

letters

Comments on a paper by D. Hofmann *et al.*
Polymer 1989, 30, 242–247

Limits to the maximum attainable modulus of poly(ethylene terephthalate)

Introduction

Recently, Hofmann *et al.*¹ published the results of an investigation on the supramolecular structure of uniaxially drawn poly(ethylene terephthalate) (PET) samples of high modulus. In their paper the authors concluded that there exists no distinct correlation between Young's modulus on the one hand and crystallite sizes and lattice distortions on the other hand. In spite of extensive variation of drawing parameters, Hofmann and co-workers were not able to produce samples with an axial Young's modulus higher than 17 GPa, which the authors stated to be ~15% of the maximum value of the crystal modulus of PET. They attributed this 'disappointing' experimental result to the detrimental effect on the axial modulus of chain entanglements, chain ends and the complex structure of the PET molecules.

In this letter we re-emphasize that it is the *finite chain length* of macromolecules that sets an upper, theoretical limit to the maximum achievable modulus of polymers *oriented through tensile drawing*. This limit can be approached, of course, only under experimental conditions where other factors that limit the draw ratios of polymers have been removed, such as crystallites and/or chain entanglements. Here, we will demonstrate that Hofmann *et al.*¹ did not reach only 15%, but, as a matter of fact, over 60% of the maximum attainable modulus in their PET tensile drawing experiments.

We employed the previously introduced, zero-parameter theory for the development of the axial Young's modulus of drawn polymers^{2,3}. The theory assumes that orientational drawing of flexible polymers proceeds in an affine fashion; its applicability is therefore limited to experimental conditions favouring affine deformation, such as relatively low drawing temperatures. In the model, the partially oriented polymer is considered to be comprised of only two types of elastic elements; 'helix' elements, that are perfectly oriented in the direction of the draw, and 'coil' elements which are unoriented. Tensile drawing is understood to increase the fraction, f_h , of helix elements at the expense of the fraction of coil elements, $(1-f_h)$. The two elements are characterized by their respective moduli: E_h , the theoretical axial chain modulus, and E_u , the modulus of the unoriented material in which, strictly speaking, $f_h=0$. Following Ward *et al.*⁴, the model assumes a uniform stress distribution in the helix and coil elements. On the basis of these assumptions the Young's modulus of a flexible polymer that is drawn to a draw ratio, λ , is given by the equation:

$$E = \left(E_u^{-1} - \left[\frac{3\lambda^3}{2(\lambda^3-1)} [1 - (\lambda^3-1)^{-1/2}] \times \tan^{-1}\{(\lambda^3-1)^{1/2}\} - \frac{1}{2} \right] (E_u^{-1} - E_h^{-1}) \right)^{-1} \quad (1)$$

which for $\lambda > 5$ to good approximation reduces to:

$$E = \left[E_h^{-1} + (E_u^{-1} - E_h^{-1}) \left(\frac{3\pi}{4} \right) \lambda^{-3/2} \right]^{-1} \quad (2)$$

Note that a plot of E^{-1} versus $\lambda^{-3/2}$, at sufficiently high values of λ , is predicted to yield a straight line with slope $(E_u^{-1} - E_h^{-1})(3\pi/4)$, and an intercept of E_h^{-1} (the reciprocal theoretical modulus) at

$\lambda^{-3/2}=0$. This implies that the model is particularly well suited to estimate theoretical axial moduli of flexible chain polymers. Equations (1) and (2) do not contain any molecular weight dependent variables or parameters. Thus the model predicts, in agreement with numerous experimental observations, the Young's modulus to depend *uniquely* on the absolute draw ratio, provided that deformation proceeds in a (near) affine mode.

