

# A fibre composite model of drawn crystalline polymers \*

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The two-phase fibre composite model proposed by us elsewhere [Barham and Arridge (1977)] is used to explain the behaviour of polyethylene and polypropylene on drawing to very high draw ratios. The basis of the theory is that, after necking, there exists a uniform distribution of aligned needle-like elements of near perfect crystallinity in a less-perfect matrix. On further drawing these reinforcing elements are supposed to elongate in a homogeneous deformation while contracting laterally. The resultant change in their aspect ratio is sufficient, using short fibre reinforcement theory, to account for the increase in the modulus on drawing. The Young's modulus of the drawn fibre is given by the expression:

$$E_f = cE_c \left( 1 - \frac{\tanh x}{x} \right) + (1 - c)E_m$$

where  $c$  is the concentration of elements,  $E_c$  the modulus of the crystalline elements and  $E_m$  that of the matrix while  $x$ , derived from shear-lag theory, depends upon the aspect ratio of the elements and the moduli of the two phases. For both polyethylene and polypropylene it is found that  $x \propto t^{3/2}$ , where  $t$  is the post-neck draw ratio. The model is applied (1) to the explanation of the observed relation between Young's modulus and draw ratio, (2) to explain the temperature dependence of drawing behaviour, (3) to postulate a mechanism for non-linear viscoelasticity and creep behaviour and (4) to explain the self-stiffening after annealing under constraint [Arridge, Barham and Keller (1977)].

## INTRODUCTION

Crystalline polymers such as polyethylene, polypropylene and nylon consist, it is thought, of regions of ordered material connected by less well ordered ones. In polymers prepared from the melt the predominant crystal form is the spherulite, which has been shown to consist of thin twisted lamellae, comprised of folded polymer chains, radiating in all directions. The spherulites grow from nuclei present in the melt and it is the number of the nuclei present in the melt at any temperature which, together with the degree of supercooling determines the number and size of the spherulites in the solid. If the solid polymer is deformed by small amounts (<0.1%) the spherulites deform viscoelastically and the overall dimensions of the sample are not permanently changed. If large deformations are applied, however, the spherulitic structure is eventually destroyed and a new fibrillar structure is found. According to the model of Peterlin<sup>1</sup> the fibrillar structure is virtually complete after a deformation of ~800% and the original spherulites are no longer detectable.

Many studies have been made of the structural changes occurring during large scale deformations, whether these are caused by tension alone (drawing), by extrusion, by rolling or by other means.

Drawing causes a pronounced anisotropy in elastic properties (as observed e.g. by Raumann and Saunders<sup>2</sup> and Ward and coworkers<sup>3</sup>). It is therefore of interest to know

what the maximum elastic modulus could be or, rather, what the ultimate values of all the elastic constants (of the anisotropic fibre) could be. Theoretical predictions based on intermolecular forces have been made for the unit cell of polyethylene by Odajima and Maeda<sup>4</sup> and by Wobser and Blasenbrey<sup>5</sup>. Predictions for polypropylene have been made by Asahina and Enomoto<sup>6</sup>. X-ray measurements of the moduli of unit crystals by Sakurada and Kaji<sup>7</sup> give the values 252 GN/m<sup>2</sup> for polyethylene and 35 GN/m<sup>2</sup> for polypropylene, both in the chain ( $c$ -axis) direction.

Caution must be exercised in accepting any, theoretical or experimental, value of the crystal modulus as being exact. The theories suffer from simplifications made in order to perform any calculation at all, whereas the experimental work based on the use of X-ray-determined lattice strains presupposes that lattice stresses are known – that is, a model of the structure has to be assumed. There is therefore a danger of circular argument in using 'theoretical' moduli to compare with predictions from a model.

