NOTE

Effect of Fiber Nonuniformity on the Dynamic Mechanical Behavior of Poly(ethylene Terephthalate)

INTRODUCTION

Occasionally, anomalous dynamic mechanical results are encountered with poly(ethylene terephthalate), PET, fibers drawn to low draw ratios. Figure 1 shows the dynamic moduli for a PET fiber nominally drawn 3×. The interesting feature is the appearance

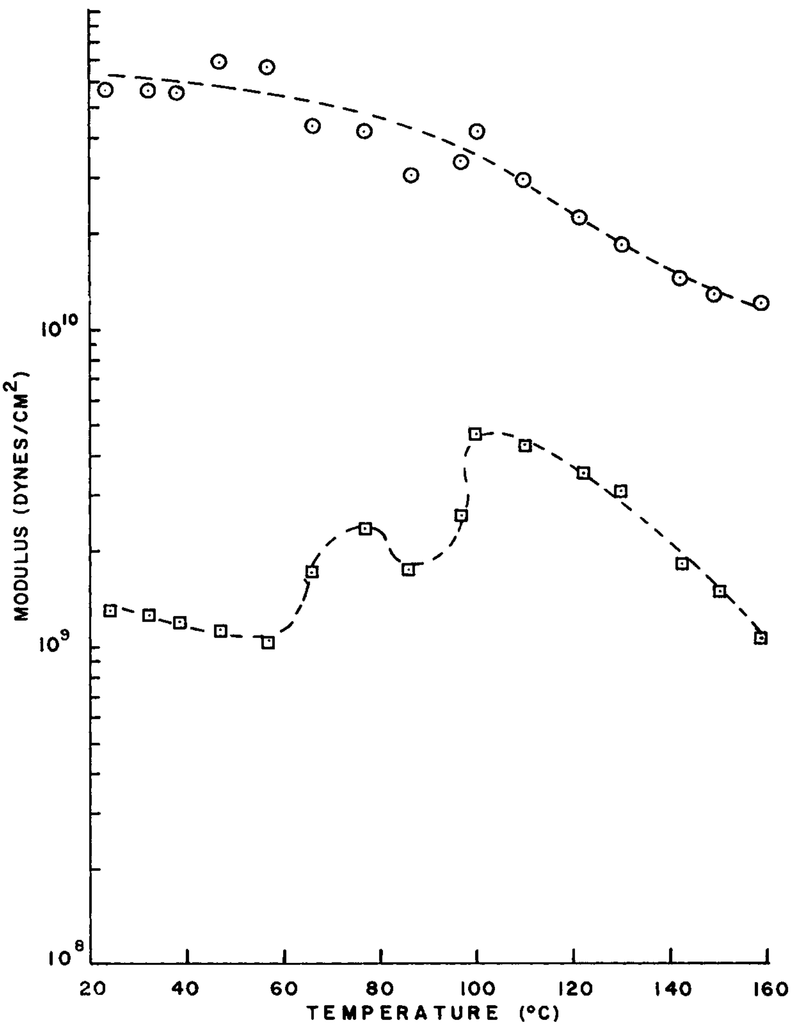

Fig. 1. Anomalous dynamic mechanical behavior of PET sample drawn 3X: (⊙) E'; (⊡) E''.

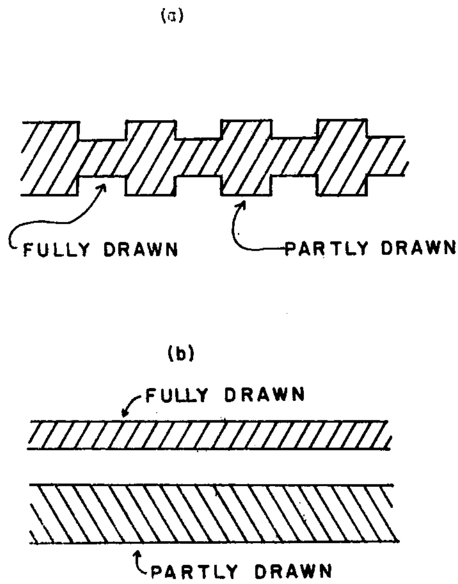

Fig. 2. Drawing nonuniformities: (a) drawn and partly drawn sections in series along fiber length; (b) drawn and partly drawn fibers.

of two maxima in the loss modulus, E'', in a region of temperature in which only one maximum is expected.[1]

Attention may be drawn to the dynamic behavior of block copolymers in which the loss modulus reflects the properties of each component separately. Since PET is a homopolymer, it is concluded that physical differences rather than chemical differences are responsible for the anomaly. The physical differences appear to be a consequence of nonuniformities introduced in the drawing process.