The molecular weight, or rather chain length, does set a limit, however, to the average maximum ratio, λ_{max} , to which a polymer chain can be elongated⁵. The latter quantity, for unperturbed chains, is given by:

$$\lambda_{max} = \frac{l_p}{l} \sqrt{\frac{n}{C_\infty}} \quad (3)$$

where n is the number of chain segments having a length l and a projected length l_p in the chain direction and C_∞ is the characteristic ratio^{5,6}. The average maximum draw ratio of a network of chains equals⁷ $\lambda_{max,net} = \sqrt{3} \lambda_{max}$. For all practical purposes, (see ref. 2 and discussion in ref. 3) the maximum draw ratio of a network of chains having a distribution in lengths, to good approximation is given by equation (3), if the weight average chain length is employed in the calculation of n . This molecular weight dependent maximum draw ratio directly translates into an *upper limit* to the achievable Young's modulus through tensile drawing. The latter value can readily be calculated from equation (1) or (2) and equation (3).

Results and discussion

Experimental data of the Young's modulus as a function of draw ratio of oriented PET used in this work were taken from literature and are represented in Figure 1. These results, which were obtained with widely different techniques, reveal surprisingly little variation or scatter. It is of major importance to note

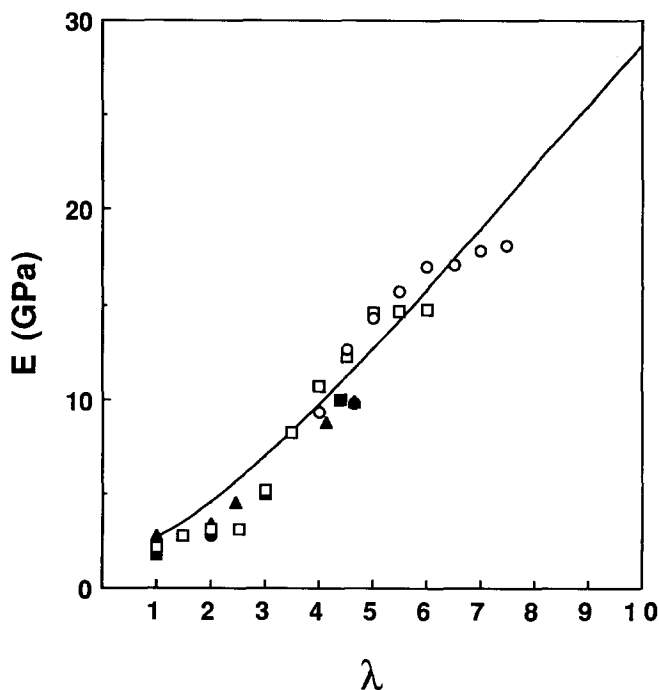


Figure 1 Axial Young's modulus E versus draw ratio λ computed for poly(ethylene terephthalate) with equation (1) ($E_h=125$ GPa and $E_u=2.6$ GPa). Experimental data points were taken from: Pinnock and Ward⁸, 'pin-only' drawn fibres (\square), 'pin-and-plate' drawn fibres (\circ); Pereira and Porter⁹, initial crystallinity 0% (\blacksquare), 30% (\bullet), 50% (\blacktriangle)

