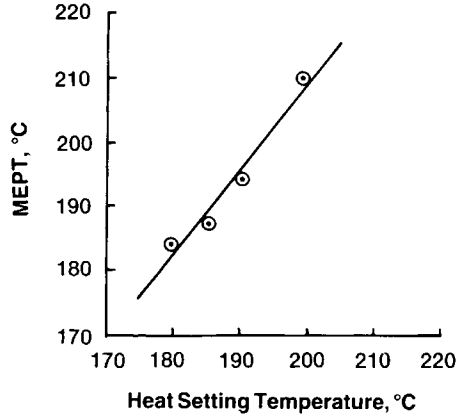


Fig. 7. MEPT vs. heat setting temperature for nylon 6 fibers heat set by Suessen method.

is due to the melting.<sup>7</sup> If the yarn is subjected to a heat treatment, a third endotherm appears between those two which we refer to as a middle endotherm peak (MEP); its temperature is termed as MEPT. Figure 6 represents the appearance of MEP for nylon 6 yarns as a result of heat treatment, i.e., heat setting. (Note: the lowest temperature endotherm due to moisture is absent when dealing with dried samples.) MEPT is found to increase linearly with increase in heat setting temperature (Fig. 7). At a given heat setting temperature, the MEPT also increases with time as shown in Figure 8; this set of data was obtained in our DSC unit, i.e., by treating a nylon 6 yarn at a given temperature for various lengths of time. In view of our own work<sup>8</sup> and the literature,<sup>9</sup> MEPT represents melting of the crystallites (nuclei) formed in the amorphous regions of the fiber microstructure during the heat setting process. An increase in heat treatment temperature or time is likely to enhance the perfection of these small crystallites,<sup>2</sup> thus resulting in an increase in MEPT.

TMA thermogram of the "control" nylon 6 yarn (Fig. 9) reveals shrinkage between the  $T_g$  ( $\sim 40^\circ\text{C}$ ) and the  $T_m$  ( $\sim 225^\circ\text{C}$ ) due to the disorientation of

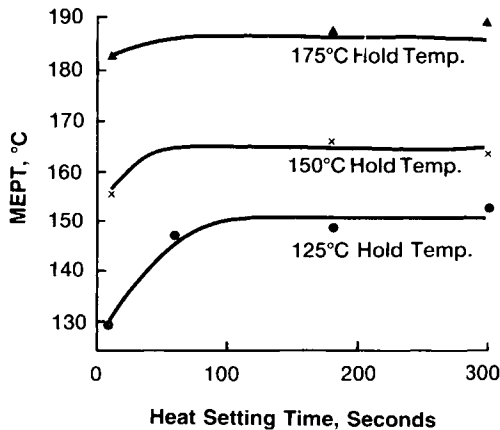


Fig. 8. MEPT vs. heat setting time at various temperatures; heat setting simulation of nylon 6 fibers in the DSC unit.

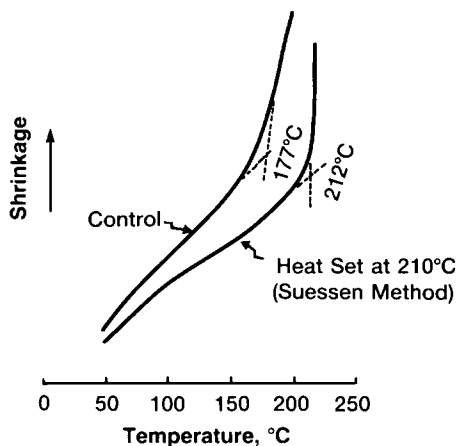


Fig. 9. TMA thermograms of nylon 6 fibers.

the amorphous fraction as well as disorientation of the crystallites.<sup>3</sup> Upon heat setting, the yarn undergoes less shrinkage at the intermediate temperatures (Fig. 9) partly due to prior shrinkage during heat setting and partly because the newly formed crystallites prevent the complete disorientation of the amorphous phase. The accelerated shrinkage (extrapolated onset) of the yarns occurs at a temperature between 180 and 220°C where the main crystal melting of the fiber begins. Interestingly, there is a linear correlation between the heat setting temperature and the onset temperature of shrinkage as demonstrated in Figure 10. Once again, this correlation originates from the formation of small crystallites. For example, heat setting for 60 s at 210°C, according to Figure 7, would lead to additional crystals melting at about 220°C (coincident with the main  $T_m$ ) which then increase the onset temperature of shrinkage until the overall melting process occurs.

