Reliable Measurements of the Nylon 6 Glass Transition Made Possible by the New Dynamic DSC

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ABSTRACT: Although it has long been known that the glass transition temperature (T_g) of nylons changes significantly with moisture content, literature to date has lacked reliable measurements of this type, primarily due to the changes in moisture during the T_g scanning experiments. Introduction of the new dynamic DSC technique has allowed us to quantify the dependence of T_g on % relative humidity for nylon 6 and nylon 66. By eliminating the possibility of moisture pickup, we have been able to separate the effect of crystallinity as well as orientation on the T_g of nylon 6. The methodology described here should be applicable to other moisture sensitive polymers as well, e.g., poly(vinyl alcohol).

Introduction

Aliphatic nylons, e.g., nylon 6, have been known since the 1930s and represent a common class of polymers with annual sales of several billion pounds. Nylons are extremely sensitive to moisture absorption; the latter being an effective plasticizer. The equilibrium moisture pickup is dependent on the relative humidity (% RH) to which it is exposed. As a consequence, there have been difficulties in determining the glass transition temperature (T_g) vs % RH since the moisture content changes while the temperature is being scanned to observe the T_g. Either the literature[1] fails to commit to a definite T_g or lists values ranging from −120 to +91 °C which, again, is of no help. Sensitive techniques for T_g detection like dynamic mechanical (DMA) and dielectric analyzers (DEA), are not totally reliable since the sample cannot be sealed. Nevertheless, thicker samples analyzed by DMA provide a T_g which is less susceptible to error arising from the absorption and diffusion of moisture. About 50 °C is the most widely accepted T_g[2] of reasonably dry nylon 6.

This paper represents the first attempt to measure, the T_g of absolutely dry nylon 6 and, more importantly, its moisture dependence. Furthermore, this study was performed on yarns which, in contrast to thicker specimens, re-equilibrate their moisture content extremely fast, i.e., during the time scale of the sample loading. The technique which made such a study possible, was introduced in 1992 under names such as modulated differential scanning calorimetry (MDSC, TA Instruments) and oscillating DSC (ODSC, Seiko Instruments). Similar techniques are under development by other instrument manufacturers like Mettler (ADSC) and Perkin-Elmer DDSC). All these technqiues involve a coupling of conventional DSC and the AC calorimetry.[3] In order to consolidate all these similar techniques, we are proposing a common name[4] of "dynamic DSC".

In brief, DDSC imposes a sinusoidal temperature ramp over a conventional linear temperature ramp and processes the resulting signal to yield a deconvoluted DSC curve. The latter is then separated into irreversible (kinetic) and reversible (specific heat) components,[3] T_g being an example of a reversible component whereas the evaporation of moisture and crystallization during heating represent irreversible components (note: ref 3 is recommended for details).

Experimental Section

Sample Preparation. Nylon 6 yarns were placed in a beaker which was then put in a desiccator set at 50, 65, and 93% RH for at least 1 week. When the samples were ready for analysis, the desiccator was opened, and about a 1 in. length (10 ± 2 mg) was cut without weighing (i.e., to save time and avoid moisture changes) and packed into a crimped aluminum pan; the total estimated time from desiccator to the ODSC unit being <45 s. For the analysis of bone-dry yarns, the samples were packed in a crimped aluminum pan with a pinhole, dried at room temperature at 10 mmHg vacuum overnight, and then conditioned in the ODSC unit at 110 °C/10 min prior to analysis. The moisture pickup at each % RH was analyzed by TGA as well as Karl-Fischer/coulometric techniques.

ODSC Method Development. Using Seiko's RDC 220 system, the yarns were analyzed at a heating rate of 5 °C/min from −60 to +150 °C in a dry nitrogen atmosphere. Not knowing the effect of frequency and amplitude, we had to optimize these variables. For a nylon 6 yarn (50% RH), at a fixed frequency of 0.02 Hz, as the amplitude increased from 1 to 10 °C, the noise decreased while the transition intensity increased. As a consequence, we adopted the maximum allowed amplitude of 10 °C. Using this amplitude, we studied the effect of frequency from the lowest allowed limit of 0.01 Hz. Surprisingly, as the frequency increased from 0.01 to 0.03 Hz, the T_g increased from −2 to +10 °C but at the cost of transition intensity and quality. As a result, a frequency of 0.01 Hz was chosen. Under these conditions of 10 °C amplitude and 0.01 Hz frequency, a quenched film of nylon 6, which exhibits a T_g of 41 °C at 5 °C/min heating rate in standard DSC, was found to show a T_g of 34 °C. In view of the quality of the transition, the above optimized conditions were adopted and a +7 °C correction imposed. Based on at least 30 runs of quenched nylon 6 film, the precision of ODSC was determined to be better than ±0.5 °C. Therefore, the scatter in the wet T_g's observed in this report has to be attributed to the minute variations in moisture content during sample preparation and/or inhomogeneous water absorption in the yarns.