BACKGROUND

It is well known that care is necessary if it is desired to draw PET uniformly to draw ratios less than about $3\times$. If drawing is carried out at too high a speed or too low a temperature, then fiber nonuniformities can occur. Typical nonuniformities are shown in Figure 2, in which some filaments are shown with drawn and partly drawn sections while still other fibers do not appear to be fully drawn along the entire length examined; this length may be 10 cm or more.

Nonuniformities such as those shown in Figure 2a are not responsible for the behavior shown in Figure 1, since the drawn and partly drawn sections are in series. The dynamic mechanical properties of an assembly of such filaments would be intermediate between the properties of the component material. Therefore, emphasis will be placed on an assembly of fibers such as is shown in Figure 2b. The mechanical properties of this parallel arrangement should show the features of the components.

Consider a yarn made up of drawn and partly drawn fibers as shown in Figure 2b. The two types of fiber are grouped into N_1 fibers of type 1 and N_2 fibers of type 2. Type 1 fibers have a cross-sectional area A_1 and a dynamic complex modulus E_1^*. A similar nomenclature applies to type 2 fibers. The complex modulus of the assembly is given[2] by

$$E^* = E_1^* + (1 - \psi)E_2^* \tag{1}$$

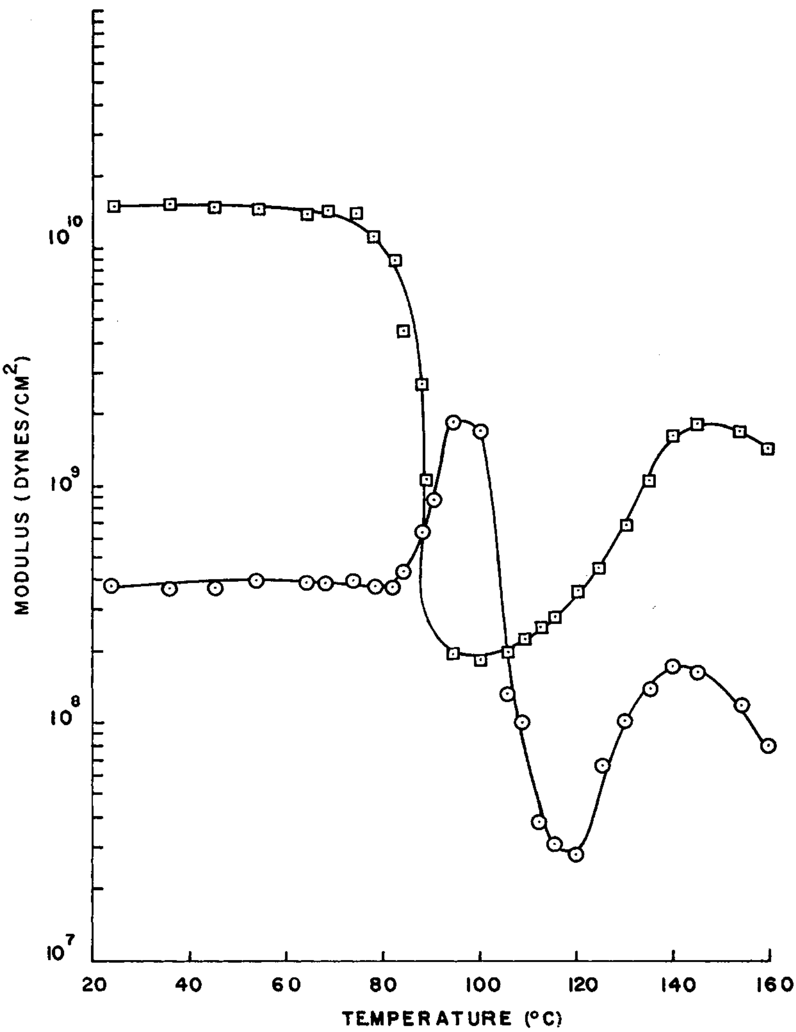

Fig. 3. Dynamic mechanical behavior of spun PET sample: (⊡) E'; (⊙) E''.

where $\psi = (N_1A_1)/(N_1A_1 + N_2A_2)$. Since $E_1^* = E_1' + iE_1''$ and $E_2^* = E_2' + iE_2''$, eq. (1) may be rewritten as follows to give the real and imaginary parts of E^*:

$$E' = E_1' + (1 - \psi)E_2' \tag{2}$$

and

$$E'' = E_1'' + (1 - \psi)E_2'' \tag{3}$$

EXPERIMENTAL

The predictions of eqs. (2) and (3) were tested on a model yarn composed of filaments of known nonuniformity. The model yarn was prepared by plying together spun fibers and fibers drawn 4×. The yarn contained 50% spun material by volume.