Heat setting either by the Suessen or the autoclave method has resulted in similar type of DSC and TMA data. However, these techniques proved unsuccess-

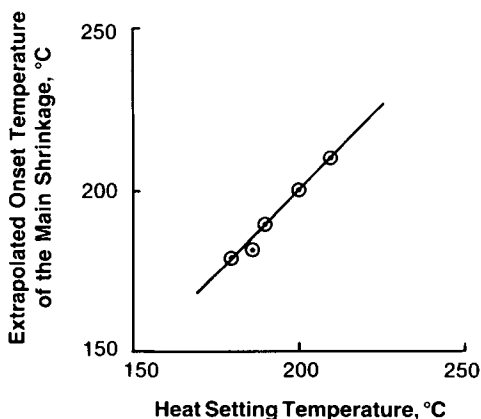


Fig. 10. Shrinkage onset temperature in TMA vs. heat setting temperature for nylon 6 fibers heat set by Suessen method.

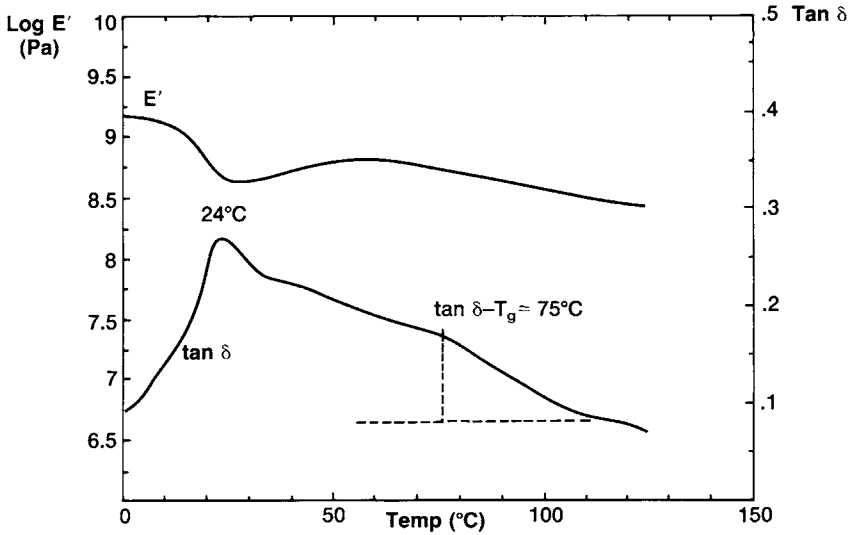


Fig. 11. DMA thermogram of a nylon 6 fiber heat set by Superba method bending mode of deformation.

cessful when applied to the Superba heat-set nylon 6 fibers. Nevertheless, DMA technique proved helpful in this case. Superba heat-set nylon 6 fibers were analyzed in the bending mode (Fig. 1) of deformation, a configuration similar to that used by Murayama.<sup>10</sup> As shown in Figure 11, a low  $\tan \delta-T_g \sim 25^\circ\text{C}$  is believed to be due to the moisture pickup during mounting and startup (e.g., large surface area/weight on the fiber). Upon continued heating, the modulus rises as the moisture is lost, and we finally observe a  $\tan \delta-T_g \sim 75^\circ\text{C}$ , which is in the range for a nylon 6. The intensity of this  $\tan \delta-T_g$  (Fig. 11) correlates

