The Effect of Heat Setting on the Structure and Mechanical Properties of Poly(ethylene Terephthalate) Fiber. II. The Elastic Modulus and Its Dependence on Structure

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Synopsis

The effects of temperature, time of heat setting, and rate of cooling on the elastic modulus of free- and taut-annealed poly(ethylene terephthalate) (PET) fibers were determined at different time scales using Instron, Rheovibron, and pulse propagation meter. The correlation of the elastic modulus with structure is critically examined in terms of the widely used simple one-phase and two-phase models for fiber modulus. It is concluded that these simple models are not universally applicable.

INTRODUCTION

Elastic modulus is a measure of the resistance to initial deformation and is one of the most important properties of textile fibers. The elastic modulus of PET fibers having widely differing structural states has been studied by a number of workers.[1-12] However, in most of these studies, the specimen were prepared by heat setting the drawn fiber in the relaxed state; moreover, the effect of the various heat setting parameters and the time scale of the experiments have not been systematically investigated. Some attempts have been made to establish qualitative and quantitative correlations between mechanical properties and structural parameters and morphology. The simplest model, postulated by Moseley,[13] considered the fiber to be a single-phase structure in which the intrinsic mechanical properties of the unit forming the fiber and their orientation determined the sonic modulus E of the fiber:

$$E = \frac{E_t^0}{\langle \sin^2 \theta \rangle_{\text{av}}} \tag{1}$$

where E_t^0 is the intrinsic lateral (transverse) modulus of the unit, θ is the angle between the molecule and the fiber axis, and $\langle \sin^2 \theta \rangle_{\text{av}}$ represents the average value of $\sin^2 \theta$. Ward[14] showed that eq. (1) represented the elastic modulus of fiber if certain approximations were made. Samuels[15,16] extended eq. (1) to two-phase systems by assuming a series coupling between the crystalline and amorphous phase and showed that

$$\frac{1}{E} = \frac{\beta}{E_{t,c}^0} \langle 1 - \cos^2 \theta_c \rangle_{\text{av}} + \frac{1-\beta}{E_{t,am}^0} \langle 1 - \cos^2 \theta_{am} \rangle_{\text{av}} \tag{2}$$

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where E is the modulus of the fiber; β is its degree of crystallinity; $E^0_{t,c}$ and $E^0_{t,am}$ are the intrinsic lateral Young's moduli for the crystalline and amorphous phases, respectively; and θ_c and θ_{am} are the angles made by the molecules in the two phases with the fiber axis.

Equation (2) was applied to Dumbleton's data[5,6] on PET samples annealed under relaxed conditions by Samuels,[16] and a good correlation was shown to exist. Prevorsek et al.[4] have stated, without giving detailed data, that in PET such a simple correlation may often exist; however, there are also numerous exceptions. Data on a limited number of samples had earlier indicated[17] that Samuels' model was not applicable, and this led to a reexamination[18] of the intrinsic birefringence values. As a result, new values were proposed. The elastic modulus data on a large number of samples having different structures are now presented and the validity of the simple one-phase and two-phase models critically examined.

EXPERIMENTAL

The experimental details of sample preparation and structural studies were given in part I.[19] In brief, commercial multifilament PET yarn was heat set in the free (FA) and taut (TA) conditions in a silicone oil bath maintained at temperatures between 100 and 220°C for times varying from 1 to 60 min. On being taken out of the bath, the samples were quenched in air. In one case, the 60-min set of samples, the cooling rate was varied by allowing the yarn to cool in the bath itself over a period of 12 hr.

For the measurement of Instron modulus, load-elongation curves of multifilament yarns of gauge length of 5 cm were taken on an Instron tensile tester at an extension rate of 100%/min. Young's modulus was obtained from the initial slope of the stress–strain curve by taking an average of 40 tests.

