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Semi-Crystalline Films

Shrinkage Stress and Thermal Recovery on Strain-Induced Semi-Crystalline Polymers

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Summary

A study of shrinkage-stress and thermal recovery on strain-induced semi-crystalline poly(ethylene-terephthalate) (PET) films has been undertaken. The residual shrinkage ratio is discussed in term of molecular disorientation in the non-crystalline region which occurs by shrinkage process, according with a composite solid model in a series coupling.

Introduction

It is well known that in the essentially unoriented non-crystalline PET films, drawn to different extensions at 80° C, two processes occur : (1) the non crystalline chains become oriented and (2) strain-induced crystallization occurs (RIETSCH et al, 1979 ; RIETSCH, 1985). If these drawn films are then subjected to increased temperature and are allowed to shrink freely for a fixed time, the orientation of the noncrystalline chains decreases (SAMUELS, 1974 ; RIETSCH). The structure produced during the initial drawing process and the subsequent structural change that occurs on thermal shrinkage are thus intimately related.

Shrinkage stress and thermal recovery

Let us considere both the amorphous and crystalline phases according with a composite solid model in a series coupling as shown in Figure I.

The isotropic sample of N elastic chains per unit volume is characterized by its initial length L_o, cross-section S_o and volume V_o (Figure I a). After homogeneous drawing at a draw-ratio λ_p the amorphous and crystalline components (of total volume $V = V_a + V_c$) are defined respectively by its lengths : L_a, L_c ; cross-sections : S_a, S_c. The amorphous phase of $N(1-\beta)$ elastic chains is drawn at a value : λ_a (Figure I b). After thermal shrinkage at a residual length L_r, the amorphous phase relax to the random state (L_r^o, S_r^o) whereas the crystalline component remains inchanged (L_c, S_c). Then the apparent extension ratio of the non-crystalline polymer, λ_a, can be defined as shown in Figure I c : $\lambda_a = L_a/L_r^o$

The extension ratio, λ_r, after the two-stage processes (total residual extension ratio) can be written as : $\lambda_r = L_r/Lo.$

Then the two-stage processes can be quantitatively expressed by the following expressions :

$$1) \quad V = L_a S_a + L_c S_c = V_o \left(1 - \beta + \beta \frac{\overline{V_c}}{\overline{V_a}}\right)$$

$$2) \quad V_a = V_o (1 - \beta) = L_a S_a$$

3) $V_c = V_o \beta \frac{\overline{V_c}}{\overline{V_a}} = L_c S_c$

4) $L_c = \lambda_p L_o - L_a$

5) $\lambda_a = L_a / L_r - L_c$

6) $\sigma = f / S_a$

7) $\lambda_p = L / L_o = (L_a + L_c) / L_o$

where β, $\overline{V_c}$, $\overline{V_a}$ are the degree of crystallinity, specific volumes of the crystalline and amorphous regions respectively.
From these relations it can be schown that the apparent draw-ratio and cross-section of the amorphous region can be expressed as follow :

$$\lambda_a = \frac{\lambda_p - \beta \frac{\overline{V_c}}{\overline{V_a}}}{\lambda_r - \beta \frac{\overline{V_c}}{\overline{V_a}}} \qquad 8)$$

$$S_a = \frac{S_o}{\lambda_p} \left(1 - \beta + \beta \frac{\overline{V_c}}{\overline{V_a}}\right) \qquad 9)$$

Then the enginnering shrinkage stress becomes :

$$\sigma = \frac{NkT}{S_a} \left(\lambda_a - \lambda_a^{-2}\right)$$

10) $$\sigma = \frac{NkT}{S_o \left(1 - \beta + \beta \frac{\overline{V_c}}{\overline{V_a}}\right)} \lambda_p \left| \left(\frac{\lambda_p - \beta \frac{\overline{V_c}}{\overline{V_a}}}{\lambda_r - \beta \frac{\overline{V_c}}{\overline{V_a}}}\right) - \left(\frac{\lambda_r - \beta \frac{\overline{V_c}}{\overline{V_a}}}{\lambda_r - \beta \frac{\overline{V_c}}{\overline{V_a}}}\right)^{-2} \right|$$

For example, a PET film extended to $\lambda_p = 2.5$ at T = 80°C, would have complete recovery or thermal shrinkage ($\beta = 0$; $\lambda_r = 1$) (DE VRIES et al, 1977 ; RIETSCH)
Thus relations 8, 9, 10 are expressed as :

$$\lambda_a = \lambda_p \qquad S_a = S_o / \lambda_p$$

$$\sigma = NkT \left(\lambda_p^2 - \lambda_p^{-1}\right)$$

It has been shown (SAMUELS, 1974) that the sample orientation return along the original extension path during shrinkage which is primarily controlled by the behavior of the non-crystalline chains. Nevertheless during thermal shrinkage (in oil or air) the samples developped a crimps or poor heat transfer. As a consequence the non-crystalline region never allowed to relax to the random state (fam = 0). Consequently, further experimental data are needed in order to obtain more precise information on the deformation of the non crystalline phase (λ_r) and thus to define more precisely tha values of λ_a and S_a. However the results described by Samuels (1974) allow us to think that λ_p is never far from the apparent amorphous draw-ratio, λ_a.

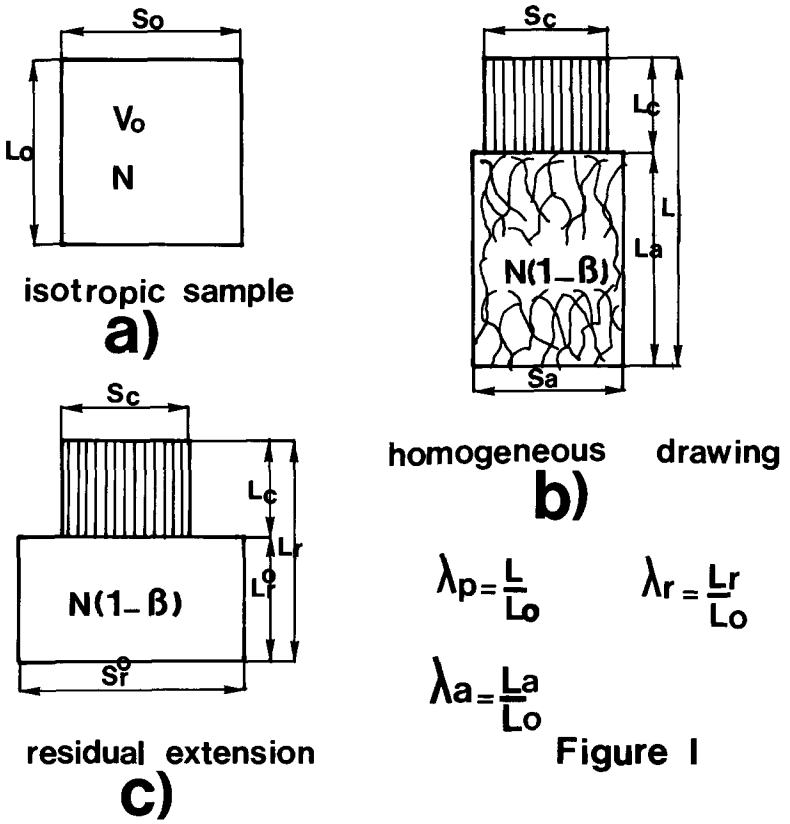

Figure I

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