It is clear then, as Frank<sup>8</sup> pointed out, that polyethylene could be as stiff as steel if the chains were fully extended, and during recent years several methods have been employed to try to achieve this condition. Drawing a fibre under simple tension has been the oldest of these methods, being employed in the textile industry. Although draw ratios of up to 30 have been achieved in the past in the laboratory (Illers<sup>9</sup>, and Meinel and Peterlin<sup>10</sup>), under conditions which now suggest high modulus may also have been attained, it is the recent work of Capaccio and Ward<sup>11</sup> and their collaborators which has drawn attention to the commercial practica-

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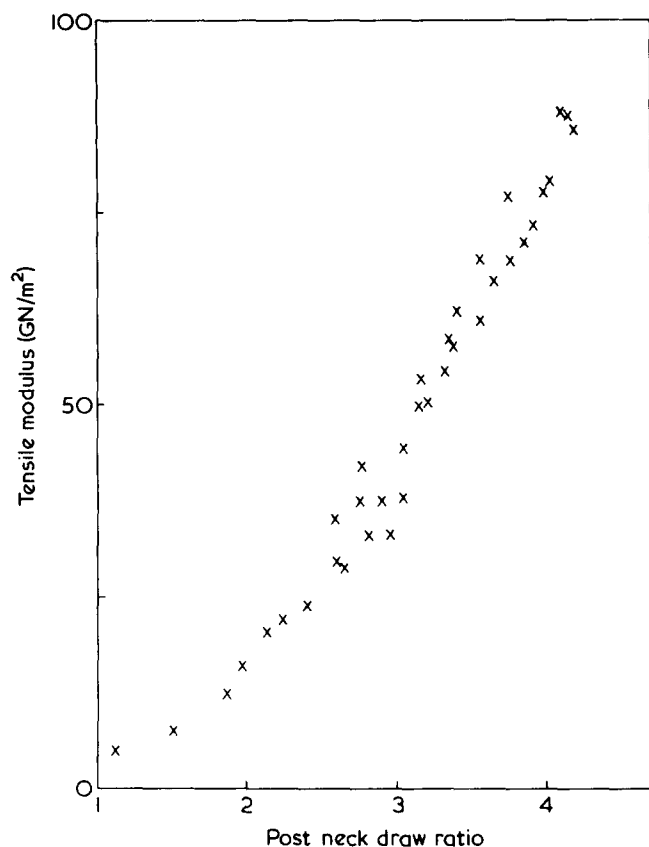


Figure 1 Tensile modulus of high density polyethylene fibres as a function of post-neck draw ratio

bility of achieving high draw ratios of up to 30, in such a way as to obtain high modulus.

It has been known for many years that the attainment of high modulus is not solely a question of achieving a high degree of orientation of polymer chains as determined by X-ray diffraction or other means. Even with very high chain orientation a high modulus need not be achieved since the chains may be folded and the oriented crystals separated by a low modulus region (of folds). The fibre structure could then be represented by a series model of alternating crystal and amorphous regions. Models for the structure of drawn polymers have therefore achieved prominence in recent years (see, for example, McCullough *et al.*<sup>12</sup>). Up to the mid 1960s the model assumed for a semicrystallized polymer was one in which the material was supposed to be made of two components, a crystalline and an 'amorphous' phase and the mechanical coupling of these was either simple series, simple parallel or a combination of both. The growth of work on composite materials such as fibre- and particle-reinforced resins, glasses and metals has, however, led to the study of much more realistic models and to an understanding of their elastic, viscoelastic and, to some extent, plastic behaviour.

One of the simpler of these models is presented here to explain the qualitative and, to an important extent, quantitative aspects of high draw ratio polyethylene and polypropylene fibres. This model is intended to form the basis of a general theory for the drawing of semicrystalline polymers.

It assumes that the crystalline fibres, referred to above, formed after deformation of the spherulitic structure, are of length to diameter (aspect) ratio, between  $\sim 2$  and  $\sim 12$ , depending on draw ratio and are embedded in a matrix of less perfect crystallinity in the manner of an oriented short fibre composite. Since the detailed account of the model is

available in a previous publication<sup>13</sup> we shall here summarize the theory and outline (a) the explanation it gives of observed facts in polyethylene and polypropylene (b) implications of the theory for non-linear viscoelasticity and creep.

## EXPERIMENTAL

### Polyethylene

Rigidex 50, moulded at 160°C, cooled at 1.5°C/min to 110°C and then quenched in water was drawn at  $75 \pm 1^\circ\text{C}$  to draw ratios up to 30<sup>11,14</sup>. The modulus obtained, measured in the fibre direction appears to be a unique function of draw ratio (Figure 1).