Sonic velocity through the yarn was measured on a pulse propagation meter (PPM-5R) at room temperature, at 5 kHz. During measurement, a constant weight of 5 g was applied to all the samples to keep the yarn in tension. The sonic modulus is given by

$$E\ (\text{dyn/cm}^2) = \rho C^2 \tag{3}$$

where ρ (g/cm^3) is the density of the fiber and C (cm/sec) is the sonic velocity.

Dynamic modulus at 110 Hz was measured on a direct-reading viscoelastometer, the Rheovibron model DDV-II, on the set of samples heat set for 30 min. The tests were performed on a strand made up of four multifilament yarns, and the length of the sample was kept approximately 4 cm. All these studies were performed in a temperature- and humidity-controlled laboratory.

Ideally, mechanical data should be obtained on single filaments to prevent complications due to the distribution of load in a multifilament yarn.[11] The present mechanical studies were however made on multifilament yarns. This was done because in the case of the Rheovibron and the pulse propagation meter, single filaments of the multifilament yarn, which are very fine, can not be used or present difficulties. For the Instron measurements also, multifilament yarn was used because comparison of data then becomes more meaningful.

RESULTS AND DISCUSSION

Effect of Heat Setting Parameters and Time Scale of Experiment on Elastic Modulus

The Instron and sonic moduli of heat-set samples are presented in Figure 1 as a function of heat setting temperature for free- as well as taut-annealed samples. The Instron, Rheovibron, and sonic moduli data for the free- and taut-annealed samples heat set for 30 min are presented in Figure 2 to highlight the effect of the time scale of the experiment on the modulus values. The main observations, with possible explanations, are given below:

(1) In all cases, the moduli of taut-annealed samples are close to the modulus of the control, while the free-annealed samples have lower values than the control and the taut-annealed samples. This suggests that orientation rather than crystallinity is important in determining the modulus.

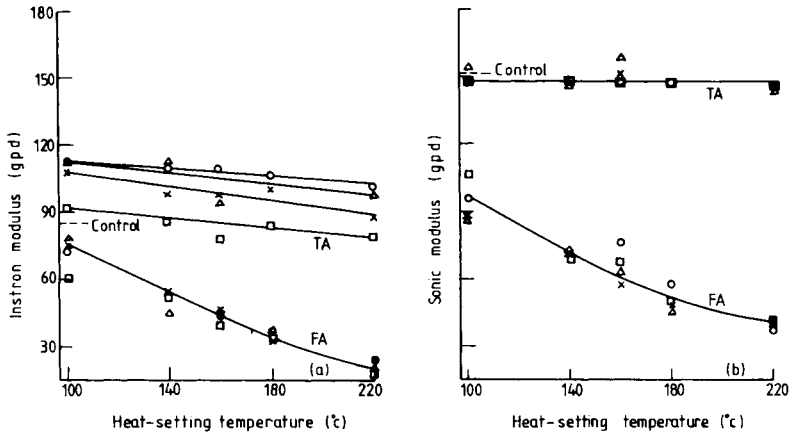

Fig. 1. Dependence of (a) Instron and (b) sonic modulus on heat-setting temperature for free- and taut-annealed samples: (○) 1 min; (△) 15 min; (□) 30 min; (×) 60 min.