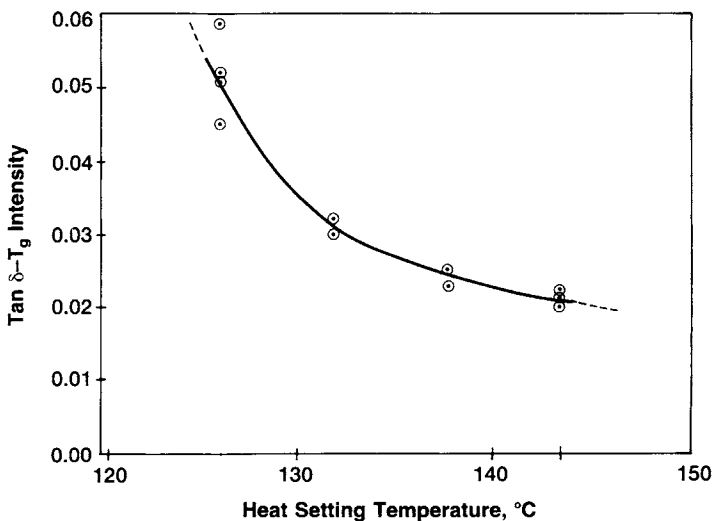


Fig. 12. Correlation between  $\tan \delta-T_g$  intensity (DMA-bending mode) and heat setting temperature of the Superba heat set nylon 6 fibers.



very well with the Superba heat setting conditions (Fig. 12). Once again, we believe that the microcrystallites formed in the amorphous regions lead to a reduced intensity of the amorphous relaxation, i.e., the basis of correlation in Figure 12. We must mention that the  $\tan \delta - T_g \sim 75^\circ\text{C}$  cannot be clearly identified when the fibers are analyzed in the conventional tensile deformation mode (Fig. 13). Based on our recent work,<sup>11</sup> we believe that, during the tensile mode, the fiber experiences elastic orientation under force (EOF) due to pre-tension, which then interferes with the relaxation phenomenon (e.g., compare Figs. 11 and 13).

As a *cautionary* note, we must mention that complications can arise if a polymeric film or fiber was subjected to complex thermal histories. For example, if a sample had been exposed, consecutively, to three temperatures such that  $T_3 > T_2 > T_1$ , the final product would have microcrystallites reflective only of the temperature  $T_3$ . Additional variations, e.g., volatiles or annealing under tension can further complicate the situation. An ideal use for the correlations described in this work is in a quality control environment where heat setting temperature/time is the only variable.

### Nature of Morphological Changes

All the correlations between annealing (heat setting) conditions and the DSC-TMA-DMA results discussed in this work are believed to originate from the formation of microcrystallites in the amorphous region during thermal treatment. Such a concept has been widely accepted.<sup>5,8,9</sup> We must mention that although the microcrystallites are too small (10–50 Å) to be characterized, there is indirect support for their existence, e.g., (a) these exhibit first-order transition unlike the known relaxations in polymers, (b) these melt 10–30°C higher than the annealing temperature for any crystallizable polymer. Assuming

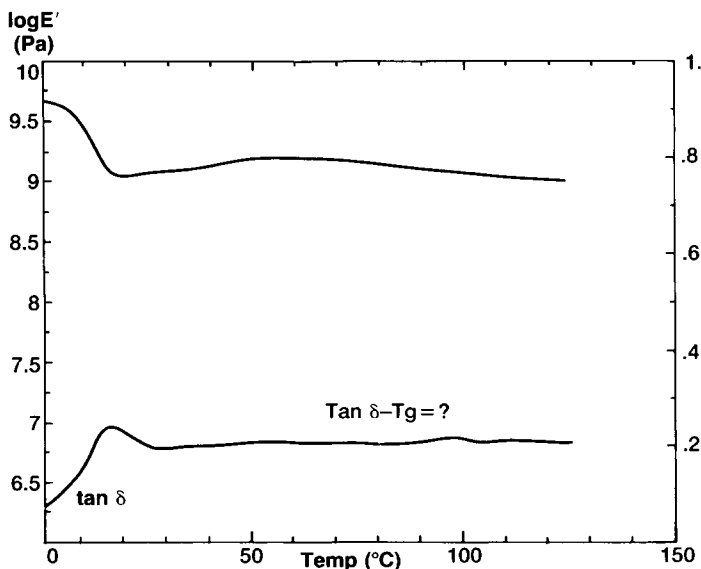


Fig. 13. DMA thermogram of a nylon 6 fiber heat set by Superba method-tensile mode of deformation.

