Thermal expansivity of oriented nylon-6 and nylon-6,6

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Measurements on the thermal expansivities along ($\alpha_{\parallel}$) and normal ($\alpha_{\perp}$) to the draw direction have been carried out from 120 to 380K for nylon-6 and nylon-6,6 with draw ratio λ between 1 and 3.6. The sharp drop in $\alpha_{\parallel}$ and the slight increase in $\alpha_{\perp}$ with increasing λ can be attributed to the gradual alignment of chain segments in both the crystalline and amorphous regions. Using the presently available expansivity data on nylon-6 crystals it is found that the observed orientation dependence below the glass transition can be quantitatively described by a two-phase aggregate model. Water acts as a plasticizer and so its absorption leads to a drop of about 80K in the glass transition temperature. At low temperature, however, water appears to form bridges between molecular chains. This gives rise to a stronger interchain interaction and hence a lowering of the thermal expansivity.

(Keywords: anisotropic thermal expansivity; nylons; rubber-elastic contraction; two-phase model; glass transition; moisture effect)

INTRODUCTION

The technical importance of isotropic and oriented nylons has long been recognized. Consequently, many of their physical properties, including mechanical moduli[1–16], have been extensively investigated. However, there have been comparatively few studies of the thermal expansivity of nylons[17–21], especially over a wide temperature range[21]. This property is important mainly for two reasons. Firstly, it is a useful parameter in various practical applications. Moreover, owing to its high sensitivity to changes in interaction strength or morphology[21–29], the measurement of thermal expansivity is helpful in elucidating the structure of a polymer.

In the present work, we have determined the thermal expansivity along ($\alpha_{\parallel}$) and normal ($\alpha_{\perp}$) to the draw axis of oriented nylon-6 and nylon-6,6 from 120 to 380 K. We will propose a two-phase aggregate model which can explain the orientation dependence of $\alpha_{\parallel}$ and $\alpha_{\perp}$. As a result of the hydrogen bonding between amide groups, nylons differ from other classes of polymers in that their physical properties are strongly affected by moisture. The change from dryness to moisture saturation gives rise to a downward shift of about 80 K in the glass transition temperature, and consequently a drastic decrease in the modulus at room temperature. At low temperature, however, water forms bridges between polymer chains, thereby leading to a slight increase in the modulus. Therefore it would also be interesting to examine the 'plasticizing' effect of water on the thermal expansivity and the 'crosslinking' effect below the glass transition.

EXPERIMENTAL

Sample preparation

Isotropic sheets of nylon-6 (Ultramid B4) and nylon-6,6 (Zytel 42) were supplied by BASF and Du Pont, respectively. Oriented samples were prepared by drawing the isotropic sheets at 150°C on an Instron tensile machine at a rate of 5 cm/min. To ensure that there was no structural changes during the course of the experiments, both the isotropic and oriented samples were initially annealed with ends free for $1\frac{1}{2}$ h at 150°C, i.e., at 40°C above the upper limit of the expansivity measurements. This thermal treatment led to very little shrinkage and so the draw ratio was essentially unchanged. The degree of chain orientation of these samples has already been studied by wide-angle X-ray diffraction and birefringence in our previous work[16].

'Dry' samples were prepared by placing in a vacuum oven at 120°C for 7 days and then storing in a desiccator. The density was determined by the flotation method using mixtures of toluene and carbon tetrachloride. From the values of density the volume fraction crystallinity was calculated to be 0.38 and 0.46 for isotropic nylon-6 and nylon-6,6, respectively. There was very little change in crystallinity after drawing[16]. 'Wet' samples were obtained by immersing the dry materials in distilled water at 25°C until they were saturated with water. The water content varied from 8 to 10% by weight.

Thermal expansion measurements

Thermal expansion measurements on dry samples were carried out from 120 to 380 K on a Perkin–Elmer thermomechanical analyser TMS II at a rate of 10 K/min. For the wet samples, measurements were made only up to 320 K since the effect of loss in water was not negligible above this temperature. The detailed procedure and method of analysis have been described previously[26]. As a result of the annealing treatment at 150°C all the samples exhibit reversible dimensional changes within the temperature range of our experiments.