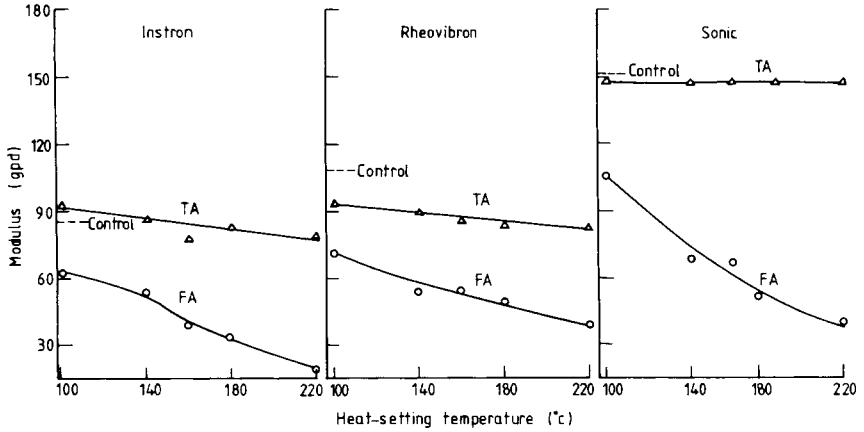

Fig. 2. Dependence of Instron, Rheovibron, and sonic modulus on heat-setting temperature for free- and taut-annealed samples heat set for 30 min.

(2) The sonic modulus values are higher than the Rheovibron modulus values, which, in turn, are higher than the Instron modulus values for free- as well as taut-annealed samples. This obviously is a result of the different time scales.

(3) The Instron and Rheovibron moduli of taut-annealed samples decrease very slightly with increase in heat-setting temperature, while the sonic modulus remains almost constant. This is apparently because the measurements involving high time scales will be influenced by the amorphous phase, while those at low time scales will reflect the state of the crystalline phase.

(4) The Instron, Rheovibron, and sonic moduli for free-annealed samples decrease with increase in heat setting temperature. Both amorphous and crystallite orientation also show a decrease for this set of samples.

(5) Compared to temperature, the time of heat setting has relatively less effect on the modulus. It was also observed that the effect of the rate of cooling on the modulus, within the range investigated, is very limited and does not show a clear trend; the data are therefore not presented. This is in reasonably good agreement with structural data.

CRITICAL EVALUATION OF THE EXISTING MODELS

One-Phase Model

Moseley postulated a one-phase model[13] for the sonic modulus which results in eq. (1) given earlier. Ward[14] showed that this had general applicability provided that certain assumptions are satisfied. These assumptions and their validity are disucssed later.

The birefringence Δn of a fiber is given by the following equation[20]:

$$\Delta n = \Delta n_{\max}\left(1 - \frac{3}{2}\langle \sin^2 \theta \rangle_{\text{av}}\right) \tag{4}$$

where $\Delta n_{\max}$ is the maximum birefringence of the fiber and $\langle \sin^2 \theta \rangle_{\text{av}}$ represents the average distribution function. Substituting for $\langle \sin^2 \theta \rangle_{\text{av}}$ from eq. (4) in eq. (1), we obtain

$$\frac{1}{E} = \frac{2}{3E_t^0} - \frac{2\Delta n}{3\Delta_{n\ \max} E_t^0} \tag{5}$$

For any given fiber, E_t^0 and $\Delta n_{\max}$ will be constant. This suggests that if the compliance $1/E$ is plotted as a function of birefringence Δn, we should obtain a straight line with negative slope if the model is valid. The plots between compliance and birefringence for Instron and sonic moduli for the taut-annealed samples are shown in Figure 3. It is seen that the compliance can even increase with increasing birefringence, which is contrary to Moseley's model. In the case of free-annealed samples, however, though the scatter in results is considerable, the compliance does decrease with increasing birefringence, and the correlation coefficients turn out to be -0.43 for the Instron compliance and -0.53 for sonic compliance. However, compliance correlates better with the amorphous orientation factor f_a, the corresponding correlation coefficients being -0.86 and -0.90. The results on free-annealed samples are in agreement with those of other workers.[16]

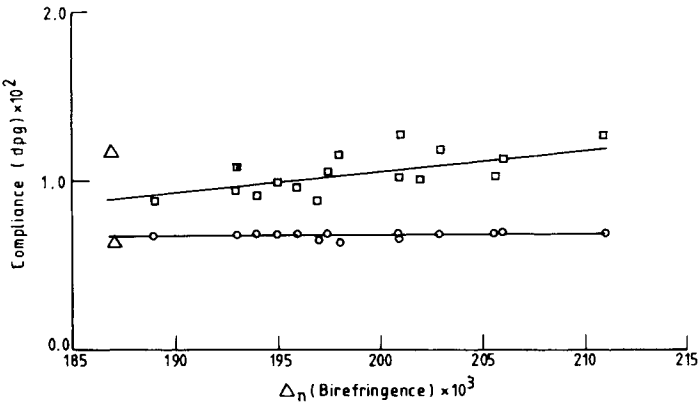

Fig. 3. Dependence of Instron and sonic compliance on birefringence for taut-annealed samples: (○) sonic; (□) Instron; (△) control.

