The elastic modulus of drawn nylon 6 fibres

Prevorsek and co-workers [1], in a previous paper on the structure and properties of nylon 6 fibres, stated that analysis of mechanical properties of fibres indicates strong lateral interactions between microfibrils. Using the Halpin–Tsai equation [2], they found from the value of the parameter ξ, that the crystal aspect ratio (length/diameter) required to predict correctly the experimental modulus from the moduli and volume fractions of the constituent crystal and amorphous phases was much smaller than the actual aspect ratio determined by small-angle X-ray scattering and electron microscopy, for a draw ratio of 3 : 1. The crystalline regions were thus considered to be behaving mechanically as wide platelets extending over several microfibrils.

The Halpin–Tsai equation predicts the overall material elastic modulus E from the moduli of the matrix (amorphous, E_A) and the inclusions (crystal, E_c)

$$E = E_A\left[\frac{1+\xi\eta\chi}{1-\eta\chi}\right], \text{ with } \eta = \frac{E_c/E_A - 1}{E_c/E_A + \xi}, \quad (1)$$

where χ is the volume fraction of inclusions. The value of the parameter ξ is of an empirical nature and depends on, for example, fibre geometry, packing geometry and loading conditions. Halpin and Kardos [3], for example, used Equation 1 to estimate the modulus in the fibre direction of a short-fibre reinforced composite for fibres of various aspect ratios. They found for l/d values from about 8 to 100 that ξ could be identified with $2l/d$, where d is the fibre diameter. When $\xi \gg 1$, Equation 1 approaches the well-known Voigt upper bound or parallel coupling case (also called the rule of mixtures)

$$E_V = E_A(1-\chi) + E_c\chi, \quad (2)$$

Prevorsek *et al.* [1], having obtained a value for ξ of about 0.02, also equated ξ to $2l/d$, and thus obtained a very small value for the effective crystal aspect ratio.

It will now be shown in the simplest manner possible that, when ξ is small, it cannot generally be identified with $2l/d$. In the limit as $\xi \to 0$, Equation 1 becomes

$$1/E_R = (1-\chi)/E_A + \chi/E_c, \quad (3)$$

which is the well-known Reuss lower bound, or the case of series connection. Here, the overall compliance is the "weighted" sum of the individual compliances. The result of Prevorsek and co-workers [1], $\xi = 0.02$, indicates that the material is behaving approximately in this way, i.e. the crystal (C) and amorphous (A) regions are coupled in series, and there are virtually no lateral constraints on the regions to prevent extension to the maximum possible amount. Hence, this is a lower bound on the modulus. The result makes no assertions about the aspect ratio of the crystals.

Let us now consider a hypothetical two-phase material in which very wide "C" and "A" platelets are stacked alternately with their normals parallel to the specimen axis. Since the "C" regions are much stiffer than the "A" regions, we shall assume here for the sake of simplicity that the crystal inclusions are rigid, and also that the "A" regions are isotropic. In the limit as $l/d \to 0$, the modulus normal to the stack of platelets is then given by

$$1/E = \frac{(1-\chi)}{E_A}\left[\frac{(1+\nu_A)(1-2\nu_A)}{(1-\nu_A)}\right], \quad (4)$$

where ν_A is Poisson's ratio of the "A" regions. Only if $\nu_A = 0$ will this equation be the same as Equation 3 (with $E_c = \infty$). For $\nu_A = 0.5$ (incompressibility condition) the modulus normal to the platelets becomes infinite. In an actual platelet composite, as we imagine the aspect ratio to decrease towards zero, the modulus normal to the platelets will thus increase. For Poisson's ratio ν_A approaching 0.5, this increase will be very marked, and large lateral forces will occur which constrain the "A" regions and prevent their extension parallel to the lamellar normals.

In conclusion to this section, there is no justification for assuming that a small value of ξ can be identified with a small aspect ratio of inclusions.

We shall now apply very simple series–parallel type coupling schemes to reassess the behaviour of nylon 6 fibres, using the actual data given by Prevorsek *et al.* [1] (see Table I). From the table, it can be seen that the modulus E increased from 4.80 to 5.50×10^5 N cm^{-2} on drawing further from 3 to 5.35 times, even though the crystallinity χ had decreased from 0.56 to 0.34. Representative volume elements (RVE) are shown (in two-

0022–2461/81/082324–03$02.30/0

TABLE I Data for nylon 6 (results adapted from Prevorsek *et al.* [1]

Parameter	Draw ratio	
	3:1	5.35:1
Microfibril diameter, d (Å) (or crystal width)	119	74
Crystal length, l_c (Å)	59	61
Amorphous length, l_A (Å)	30	32
Long period, $(l_c + l_A)$ (Å)	89	93
Crystal aspect ratio, l_c/d	0.48	0.8
Crystal modulus, E_c (10^5 N cm^{-2})	25	25
Amorphous modulus, E_A (10^5 N cm^{-2})	2.34	3.26
Crystal volume fraction, χ	0.56	0.34
Experimental modulus, E_{exp} (10^5 N cm^{-2})	4.80	5.50

dimensions) in Fig. 1. The crystals (C) are lined up at equal heights in the microfibrils along the fibre direction (Z) in accordance with Prevorsek and co-workers [1]. "A" represents amorphous material between the crystals within the microfibrils, while "I" represents the noncrystallized, intermicrofibrillar matter. The volume fractions of the three regions can be calculated from the data given in Table I for the two draw ratios considered. In what follows, it is assumed that the modulus of the I regions is the same as that of the A regions.