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RESULTS AND DISCUSSION

General features

The thermal expansivity along ($\alpha_{\parallel}$) and normal ($\alpha_{\perp}$) to the draw axis are plotted against temperature at various draw ratios (λ) in *Figures 1* and *2*. At low temperature the temperature dependence is weak, and the most important feature is that $\alpha_{\perp}$ increases slightly and $\alpha_{\parallel}$ drops substantially with increasing draw ratio. As a polymer is drawn the chains are preferentially aligned so that $\alpha_{\parallel}$ becomes increasingly dominated by the small negative value of the expansivity along the chain axis ($\alpha_{\parallel}^{c} \simeq -1.5 \times 10^{-5}\ \mathrm{K}^{-1}$)[29–31]. In the transverse direction the effect of orientation is small since both the expansivity of the isotropic sample (α_{iso}) and $\alpha_{\perp}$ are largely determined by weak interchain forces[21–29].

Figures 1 and *2* also reveal that the thermal expansivity increases abruptly in the glass transition region, but the step in $\alpha_{\parallel}$ becomes smaller with increasing λ and is hardly noticeable at $\lambda \geqslant 3$. This is because the presence of oriented chains and taut tie molecules in the amorphous regions tends to inhibit the large-scale segmental motion responsible for the transition. The temperature dependence above T_g is especially interesting. α_{iso} and $\alpha_{\perp}$ continue to rise but $\alpha_{\parallel}$ exhibits a sharp drop, particularly for the sample at the highest draw ratio. The increase at T_g combined with the subsequent drop at higher temperature leads to a peak in $\alpha_{\parallel}$ at intermediate draw ratio ($\lambda \simeq 2$).

Upon careful examination of the $\alpha_{\parallel}$ data for the highly oriented materials ($\lambda \geqslant 3$) it is apparent that $\alpha_{\parallel}$ actually starts to decrease at 200 K but the drop is not dramatic until above the glass transition. This indicates that there is already a small rubber-elastic contraction of the tie molecules above the subglass transition (β relaxation at 200 K) where the non-hydrogen bonded amide groups begin to move, but this effect is not sufficient to overwhelm the expansion of the adjacent amorphous components. Above the glass transition, however, the entropic effect becomes dominant. The very large contraction along the draw direction and the accompanying transverse expansion lead to an even larger anisotropy in the thermal expansivity.

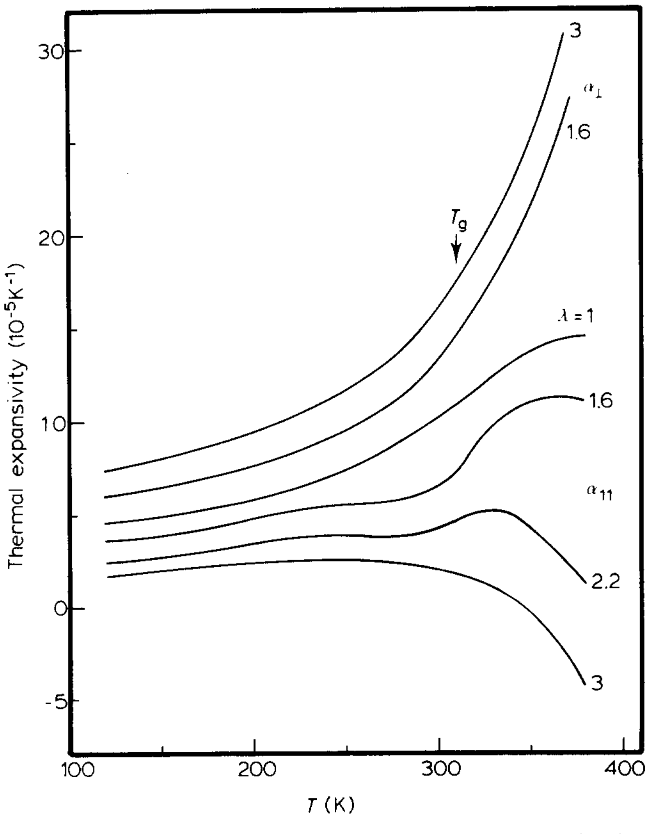

Figure 1 Temperature dependence of thermal expansivities for dry nylon-6. λ is the draw ratio and T_g denotes the glass transition