The dynamic mechanical properties of the model yarn were determined with a Vibron viscoelastomer at 11 c/sec. A nitrogen atmosphere was used, and data were collected every 5°C except near the maxima where readings at 1°C intervals were made. The yarn was allowed to shrink on heating between each measurement up to the maximum tem perature used of 140°C. A problem encountered with the model yarn was yarn crimpin

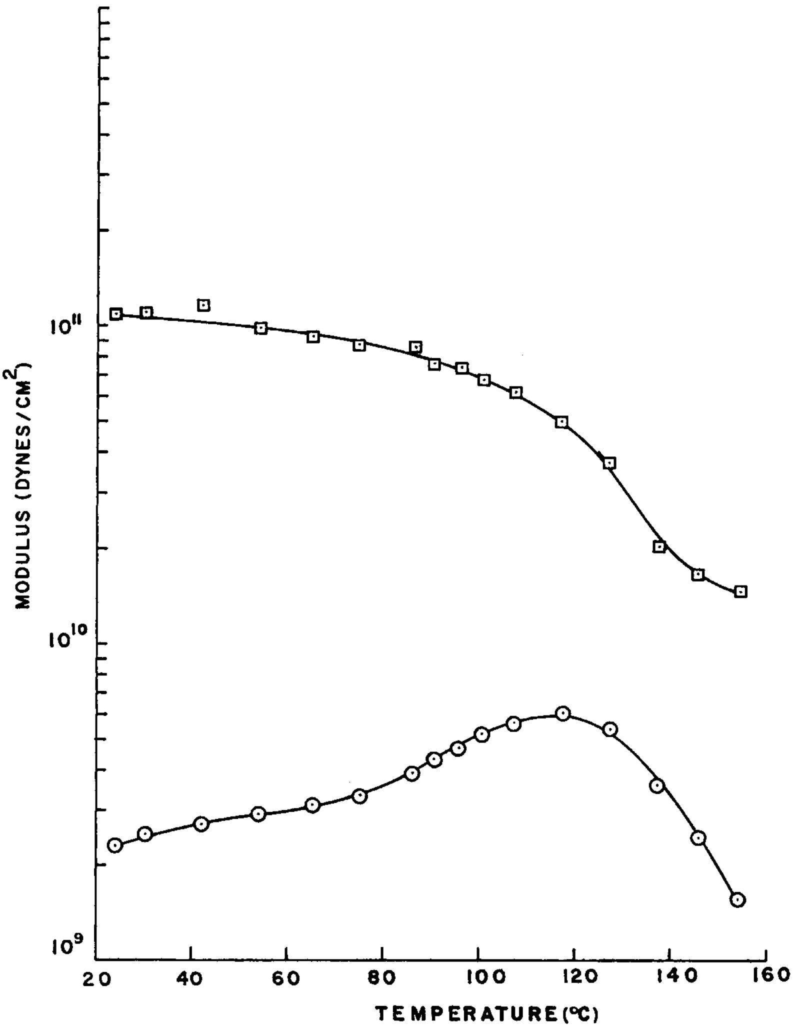

Fig. 4. Dynamic mechanical behavior of PET sample drawn 4X: (⊡) E'; (⊙) E''.

as the temperature was increased. This was caused by a disparity in the shrinkage between the spun and drawn fibers. The problem was minimized by choosing a spun yarn which had received orientation during the spinning process; the birefringence of this spun yarn was 0.004. The shrinkage behavior of the spun fibers closely paralleled that of the drawn fibers.

The appropriate moduli for substitution in eqs. (2) and (3) were obtained from dynamic measurements on the spun yarn and on yarn drawn to 4×.