### Polypropylene

The material used was high purity homopolymer supplied by ICI Ltd with a melt flow index (at 230°C under 2.16 kg) of 4.5. This was melted under pressure at 250°C and allowed to cool slowly ( $\sim 3$  h) to room temperature. Dumb-bell specimens with a gauge length of 10 mm, width 2.48 mm and thickness 0.86 mm were then cut from the sheet and drawn at 50 mm/min. Similar experiments have been reported by Cansfield *et al.*<sup>15</sup>. There appeared to be three regions of drawing behaviour with polypropylene.

(a) Below 50°C the material failed in a brittle manner with neck formation.

(b) Between 50°–100°C a stable neck formed running through the specimen and producing a white fibrous material.

(c) Above 110°C a stable neck was formed and the drawn material remained transparent. Whitening again occurred however at high deformation. However, if material partly drawn at 110°C, remaining transparent, was then heated to higher temperatures it was found possible to draw it further without whitening.

Figure 2 summarizes the types of deformation found possible, with their temperature ranges. It is seen that the modulus attainable with polypropylene is much lower than with polyethylene, for a given draw ratio. The reason for this is as follows. The crystal lattice in polyethylene is orthorhombic with the *c*-axis containing the polymer chains. Under *c*-axis

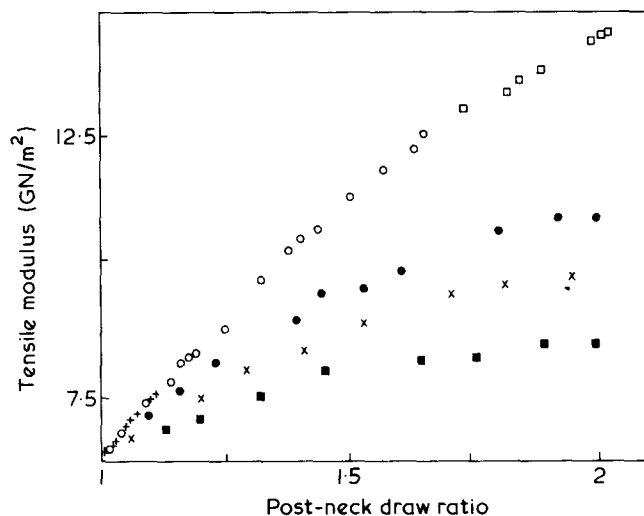


Figure 2 Tensile modulus of polypropylene fibres as a function of post-neck draw ratio for various temperatures of drawing. +, 110°C (drawn to break); O, 115°C; □, first draw 115°C, subsequently at higher temperatures; ●, 122°C; X, 138°C; ■, 145°C

extension the polymer chains are directly extended and the modulus is consequently a function of bond bending and stretching, as was first shown by Treloar<sup>16</sup>. The theoretical modulus along the chain axis for polyethylene probably lies between 250 and 350 GN/m<sup>2</sup> and is the highest attainable for a polymer since the cross-section of any other polymer is larger, because of side groups<sup>17</sup>. In polypropylene the molecule adopts a helical configuration in the crystal unit cell, so that a stretch along the chain leads to some untwisting of the helix as well as to bond rotation, bending and stretching.

#### Thermal behaviour of drawn fibres

The 'elastic' moduli of drawn polymers are highly temperature dependent. The viscoelastic properties of highly drawn polyethylene have been investigated by Smith *et al.*<sup>18</sup> and by ourselves<sup>19</sup>.

At high temperatures, irreversible changes occur and the fibre contracts unless it is held under constraint. If high-drawn polyethylene is held at constant strain at temperatures between 129° and 132°C the contractile forces are relaxed and the fibre when cooled under constraint to room temperature is found to have lost its high modulus. After a period of some hours at room temperature, however, the high modulus is partly (up to 75%) regained. We have termed this 'self-hardening' in a previous publication<sup>20</sup>, (more properly 'self-stiffening'). The higher the temperature of annealing under constraint, the more complete is the regaining of high modulus. The self-stiffened material does not contract on reheating. A similar effect can be seen in polypropylene although the magnitudes of the changes are much smaller than those in polyethylene.