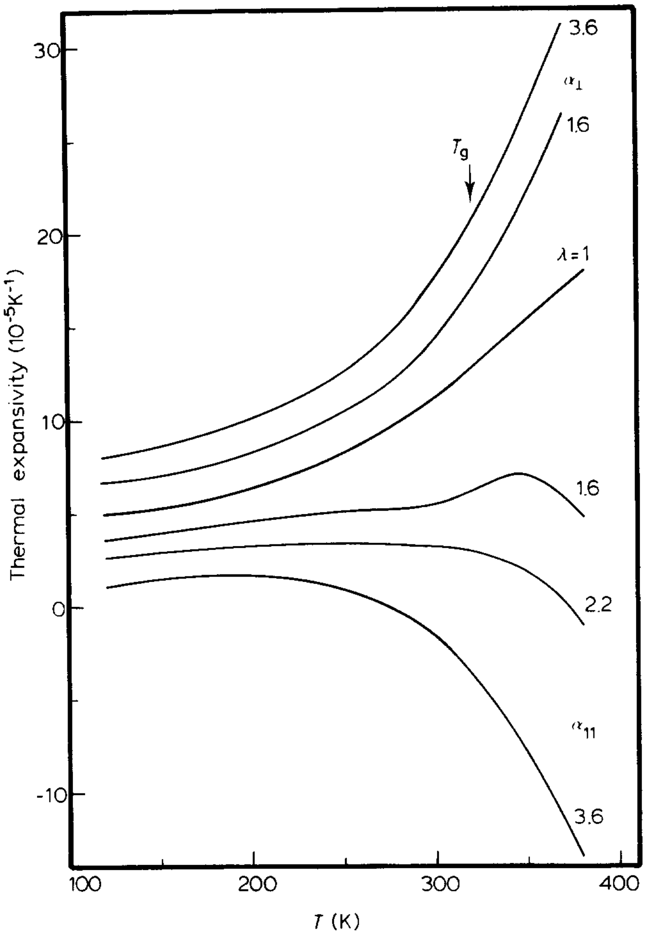

Figure 2 Temperature dependence of thermal expansivities for dry nylon-6,6. Legends as in *Figure 1*

Two-phase aggregate model

One important model often used in the analysis of the effect of orientation is the aggregate model[32–34]. According to this model a polymer may be considered as an aggregate of anisotropic intrinsic units, whose properties remain unchanged, but are increasingly aligned as the polymer is drawn. If the degree of orientation of the intrinsic units is known, the physical properties of the polymer can be calculated. Early studies[32–34] were concerned with amorphous or slightly crystalline polymers and so only a single-phase model was required. More recently, Samuel and coworkers[35,36] have extended the aggregate model to a two-phase model so as to analyse the elastic modulus of highly crystalline polymers. The calculation of elastic constants can be made in two ways, either by assuming uniform stress (the Reuss average) or uniform strain (the Voigt average), both within each phase and between the crystalline and amorphous phases. However, the Reuss averaging procedure is more commonly employed since the theoretical results agree much better with data[35–37].