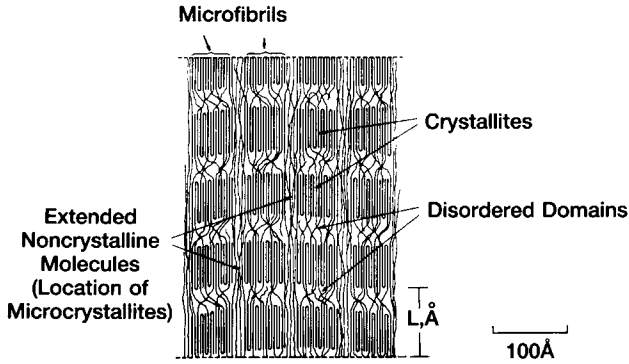


Fig. 14. Schematic representation of the microstructure of nylon 6 fibers as per Prevorsek et al.<sup>10</sup>

a three-phase model of Prevorsek et al.<sup>12</sup> for oriented fibers, the microcrystallites are believed to be located somewhere in the amorphous domains (Fig. 14).

X-ray studies from our laboratory<sup>3</sup> have shown that the modifications of the crystalline phase occur above a critical temperature of 170°C (under dry conditions) or 100°C (saturated steam-plasticized). Now we wish to report a relaxation mechanism occurring at about 170°C in dry nylon 6, which we believe is responsible for the crystalline changes taking place above 170°C under dry conditions. Takayanagi<sup>13</sup> has reported a minor peak (shoulder) at about 190°C in the DMA thermograms of nylon 6. Since this shoulder was most pronounced for samples of highest crystallinity, it was attributed to a crystalline relaxation. This type of relaxation in nylon 6 has not received much recognition because its identification has been masked by factors such as simultaneous premelting of imperfect crystals, further crystallization, crystal thickening and perfection,

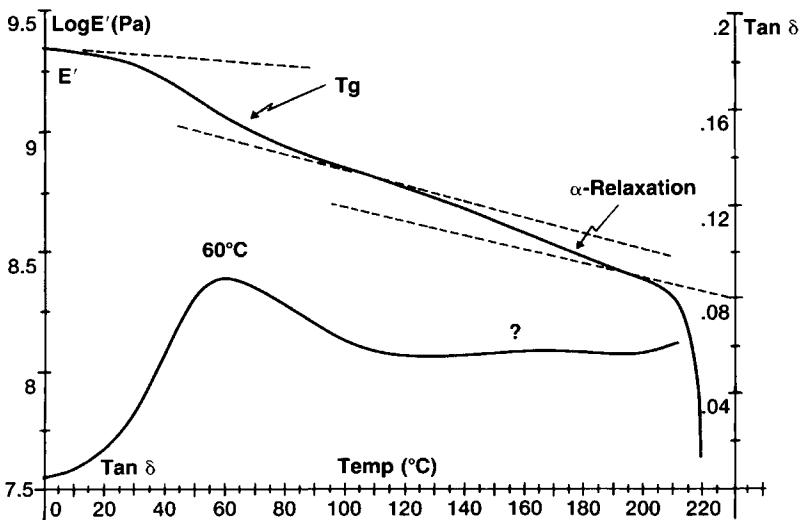


Fig. 15. Representation of the  $\alpha$ -relaxation in the DMA thermogram of a nylon 6 sheet annealed at 220°C for 62 h.

conversion of  $\gamma$ -to- $\alpha$ -crystal form, etc. In accordance with our recently developed annealing scheme,<sup>14</sup> a nylon 6 plaque was annealed in the mold at 220°C for 17–65 h, resulting in a  $T_m$  of > 240°C. This process eliminated any premelting and any crystalline metastability up to 220°C. DMA thermogram of the nylon 6 plaque annealed under these conditions, reproducibly, exhibits a broad  $\alpha$ -relaxation centered at about 170°C (Fig. 15). In analogy with published studies on semicrystalline polymers, e.g., polyethylene,<sup>15</sup> poly(vinyl alcohol),<sup>16</sup> and ethylene-chlorotrifluoroethylene copolymer,<sup>17</sup> we tentatively assign the 170°C relaxation in nylon 6 as its  $\alpha$ -relaxation representing the mobility of the interfacial amorphous domains; crystal mobility being a prerequisite for  $\alpha$ -relaxation to occur.<sup>15–17</sup> The relationship between  $\alpha$ -relaxation and the crystalline phase changes occurring in nylon 6 will be the subject of a future manuscript.<sup>18</sup>

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