The fact that polyethylene does not melt completely at 129°–132°C, while some component of it clearly is melting (or relaxing) suggests strongly that a component exists that is not melted out and that this must be an extended chain or fibril. Since there cannot be complete connectivity throughout the fibre (for practical molecular weights) something akin to a fibre composite seems an obvious texture to postulate for drawn polyethylene. Here the fibrils making up the composite could be thought of as small crystals of near perfect structure and orientation, embedded in a less perfect matrix. On cooling to room temperature recrystallization could occur with these fibrils acting as nuclei. In order to avoid a multiplicity of assumptions we choose to take the following.

- (1) The fibrils are formed on drawing and remain unchanged with temperature up to their melting point.
- (2) The matrix material in which they are embedded and which connects them is partly crystalline, probably with highly oriented amorphous material present which relaxes on annealing.
- (3) The self-stiffening effect is due to the oriented recrystallization (cf. row nucleation) of the matrix material on the fibrils as nuclei thereby increasing the shear modulus of the matrix.
- (4) The simple shear lag theory of fibre composites may be applied for calculation of elastic moduli and yield behaviour.

#### THEORY

The model we are applying is the well-known shear lag theory of fibre composites in which the fibres carry tensile

stresses only and the matrix in which they are embedded carries no tensile stress but transfers load from fibre to fibre by shear. It was used by Cox<sup>21</sup> to explain the properties of paper and together with more recent modifications is detailed in several textbooks e.g. Kelly<sup>22</sup>. The principal results are as follows<sup>13</sup>. The fibre Young's modulus  $E_f$  is given by:

$$E_f = cE_c(1 - \tanh x/x) + (1 - c)E_m \quad (1)$$

where  $E_c$ ,  $E_m$  are the fibril and matrix Young's moduli, respectively and  $c$  is the volume concentration of fibrils.

For hexagonally packed fibrils:

$$x = \frac{L_c}{r_c} \left\{ \frac{G_m}{E_c \ln [2\pi/(3^{1/2}c)]} \right\}^{1/2} \quad (2)$$

where  $G_m$  is the shear modulus of the matrix,  $L_c$  the fibril length and  $r_c$  its radius. In shear lag theory the tensile stress,  $\sigma$ , in the fibril depends upon the distance from the end,  $z$ , by the relation:

$$\sigma = e_f c E_c \left[ 1 - \frac{\cosh \beta(z - L_c/2)}{\cosh \beta L_c/2} \right]$$

where  $e_f$  is the overall strain in the fibre. It is therefore possible, using shear lag theory, to make estimates of the distribution of stress within a semicrystalline polymer when it is highly drawn. Such estimates have a bearing on the determination of crystal strain by X-ray methods<sup>7</sup> and on the nature of such deformation processes as non-linear viscoelasticity and creep.

Predictions should not however, be taken too far. Shear lag theory is an approximation only since it neglects factors such as normal stresses and the distribution of stress within a fibril which may not be uniform when such high anisotropy is present<sup>23</sup>. It has however been found to be reasonably correct except near fibre ends and the  $z$ -dependence of  $\sigma$  is of the correct form<sup>24</sup>. Short fibre composite theory also allows us to make a further prediction which is supported by experiment, namely of the way in which a composite will deform plastically. A detailed account of this is contained in another publication<sup>25</sup> but the essentials are as follows.

Consider a fibril embedded in a matrix of lower elastic modulus and let the system be strained in the fibre direction. Three events may occur.

(I) The matrix may extend elastically while constraining the fibril to deform with it until plastic deformation occurs. On removal of the stress the matrix will return to its former dimensions and the fibril will deform with it at first elastically and then under plastic compression. The system is then a model for a viscoelastic composite in which the fibril undergoes a hysteresis loop of cyclic extension and contraction.

(II) Matrix and fibril may deform elastically and yield simultaneously. This deformation will be permanent and, we suggest, is what occurs in drawing past the neck in highly drawn polyethylene and polypropylene.