Several workers[27,37–39], including ourselves, have applied the single-phase aggregate model to understand the thermal expansion behaviour of amorphous polymers. In our previous analysis[26,28,29] of semicrystalline polymers a two-phase model was used but the amorphous phase was assumed to be isotropic. Although the agreement between prediction and experimental data is reasonable for $\alpha_\perp$, this model gives $\alpha_\parallel$ values which are much too high. This discrepancy arises largely from the over simplifying assumption of an isotropic amorphous phase since it is well known[10,12,16,35] that there is appreciable amorphous orientation even at low draw ratio. Therefore, for a more meaningful comparison with experimental results, we will express $\alpha_\parallel$ and $\alpha_\perp$ in terms of the orientation functions of the amorphous (f_a) and crystalline (f_c) phases, as well as the intrinsic expansivities of the two phases. If we assume uniform temperature change (analogous to the Reuss averaging procedure in the mechanical case), then the calculation involves averaging the thermal expansivities to give

$$\alpha_\parallel = X[(1+2f_c)\alpha_\parallel^c + 2(1-f_c)\alpha_\perp^c]/3 \\ +(1-X)[(1+2f_a)\alpha_\parallel^a + 2(1-f_a)\alpha_\perp^a]/3 \qquad (1)$$

$$\alpha_\perp = X[(1-f_c)\alpha_\parallel^c + (2+f_c)\alpha_\perp^c]/3 \\ +(1-X)[(1-f_a)\alpha_\parallel^a + (2+f_a)\alpha_\perp^a]/3 \qquad (2)$$

where X is the volume fraction crystallinity, $\alpha_\parallel^p$ and $\alpha_\perp^p$ are the thermal expansivities of phase p (p = amorphous or crystalline) along and normal to the chain axis, respectively. For the isotropic sample, $f_a = f_c = 0$ and either equation (1) or (2) reduces to

$$\alpha_{iso} = [X(\alpha_\parallel^c + 2\alpha_\perp^c) + (1-X)(\alpha_\parallel^a + 2\alpha_\perp^a)]/3 \qquad (3)$$

It should be noted that, in an aggregate model, the chain segments are regarded as rigid units, an assumption which may not hold above the glass transition where there is large-scale segmental motion in the amorphous regions. Therefore, equations (1)–(3) are expected to be valid only below T_g. Another factor which hampers the application of the two-phase aggregate model is the scarcity of data on intrinsic expansivities. The expansivities of the crystalline phase can be obtained from wide-angle X-ray diffraction measurements but, unfortunately, data are available over a wide temperature range (100–330 K) only for two polymers, polyethylene[40] and nylon-6[31,41]. There is no obvious method for determining the intrinsic expansivities of the amorphous phase. However, theoretical results[21,30,42] and the observation that $\alpha_\parallel$ and $\alpha_\perp$ for a large variety of amorphous and semicrystalline have similar orientation dependence[29] suggest that the intrinsic parameters for the two phases should have similar values, at least below T_g.

With the above consideration in mind we attempt to understand the expansion behaviour of nylon-6 in terms of equations (1)–(3). *Figure 1* shows that the draw ratio dependence of $\alpha_\parallel$ and $\alpha_\perp$ is scarcely dependent on temperature in the region 120–260 K, i.e., below the onset of the glass transition. It is therefore sufficient to consider the orientation dependence at only two temperatures, namely, 120 K and 260 K (*Figure 3*). First, the crystal parameters $\alpha_\parallel^c$ and $\alpha_\perp^c$ are taken from the literature[31,41]. Furthermore, theoretical studies[21,30,42] indicate that the axial expansivity is rather insensitive to intermolecular interaction, so it is reasonable to assume that $\alpha_\parallel^a = \alpha_\parallel^c$. Then the remaining parameter $\alpha_\perp^a$ can be found by fitting equation (3) to the data for isotropic nylon-6. We see from *Table 1* that $\alpha_\perp^a \sim \alpha_\perp^c$, i.e., the crystalline and amorphous phases have similar expansivity values, as we have discussed above. Therefore, the reason for introducing a two-phase aggregate is mainly to account for the significant difference in the degree of orientation in the two phases. As an example, for the nylon-6 sample at $\lambda = 3$, $f_c \sim 0.9$ whereas $f_a \sim 0.3$[16].