Two-Phase Model

Samuels[16] extended the simple one-phase model to a two-phase system, and eq. (2) given earlier correlates modulus with structural parameters. For calculating modulus on the basis of this model, intrinsic values of the lateral moduli $E^0_{t,c}$ and $E^0_{t,am}$ are required. Intrinsic modulus values can be found using the following equation[16]:

$$\frac{3}{2E_u} = \frac{\beta}{E^0_{t,c}} + \frac{1-\beta}{E^0_{t,am}} \tag{6}$$

where E_u is the measured modulus of unoriented PET fiber and β is its degree of crystallinity. This equation can be written as

$$\frac{3}{2E_u} = \frac{1}{E^0_{t,am}} - \beta\left[\frac{1}{E^0_{t,am}} - \frac{1}{E^0_{t,c}}\right]. \tag{7}$$

A plot between $1/E_u$ and β should give a straight line; the values of $E^0_{t,am}$ and $E^0_{t,c}$ are computed from the intercepts of $\beta = 0$ and $\beta = 1$, respectively. Such a plot, based on the data of Dumbleton,[21] Thompson and Woods,[1] and Kawaguchi,[2] is shown in Figure 4 and leads to the values of intrinsic moduli quoted in Table I.

Using the values of the intrinsic lateral moduli given in Table I, the modulus of a fiber can be predicted on the basis of Samuels' two-phase model by making use of eq. (2) if the structural parameters and the intrinsic birefringence values are known. For the free- and taut-annealed samples heat set for 30 min, the widely used intrinsic birefringence values[16,22] of $\Delta^0 nc = 0.212$ and $\Delta^0 na = 0.275$ were used, and it was found[17] that the predicted curves showed no resemblance to the experimental curves. This is also the case when the analysis is extended to Instron and sonic modulus data for all the samples studied.

To understand the cause of this discrepancy, the intrinsic birefringence values of PET were computed[18] from the present data and were found to be $\Delta^0 nc = 0.29$ and $\Delta^0 na = 0.20$. The predicted moduli using these values of intrinsic birefringence are shown in Figure 5 as a function of heat-setting temperature for the 30-min set of samples. The predicted values and the trends now compare quite well with the experimental data (Fig. 2) for the free-annealed samples but not for the taut-annealed samples.

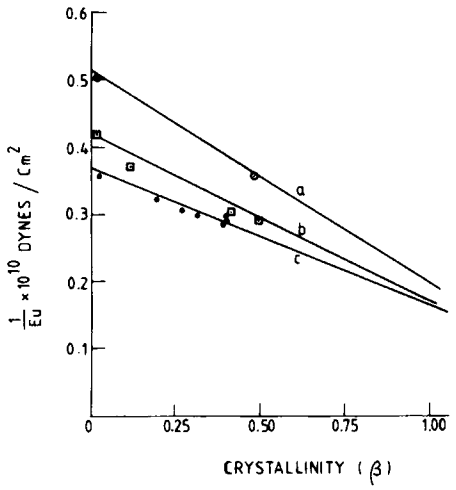

Fig. 4. Plot between compliance and crystallinity for unoriented PET based on data of (a) Thompson and Woods,[1] (b) Kawaguchi,[2] and (c) Dumbleton.[21]