(III) The matrix may yield before the fibrils do in which case drawing will occur but the fibrils will not extend permanently. In ref 25 we refer to these three events as Regions I, II and III and suggest that a polymer may deform in one or other of these regions depending upon the temperature and rate of drawing.

For a full understanding of the deformation modes it is necessary to assume that a distribution of fibril aspect (length/diameter) ratios exists. Whether or not a fibril will

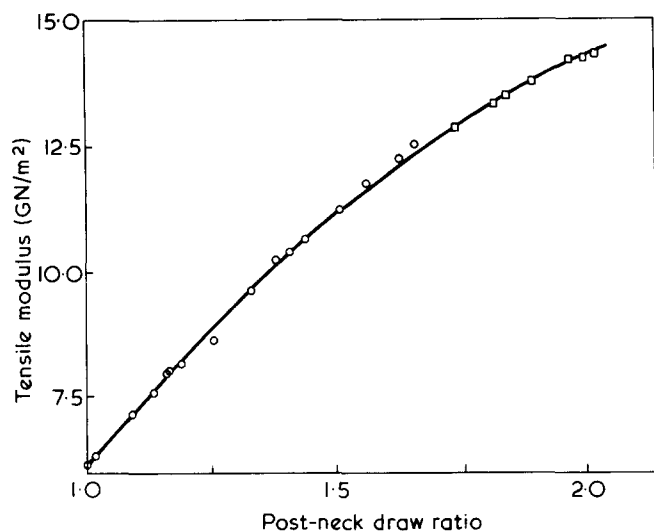


Figure 3 Tensile modulus of polypropylene fibres (○ drawn at 115°C; □, redrawn at higher temperatures) as a function of post-neck draw ratio. —, derived from equation (1) using  $x = 1.1$ ,  $c = 0.58$  and  $E_m = 1.41 \text{ GN/m}^2$

yield is then dependent upon the relation between the fibril aspect ratio  $A$  and the yield ratio:

$$Y_R = \frac{\text{Yield stress of fibril}}{\text{Yield stress of matrix}}$$

If  $A_0 \geq Y_R$  the fibrils will yield whereas if  $A_0 < Y_R$  they will not. (This follows from the simple equating of the tensile force gradient in the fibril to the mean shear traction at yield on its surface.)

#### APPLICATION OF THE MODEL

##### Modulus—draw ratio relation

Since our concern is with already-oriented material, that is material in which fibrils have formed, for example by the means described by Peterlin, the fibre composite model must explain the increase in modulus after necking. This cannot be by further orientation since it is well known that orientation is virtually complete after the neck in drawn crystalline polymers. The basis of the theory propounded in refs 13 and 20 is that the needle-like fibrils deform homogeneously with the fibre, increasing their length by the post-neck draw ratio  $t$  and becoming thinner by (approximately)  $(t)^{1/2}$ . [If the fibrils were incompressible the thinning would be exactly  $(t)^{1/2}$ ] The aspect ratio at draw ratio  $t$ ,  $A_t$  is given by:

$$A_t = A_0 t^{3/2}$$

Now equation (2) may be written:

$$x = 2A_0 K$$

where  $K$  depends upon  $G_m$ ,  $E_c$  and  $c$ . We assume  $K$  to be constant during drawing. Hence, at draw ratio  $t$ :

$$x_t = 2A_t K = 2A_0 t^{3/2} K = x_0 t^{3/2}$$

and equation (1) becomes:

$$E_{ft} = cE_c \frac{(1 - \tanh x_0 t^{3/2})}{x_0 t^{3/2}} + (1 - c)E_m$$

That is, the increase in modulus on drawing past the neck is due to the increase in aspect ratio of the fibrils. This relation has been tested experimentally for polyethylene<sup>13</sup> and polypropylene<sup>20</sup>. A very good fit of experimental data to theory is found in each case, this is illustrated in Figure 3 where the fit for polypropylene is shown. A more exact treatment, taking fibril length variability into account has been performed for polypropylene and also gives a very good fit (see ref 25).