Results and Discussion

We shall present this section in two parts, each of which leads to a particular conclusion.

Glass Transition vs % Moisture. The results for nylon 6 yarns are presented in Figures 1 and 2. The

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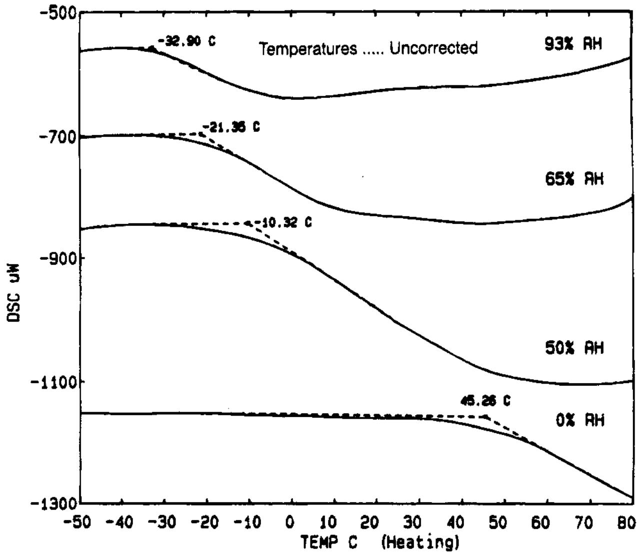

Figure 1. Oscillating DSC thermograms of nylon 6 yarns at various % RH levels (note: uncorrected temperatures, one typical scan at each RH).

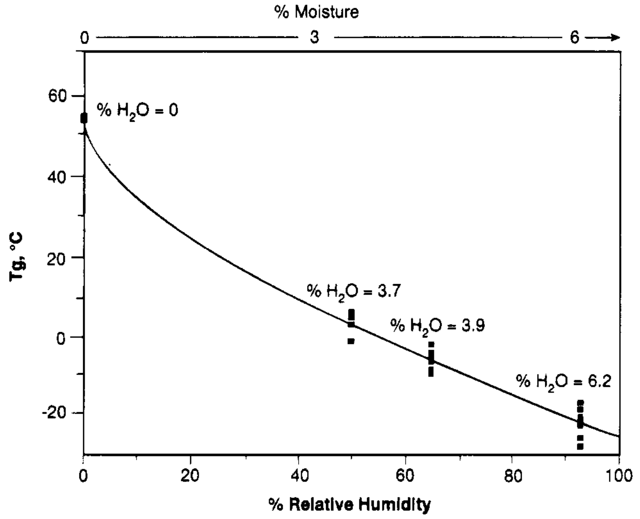

Figure 2. Dependence of T_g on the % RH for nylon 6 yarns (note: corrected temperatures, 10–15 measurements at each RH).

data for this as well as other related systems could be described by the following empirical equation although we cannot comment on its physical significance:

$$T_g = a + b\,(\%\ \mathrm{RH}) + c\sqrt{\%\ \mathrm{RH}}$$

where $a = 53.67$, $b = -0.168$, and $c = -6.208$ are empirical constants.

Following are the reasons why we believe the data in Figures 1 and 2 to be highly reliable: (1) for the bone-dry T_g, the sample was crimped and dried under ultrahigh vacuum. During transportation to the ODSC unit in a desiccator, the sample could not have picked up any moisture since it was not exposed to the surrounding atmosphere. Moreover, prior to the T_g scanning, the sample was conditioned at 110 °C/10 min in the ODSC unit. (2) The moist samples were packed within 45 s while in the desiccator of a particular % RH and then crimped (not hermetically sealed) in an aluminum pan. Since the sample holder did not expose the sample to the surrounding atmosphere and was loaded in the ODSC unit a <-50 °C, it could not have changed in moisture content during temperature scanning as the wet T_g's are below the room temperature. Figure 2 has a pattern similar to those typically known for T_g vs % plasticizer dependence. Moreover, if the moisture content was changing during the handling or during the ODSC experiment, we would not have been able to differentiate the samples of varying % RH, especially the 50% RH and the 65% RH.

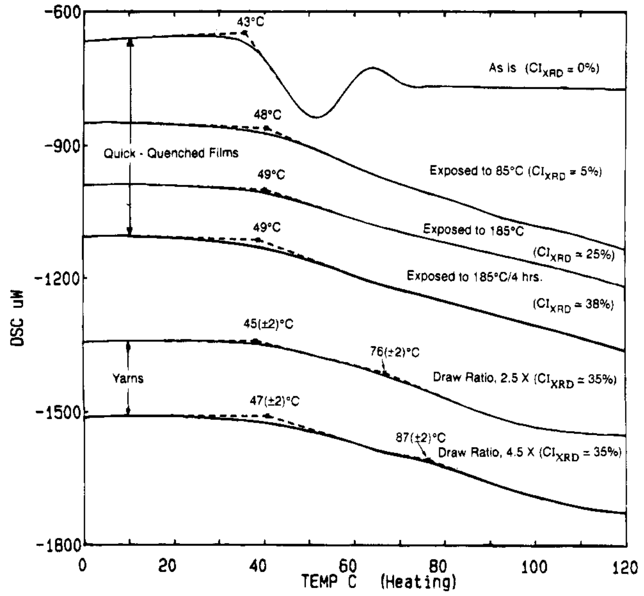

Figure 3. Oscillating DSC thermograms of nylon 6 at various crystallinities (films) and draw ratios (yarns).