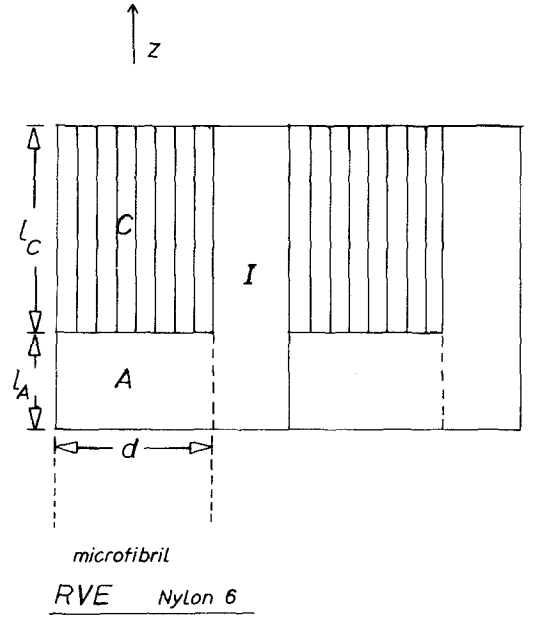


Figure 1 Representative volume element for nylon 6 fibre.

Scheme 1: Paul's approximate method. Firstly, the data is analysed by applying Paul's approximate method [4] to evaluate the predicted modulus E. The RVE is divided into infinitesimal slices with normals parallel to the specimen direction Z. In each slice the strain is assumed to be uniform. The slices are then integrated in series to cover the RVE, i.e.

$$\frac{1}{E} = \int \frac{dZ}{E_A + (E_c - E_A)A_c(Z)}, \qquad (5)$$

where $A_c(Z)$ is the distribution of the crystalline "inclusion". For our case this type of coupling is shown in Fig. 2.

Scheme 2: Microfibrillar model. As a second approach, the coupling scheme will be adopted in which the C and A regions are coupled in series, and the I material is coupled in parallel to the microfibril. The appropriate equation for the modulus E is

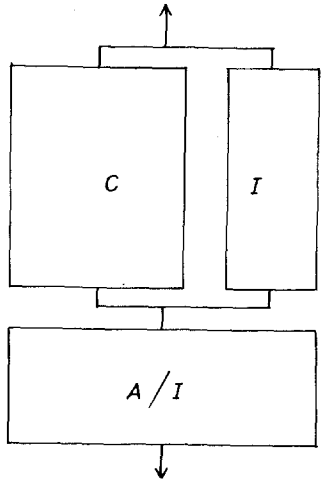
$$E = \frac{V_I}{V}E_A + \left(1 - \frac{V_I}{V}\right) \times \left[\frac{\left(\frac{V_A}{V_A + V_c}\right)}{E_A} + \frac{\left(\frac{V_c}{V_A + V_c}\right)}{E_c}\right]^{-1}, \qquad (6)$$

where V_I, V_A, V_c and V are the volumes of I, A, C and total material in the RVE, respectively.

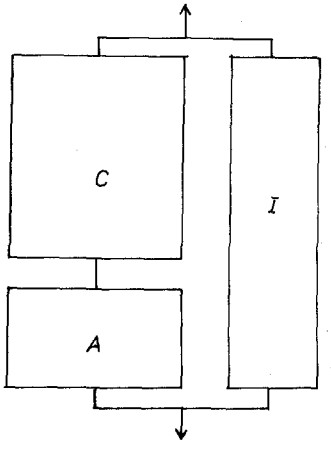
It is important to note that, although these models appear to resemble the model of Takayanagi, Imada and Kajiyama [5], they differ in a major way. In the Takayanagi model, the parameters ϕ and λ indicate the extent to which the material is showing series or parallel coupling, rather like the parameter ξ in the Halpin–Tsai equation. The parameters ϕ and λ bear no direct link to the geometry of the individual phases in the RVE, except that $\phi \cdot \lambda = 1 - \chi$.

In the models described here, definite regions of the RVE have been assumed to couple so as to satisfy one or the other of the series or parallel bounds.

The predictions of these models are shown in Table II. It appears that the coupling Scheme 2 agrees best with the experimental results. It is inferred from this finding that each microfibril should be regarded as a series connection of crystal and amorphous components with relatively



Scheme 1



Scheme 2

Figure 2 Coupling schemes used in the analysis.

little lateral constraint, such that its behaviour approaches the Reuss lower bound. The assembly of long microfibrils is interspersed with intermicrofibrillar regions, the behaviour of which approaches the Voigt upper bound, as expected for long, parallel constituents. These considerations seem to argue against being able to describe drawn nylon 6 fibres as a composite material where the crystals are embedded in a homogeneous amorphous matrix.

TABLE II Elastic modulus predictions

Predicted modulus (10^5 N cm^{-2})	Draw Ratio	
	3:1	5.35:1
Halpin–Tsai equation (with measured aspect ratios)	6.34	6.02
Scheme 1: Paul's approximate method	5.71	6.65
Scheme 2: Microfibril model	5.31	5.50
Experimental value	4.80	5.50

Acknowledgement

The author wishes to thank the Deutsche Forschungsgemeinschaft for financial support for this work.

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Received 26 November
and accepted 12 December 1980

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