The Vibron allows direct measurement of the real part of the modulus E' and of the loss factor tan δ. The loss modulus E'' is obtained from the equation

$$E'' = E' \tan\delta.$$

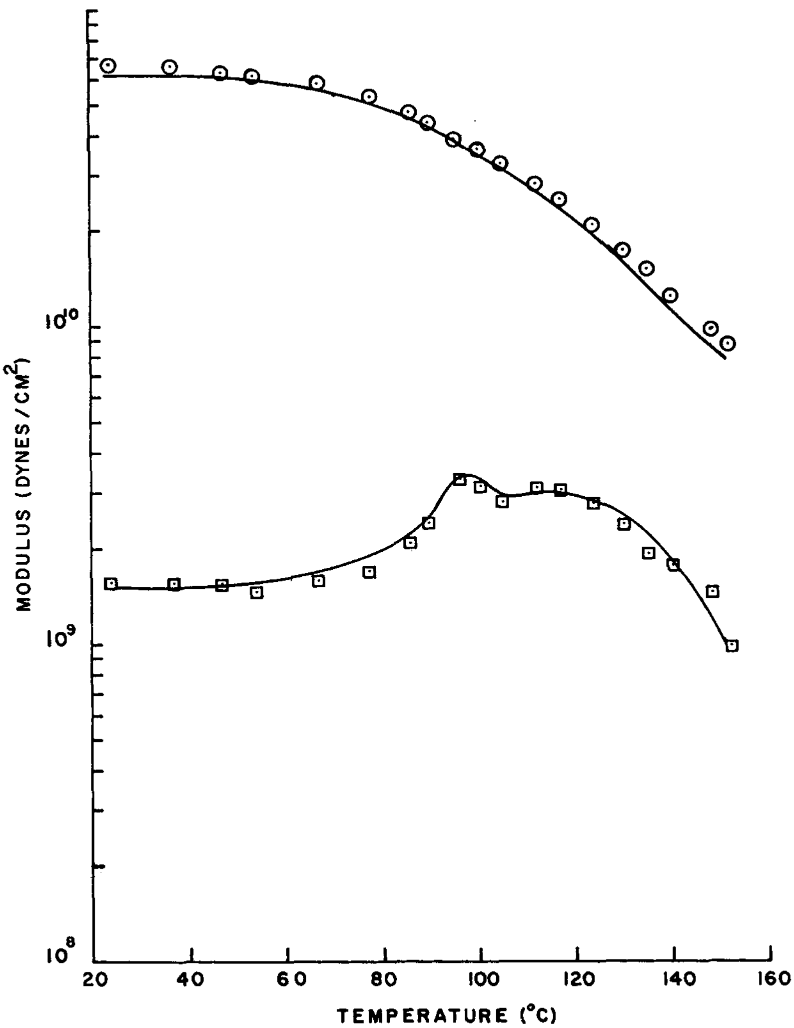

Fig. 5. Observed and calculated dynamic mechanical data for model PET sample: (—) calculated; (⊙) E' experimental; (⊡) E'' experimental.

The E'' values have an error which depends on the error in both E' and tan δ. For this reason it is advisable not to calculate E'' directly from the E' and tan δ values. Instead, E' and tan δ are plotted versus temperature, and a smooth curve is drawn through each set of data. At any given temperature the smoothed values are used to calculate E''. This procedure was followed in the present work.

DISCUSSION

Figure 3 shows the dynamic properties of the spun yarn. There is a maximum in E'' at 95°C and a corresponding steep fall in E'. Usually the experiment would be terminated at this temperature, but in the present case the measurements were continued up to 140°C. It is found that there is a partial recovery in E' at higher temperatures and also a further small peak in E''. This behavior is caused by crystallization. The crystals exert a stiffening effect and also inhibit motion in parts of the noncrystalline regions. The density of the spun sample was 1.335 g/cm^3 before the Vibron measurements and 1.377 g/cm^3 after the measurements. The crystallinity, therefore, changed from 0% to 27%. The sample was unoriented since the birefringence was zero after heating.

Figure 4 shows the dynamic properties of the 4× yarn. The sample has a maximum in E'' at 119°C, and the decrease in E' is moderate. The 4× sample is both oriented and crystalline, and this accounts for the position of the E'' maximum and the smaller decrease in E'.[3]

Figure 5 gives the dynamic properties of the model yarn. The E'' curve has two peaks, in positions corresponding to the peak from the 4× sample and the main peak from the spun sample. Also shown in Figure 5 are the E' and E'' values calculated from eqs. (2) and (3). There is good agreement between the observed and calculated curves. It is therefore proposed that nonuniformities such as shown in Figure 2b are responsible for the behavior shown in Figure 1. In the general case, other nonuniformities may be present, and the dynamic behavior would be correspondingly changed. However, the method used to obtain eq. (1) could be extended to cover these other cases.

References

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