The mechanical and optical properties of oriented fibres of semicrystalline polymers

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Abstract: The mechanical properties of semicrystalline polymers are very much dependent on the molecular orientation. The orientation function to deal with the elastic moduli data of Hadley et al. (1969) are treated under new aspects. To determine the nature of orientation function from empirical data a relation of the form \( \sin \theta = f(n) \sin \theta' \) is assumed to describe the change in the orientation angle of a unit from \( \theta' \) to \( \theta \) for the draw ratio \( n \). Birefringence experimental data are used to find the orientation function \( f(n) \) which is then used to calculate elastic properties. The agreement of the experimental values of \( E_0 \) and \( E_{90} \) over the entire draw ratio range is found to be satisfactory for Nylon, low density polyethylene and polyethylene terephthalate. This furnishes strong empirical evidence for the validity of the orientational model for the above substances.

Key words: Orientation of polymer chains, birefringence, mechanical properties, semicrystalline polymers.

1. Introduction

It is well known that crystallinity and orientation are the two most important factors on which the mechanical properties of semicrystalline polymers depend. If the crystallinity remains practically constant it is reasonable to expect that the aggregate model [1] would give a fairly good account of the development of mechanical anisotropy on drawing. But it has been found that in the case of low density polyethylene (LDPE) where the crystallinity remains practically constant [2] the aggregate model predicts the experimental results only qualitatively and the quantitative agreement is far from satisfactory [3]. The limitation of the aggregate model has been mainly assigned to the use of an affine deformation scheme [3, 4]. It is also seen that the non affine deformation proposed by Rataty [5] is also inadequate to interpret the elastic moduli data of LDPE at all temperatures and over the entire draw ratio range. From an analysis of the experimental results on elastic moduli of LDPE it has been shown [6] that the mode of change of orientation with draw ratio is different at different temperatures. It seems therefore unlikely that the pattern of change of orientation on drawing for different polymers will be the same. Our aim in the present paper is to examine this question on the basis of the available empirical data on birefringence. It is seen that these data very clearly indicate that the model of change of orientation takes different patterns for different polymers.

In the next section we present a method of extracting information regarding change of orientation from birefringence data. The corrections of these orientation functions are then tested by applying them to calculate the elastic moduli for semicrystalline polymers which are considered as transversely isotropic elastic bodies. Excellent agreement between the calculated and experimental values give strong evidence for the essential correctness of the orientation function obtained from the birefringence data and confirm the conjecture that this function is different for different materials.

2. Mechanical properties

The expressions for Young’s modulus along the draw direction \( (E_0) \) and perpendicular to the draw direction \( (E_{90}) \) are given by [1]

\[
\frac{1}{E_0} = I_1 S_{11} + I_2 S_{33} + I_3 (2 S_{13} + S_{44})
\]
and

$$\frac{1}{E_{90}} = \frac{1}{8} \left( 3 I_2 + 2 I_5 + 3 \right) + \frac{3}{8} I_1 S_{33} +$$

$$+ \frac{1}{8} \left( 3 I_3 + I_4 \right) \left( S_{44} + 2 S_{13} \right).$$

Where $S_{ij}$ etc. are the compliance constants of the basic unit of which the polymer is supposed to be composed of and

$$I_1 = \langle \sin^4 \theta \rangle, \quad I_2 = \langle \cos^4 \theta \rangle, \quad I_3 = \langle \sin^2 \theta \cos^2 \theta \rangle,$$

$$I_4 = \langle \sin^2 \theta \rangle, \quad \text{and} \quad I_5 = \langle \cos^2 \theta \rangle.$$

Of the five $I$'s knowing $I_1$ and $I_2$ the others can be evaluated. This follows from the following relations

$$I_1 + I_2 + 2 I_3 = 1, \quad I_4 + I_5 = 1, \quad I_1 - I_4 + I_3 = 0.$$

The expressions for $E_0$ and $E_{90}$ can be expressed as

$$\frac{1}{E_0} = \frac{1}{2} \left[ I_1 (2 S_{11} - Z) + I_2 (2 S_{33} - Z) + Z \right]$$

and

$$\frac{1}{E_{90}} = \frac{1}{8} \left[ I_1 (3 S_{33} - S_{11} - Z) + 2 I_2 (2 S_{11} - Z) +$$

$$+ 4 S_{11} + 2 Z) \right]$$

with $Z = 2 S_{13} + S_{44}$.

It is assumed that for the draw ratio $n$ the change of orientation is described by the relation

$$\sin \theta = f(n) \sin \theta'$$

where $\theta$ and $\theta'$ are the angles made by the c-axis of the unit with the draw direction at the drawn and undrawn state respectively.

It is well known that birefringence provides a simple and very useful method of finding the orientation in polymers. It has been shown [1] that the value of birefringence ($\Delta n$) at any draw ratio is connected with the maximum birefringence ($\Delta n_0$) by the relation

$$\Delta n = \Delta n_0 \left[ 1 - \frac{3}{2} \langle \sin^2 \theta \rangle \right].$$

From this we get,

$$I_4 = \langle \sin^2 \theta \rangle = \frac{2}{3} \left( 1 - \frac{\Delta n}{\Delta n_0} \right).$$

With the help of (3) and (5) we get,

$$f^2(n) = 1 - \frac{\Delta n}{\Delta n_0}.$$

Thus we find that the birefringence data leads directly to a knowledge of orientation function $f(n)$. Knowing $f(n)$ we can evaluate $I_1$ and $I_2$ from the relations

$$I_1 = \frac{8}{15} f^4(n)$$

and

$$I_2 = 1 - \frac{4}{3} f^2(n) + \frac{8}{15} f^4(n).$$

Using $I_1$ and $I_2$ calculated from the birefringence data it is possible to calculate $E_0$ and $E_{90}$ by using equations (1) and (2).

3. Application

Hadley et al. [7] have measured the birefringence and elastic moduli for low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET) and Nylon. We have tried to apply the present method and found that it is adequate to interpret the elastic moduli of LDPE, PET and Nylon.

The maximum birefringence ($\Delta n_0$) for these polymers calculated by extrapolating the birefringence vs draw ratio data to infinite draw ratio. The variation of $f^2(n)$ with draw ratio as derived from birefringence data is shown in figure 1. The compliance constants $S_{11}$ and $S_{33}$ for the basic unit is evaluated as the reciprocals of the $E_0$ and $E_{90}$ values corresponding to the maximum birefringence. The only parameter in the present calculation is $Z = 2 S_{13} + S_{44}$ which is estimated to give exact fit at the undrawn state. The data used in the present calculation is presented in table 1. The results on the calculation of $E_0$ and $E_{90}$ for LDPE, PET and Nylon are furnished in figures 2 to 4.