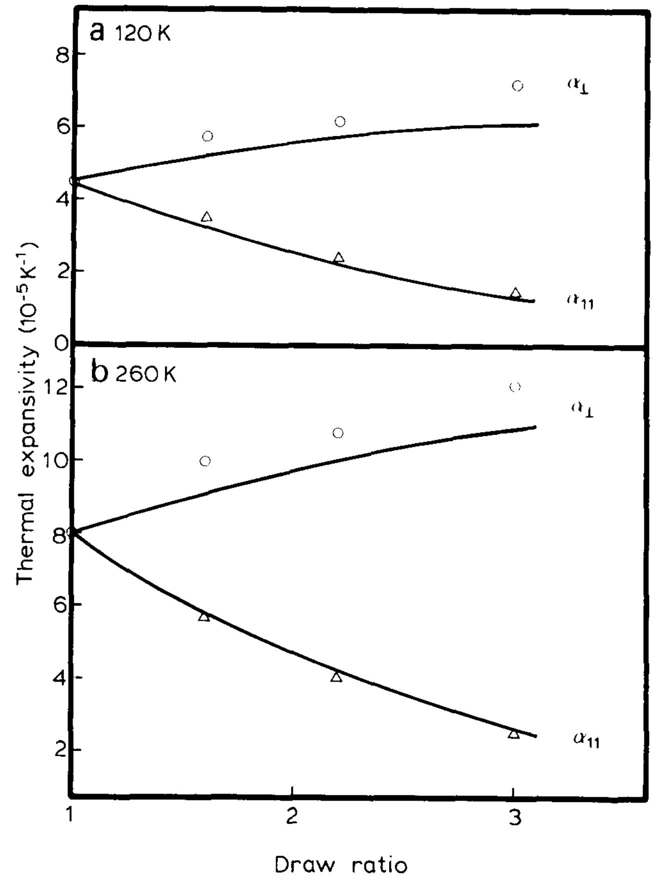

Figure 3 Draw ratio dependence of thermal expansivities for dry nylon-6 at (a) 120K and (b) 260K. The curves denote theoretical predictions according to equation (1) and (2)

Table 1 Values of intrinsic parameters (in units of 10^{-5} K^{-1}) used for the calculation of observed expansivities

T(K)	$\alpha_\parallel^c$	$\alpha_\parallel^a$	$\alpha_\perp^c$	$\alpha_\perp^a$
120	−1.1	−1.1	8.0	6.9
260	−1.5	−1.5	14	12

Using the parameters in *Table 1* and the f_c and f_a values from our previous work[16], $\alpha_\parallel$ and $\alpha_\perp$ have been calculated according to equations (1) and (2) and shown in *Figure 3*. It is apparent that the agreement with experimental results is better than 15%, indicating that the two-phase aggregate model provides a useful framework for understanding the orientation dependence of the thermal expansivities below the glass transition. However, to find out whether this model has general validity it is necessary to apply it to several polymers. Unfortunately, this will not be possible until more data on the expansivity of polymer crystals are available.