Some Comments on the Models

The above analysis shows that the simple one-phase model considered here cannot predict the elastic modulus of taut-annealed samples, though it does succeed to some extent in the case of the free-annealed samples. This is because while in free-annealed samples both average molecular orientation and elastic modulus measured at different time scales decrease with increase in heat-setting temperature, in taut-annealed samples the birefringence increases while the elastic modulus may decrease. The amorphous orientation factor correlates better with the elastic modulus, as stated earlier. In taut-annealed samples, the amorphous orientation factor was shown[19] to decrease with increase in heat-setting temperature and would therefore appear to be better correlated with Instron and Rheovibron moduli, which also decrease with increasing heat-setting temperature (Fig. 2), but not with the sonic modulus, which remains almost constant. This suggests that the structural parameters that are important at low frequencies of measurement may not necessarily be of equal importance at high frequencies. Thus, the analysis of the data based on different measurement techniques in terms of a single model may be open to criticism.

The assumptions that are implicit in Moseley's model are[13,14] (1) The extensional compliance is very small compared to the transverse compliance, which in turn is close to the torsional compliance; and (2) the sample has relatively low orientation. The validity of the first assumption has not been tested for the samples under investigation, while the second assumption does not apply to them.

TABLE I
Intrinsic Values of Transverse Moduli

	Modulus, gpd	
	$E^0_{t,c}$	$E^0_{t,am}$
Instron modulus (extension rate 100%/min)	26.6	11.2
Rheovibron modulus (110 Hz)	30.5	13.7
Sonic modulus (5 kHz)	31.9	15.3

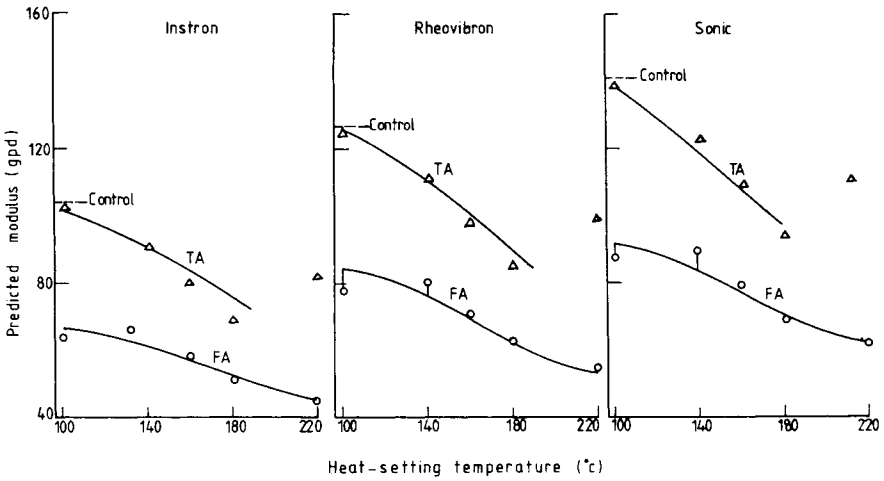

Fig. 5. Modulus predicted by Samuels' two-phase model (using $\Delta_{nc}^{0} = 0.29$ and $\Delta_{na}^{0} = 0.20$) vs. heat-setting temperature.

It is also clear from the analysis presented in this report that the two-phase model is relatively less successful with taut-annealed samples. This model assumes that there is series coupling between the two phases. In view of this, it is not surprising that it gives good correlation for free-annealed samples but not for the taut-annealed samples. This aspect will be taken up in greater detail in part III,[23] where the type of coupling for the two sets of samples will be shown to be different.

In conclusion, it may be stated that various structural and morphological factors determine the elastic modulus of PET fibers and that the role played by these various factors is a function of the time scale of the method by which the modulus is measured. In addition to the degree of crystallinity, crystallite orientation, and amorphous orientation, which have been included in Samuels' two-phase model, the size and distribution of the crystallites and their connectivity with the amorphous regions must also be taken into account. Finally, it must be appreciated that the intrinsic birefringence affects the predictions considerably, and hence "correct" values must be used.

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