##### Temperature dependence of drawing behaviour

On the fibre composite model this arises from the assumed difference in the temperature dependence of yield in fibrils and matrix, respectively. It is a plausible assumption that the fibril yield stress changes with temperature more slowly than the matrix yield stress. If their ratio  $Y_R$  is low and less than the fibril aspect ratio then fibril yield cannot occur and the fibre composite will deform viscoelastically until matrix failure occurs, if it does not yield. This behaviour is common to any fibre composite system and may be demonstrated, for example, in epoxy resin containing short copper wires. Again, the fibrils may break before yielding. This type of behaviour occurs in brittle fibre reinforced materials such as glass-reinforced aluminium and tungsten reinforced copper. It is probable that fibril breakage, or matrix brittle fracture is responsible for the failure to draw polypropylene below 50°C and for the fact that polyethylene requires a temperature of ~75°C before ultra-high drawing can be done.

If the temperature is too high so that the yield ratio is greater than the aspect ratio of the longest fibrils then those fibrils cannot be plastically deformed, although the matrix may extend plastically, flowing over the strained but unyielded fibrils. This is a possible explanation for the lower modulus obtained, even at high draw ratios, in polypropylene drawn at temperatures of 143°C, as shown in ref 25. Since the variables in the fibre composite theory of oriented polymers are many it is possible that some polymers may never be capable of achieving high modulus by drawing (though possibly by other means) while in other cases the temperature and speed ranges for successful drawing remain undetermined.

##### Non-linear viscoelasticity and creep

Although it is too early to make valid predictions of these properties it is worth pointing out that the inhomogeneity of the stress distribution in fibrils and matrix must lead inevitably to a non-linear viscoelastic behaviour since the position within the fibril at which yield will occur will depend upon the overall strain in a non-linear fashion. Similarly for matrix yield. Preliminary calculations of the expected behaviour during cyclic strain in Region I indicate that this is the case. Assumption of a fibre composite model for the structure of a crystalline polymer will also allow calculation of creep behaviour for comparison with experiment.

##### Self-stiffening

The application of the model to this effect in qualitative terms is quite simple: we assume that at the high temperature there is some melting or relaxation process in the matrix which causes a severe drop in shear modulus. This reduced shear modulus is retained even at room temperature when the

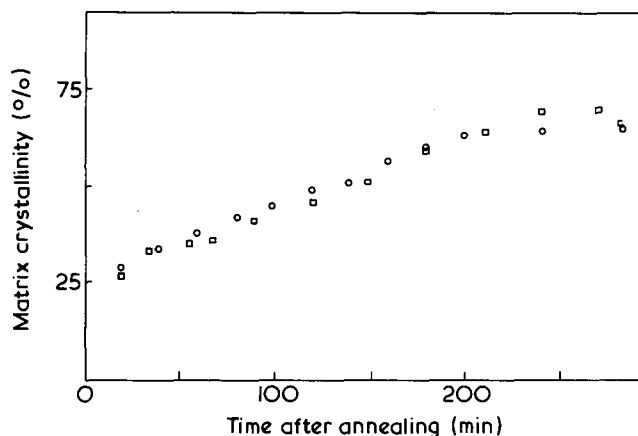


Figure 4 Matrix crystallinity in a polyethylene fibre as a function of time after annealing under constraint. O, Calculated from tensile modulus measurements; □, calculated from density measurements

specimen is cooled. Then the relaxed material in the matrix is assumed to recrystallize slowly in a lamellar form, this is manifested by an increasing density and by changes in the Raman spectrum and low-angle X-ray diffraction. We are able to make some quantitative predictions from the model about such a system. We can measure both the increase in density and the increase in tensile modulus as functions of time after the annealing process (see ref 20, Figures 4 and 7). Fibre composite theory connects these two sets of measurements if it is assumed that the fibril concentration,  $c$ , and aspect ratio  $L/r$ , remain unchanged. Then the increase in density implies a change in matrix crystallinity, which can be calculated from these measurements. The changes in tensile modulus are then associated with changes in matrix shear modulus which can also be associated with the matrix crystallinity as described in ref 10. If we use the data obtained a long time after hardening to determine the fibril aspect ratio then we may plot the matrix crystallinity as a function of time calculated from these two separate experiments; such a plot is shown in Figure 4. It can be seen that there is

very good agreement between the two sets of data, which gives us some confidence in this approach to the problem.

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