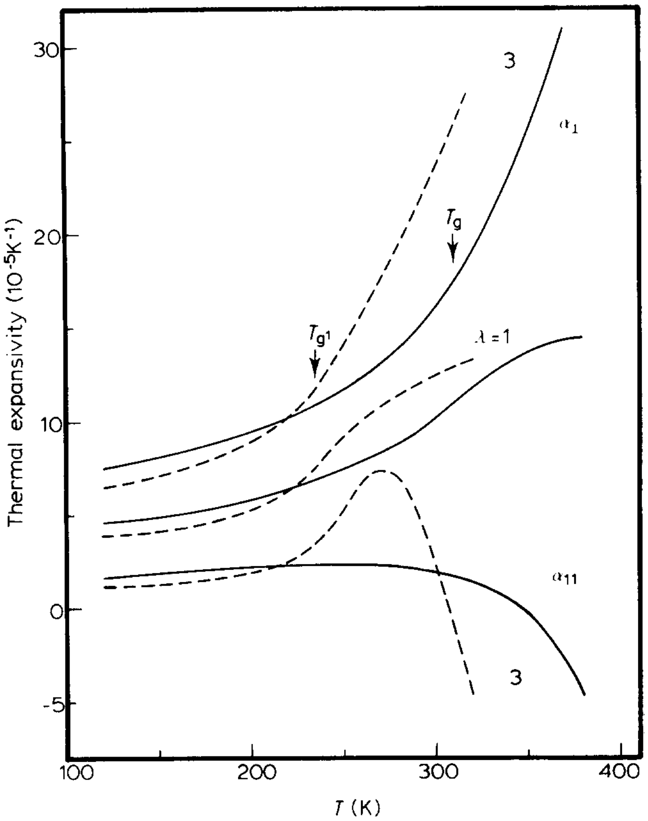

Figure 4 Effect of water on the thermal expansivities of nylon-6. The full and broken curves denote data for dry and wet samples, respectively. T_g and T_g' are the glass transition temperatures of dry and wet nylon-6, respectively

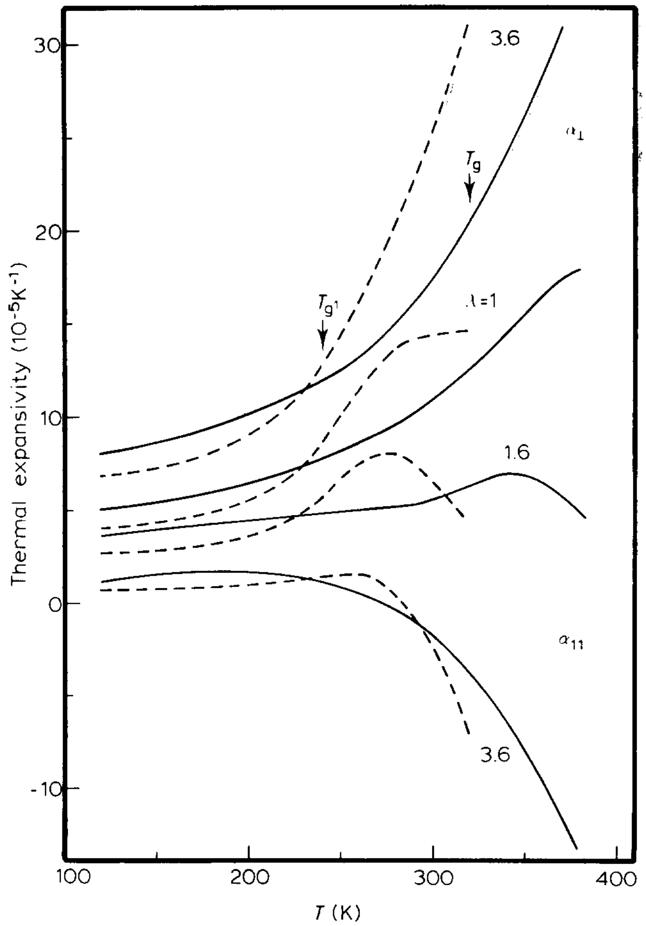

Figure 5 Effect of water on the thermal expansivities of nylon-6,6. Legends as in *Figure 4*

Effect of water

Figures 4 and *5* show the comparison between the thermal expansion behaviour of dry samples and samples saturated with water. It is seen that the temperature and orientation dependence are similar for dry and wet samples. However, the glass transition temperature of the wet samples is 80 K lower, indicating that water is a good plasticizer for nylon-6 and nylon-6,6. As a result, the rubber-elastic contraction along the draw axis and the accompanying large transverse expansion are prominent even at room temperature. We have already mentioned that water forms crosslinks between chain segments at low temperature. This leads to an increase in the strength of interchain interaction and hence a reduction in the thermal expansivity. These changes induced by water absorption are consistent with the behaviour of mechanical moduli investigated previously[5,8,16].

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