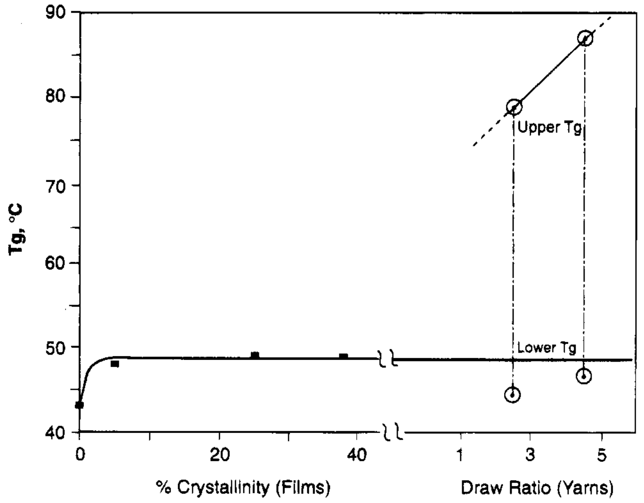

Figure 4. Dependence of T_g on the crystallinity (films) and draw ratio (yarns) for nylon 6.

To our knowledge, Figure 2 represents the first attempt to obtain reliable T_g vs % moisture data. The bond-dry T_g of 54 °C (Figure 2) is slightly higher than the literature reported dry T_g of about 50 °C[2] because our samples were thoroughly dried in two stages; step I involved drying overnight at room temperature under ultrahigh vacuum while crimped in an aluminum cup with a pinhole, and then step II involved redrying at 110 °C/10 min in the ODSC unit. Although, it is well-known that a complete description of the T_g requires its onset, midpoint, and end temperatures,[5] we have presented only the onset temperature of the T_g's; the midpoint and end temperatures, being dependent on the crystallinity, orientation, and % moisture, would have complicated the interpretation. Moreover, for the moist samples, diffusion of moisture will begin during the

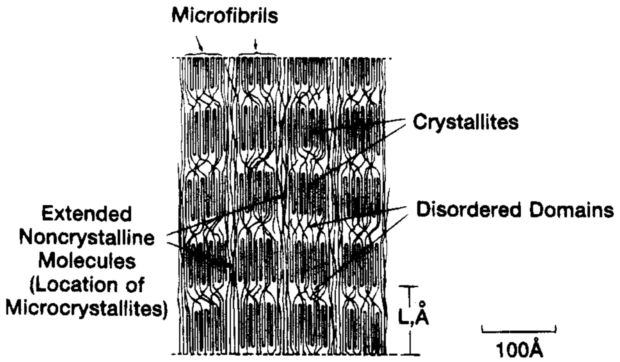

Figure 5. Schematic representation of the microstructure of nylon 6 fibers as per Prevorsek et. al.[6]

temperature span of the transition, thus causing a transition broadening. Therefore, it is felt that only the onset temperature of the T_g will be reliable.

Glass Transition vs Crystallinity/Orientation. Due to the much enhanced sensitivity of ODSC and the ability of DSC to protect the sample from surrounding atmosphere after ultra vacuum drying, we have been able to obtain information on the T_g as a function of crystallinity and orientation. Figures 3 and 4 show that the T_g of dry nylon 6, defined as the onset temperature, is 43 °C for an undrawn amorphous film and reaches a limiting value of about 49 °C at 5–10% crystallinity. Note that the limiting T_g of 49 °C for dry samples in Figure 3 is about 5 °C lower than the dry T_g of 54 °C in Figure 2 because the samples in Figure 3 were not subjected to the step II drying due to concerns of altering the crystallinity and/or orientation. In addition, it appears that there is a doublet T_g for the drawn samples (note: this has been demonstrated by at least five measurements on each sample). On the basis of the three phase model,[6] the lower T_g, which is the same as that in the unoriented but crystalline film samples, is being assigned to the interlamellar amorphous regions while the upper T_g is reflective of the interfibrillar (oriented amorphous phase) regions, and thus sensitive to the draw ratio (Figure 5). Note that for systems of differing degrees of orientation, the disorientation (e.g., shrinkage by thermomechanical analysis) begins to occur at the same temperature (T_g), but the extent of disorientation will depend on the degree of initial orientation. On the basis of this argument, we feel the doublet T_g is real rather than an artifact from the relaxation process.

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