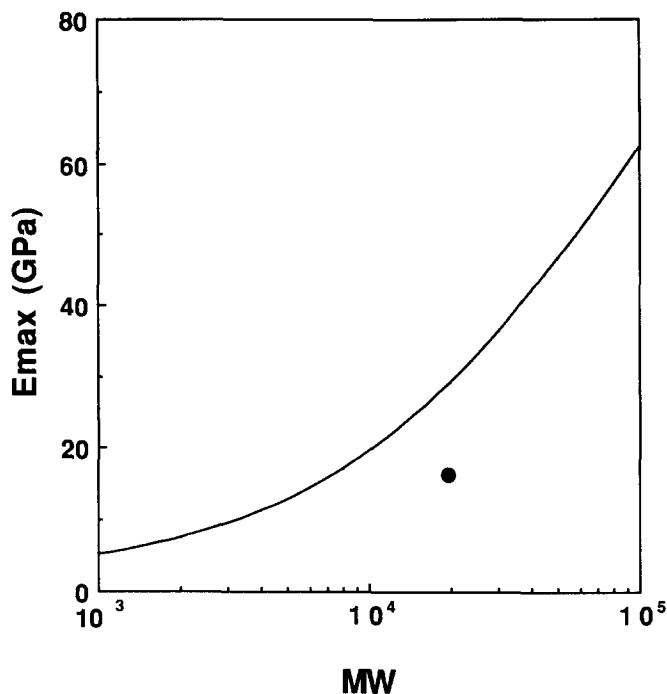


Figure 2 Maximum axial Young's modulus achievable through tensile drawing as function of molecular weight, calculated for poly(ethylene terephthalate) with equations (1) and (3). Experimental data point was taken from Hofmann *et al.*¹

that the initial crystallinity (0–50%) (ref. 9) as well as the drawing procedure⁸ of the samples barely affected the development of the Young's modulus with draw ratio. This finding, of course, justifies one of the prime assumptions in the development of the presently employed theory².

From the intercept of a plot of E^{-1} versus $\lambda^{-3/2}$, the value of the theoretical modulus, E_h , of 125 GPa was obtained and from the slope of the curve $E_u = 2.6$ GPa was calculated. Despite the expected scatter of the data at the relatively low draw ratios, the calculated axial modulus shows gratifying accord with the theoretical modulus determined by many other authors^{10–17}. The development of the axial Young's modulus with draw ratio calculated according to equation (1), with $E_h = 125$ GPa and $E_u = 2.6$ GPa, is represented by the solid line in Figure 1. The results in this graph illustrate that equation (1) accurately describes the experimental data.

The molecular weight dependence of the maximum modulus, achievable through tensile drawing, calculated with equations (1) and (3), is presented in Figure 2. In this figure we also plotted the maximum Young's modulus obtained by Hofmann *et al.*¹. The graph clearly shows that their highest modulus is within

60% of the upper limit that is expected for a PET sample of molecular weight (M_w) of 20 000.

Conclusion

The results presented in this paper clearly demonstrate that the molecular weight sets a theoretical upper limit to the maximum draw ratio of flexible polymers, and, therewith, also to the maximum axial modulus that can be achieved through tensile drawing. This limit can be surpassed only if processes other than tensile drawing are applied, that lead to superior uniaxial order, such as in-situ growth of extended chain polymer whiskers (e.g. ref. 18). As yet, such processes have not been developed for PET.

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Reply to comments

In their comment on our paper¹ Postema and Smith discuss the maximum attainable longitudinal modulus of tensile drawn PET samples as a function of the weight average molecular weight \bar{M}_w . But the model used by these authors is limited to affine drawing. Crystallization processes in particular are neglected. That means that this treatment is suited mainly for our cold and slow drawn PET strips 1 and 8 (see Table 1 in ref. 1). For the hot zone drawn samples, however, a semicrystalline structure is present (i.e. the molecular chains are fixed segment-wise in crystalline regions). These materials can be assumed to be composed of microfibrils with each microfibril being an arrangement of structural unit elements. The elements have an average length L and contain in each case one crystallite with one longitudinally adjoining non-crystalline region (see Figure 6 in ref. 1). The cross-sectional area A of a structural unit element

can be obtained roughly from $A = L_{100} L_{010}$ with L_{100} and L_{010} being lateral crystallite dimensions as obtained from WAXS (see Table 2 in ref. 1). Then $A/0.25 \text{ nm}^2$ gives the number n of molecular chain segments leaving the crystalline part of a structural unit element. (Note that 0.25 nm^2 is the average cross-sectional area per PET chain in the crystalline lattice.). L , A and n are given in Table 1.

Since there are also chain ends and entanglements in the non-crystalline regions, the number of intrafibrillar tie molecules is smaller than n . The relative fraction e of chain ends in the non-crystalline part of a structural unit element can be calculated from:

$$e \approx 2L/L_0 \quad (1)$$

(see refs 2 and 3) with $L_0 = 84 \text{ nm}$ being the average length of a