

# Elastic extension of an oriented crystalline fibre

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The elastic extension of an oriented and crystalline fibre built up of rigid-rod chains is analysed. A formula for the stress-strain curve is derived. It is shown that the shape of the initial crystallite orientation distribution and the modulus for shear parallel to the chain direction are important factors determining the stress build-up during extension of the fibre. The relations predicted by this analysis agree well with the experimental data obtained from poly(*p*-phenylene terephthalamide) fibres.

(Keywords: fibre; elasticity; crystalline; aramids)

## INTRODUCTION

The orientation process during uniaxial drawing of a polymer has long been the subject of many theoretical and experimental studies. In one of the earliest investigations Kratky introduced the affine deformation principle<sup>1</sup> which denotes a spatial transformation in which every element of unit volume changes its shape in the same proportion as the macroscopic dimensions do. Relations between the orientation distribution and the extension ratio were derived for systems consisting of rigid rodlets freely suspended in a plastic medium. On the basis of studies on the deformation of regenerated cellulose fibres Kratky and Mark formulated the orientation process of a second case<sup>2,3</sup>, viz. the deformation of a network of rodlets held together by crosslinks. These approaches are of a purely geometric nature. In an attempt to depart from this path J. J. Hermans introduced forces acting on the ends of the chain elements<sup>4</sup>. Kuhn and Grün extended the affine deformation model for rubber-like polymers by introducing chains with intrinsic anisotropic properties<sup>5</sup>. Further development took place along two different paths. One is the development of the rubber elasticity theory and the other is the formulation of the orienting aggregate model which is used for describing the orientation mechanism in semi-crystalline polymers. The latter was formulated first by Crawford and Kolsky<sup>6</sup> who modified the Kuhn and Grün theory into a so-called pseudo-affine deformation scheme, which differs from the original model in that the rotating aggregates do not change in length. Ward further developed the aggregate model and verified its results by investigating the deformation of semi-crystalline polymers<sup>7,8</sup>. This model provides relations between the extension ratio, the macroscopic elastic constants, the orientation parameters such as the second and fourth moment of the distribution of the chain directions and the elastic constants of the anisotropic aggregate.

The advance of wholly paracrystalline fibres composed of rigid-rod chains with a narrow orientation distribution, like the aromatic polyamides and polyesters, raises the

question whether previously developed deformation theories for semi-crystalline fibres provide a proper description for the tensile deformation of these fibres. In earlier work<sup>9</sup> an analysis of the tensile deformation of poly(*p*-phenylene terephthalamide), abbreviated as Pp-PTA, fibres was presented. This analysis was partly based on the results obtained from the aggregate theory. Since in our opinion this approach was not flawless, we present here a new derivation for the stress-strain curve. Only the elastic part of the tensile deformation of wholly crystalline and oriented fibres is considered, and only small strains are admitted.

## THEORY

The fibre is considered as being built up of a parallel array of identical fibrils which are subjected to a uniform stress along the fibre axis. Each fibril consists of a series of crystallites arranged end to end. A crystallite is composed of rigid-rod polymer chains running parallel to the symmetry axis. All crystallites have identical mechanical properties and are transversely isotropic. These assumptions are similar to those of the aggregate theory, which in addition excludes the distortion of the crystallites under tension.

In the fibre model considered here the crystallites are of equal length as measured along their symmetry axis and resemble packs of non-bending and parallel oriented pencils. The elastic extension of the fibril is the result of the distortion of the crystallites which is determined by two dominant processes, viz. the extension of the chain and the shear between adjacent chains. We assume that this distortion does not substantially change the symmetry of the crystallite.

The orientation angles  $\theta$  of the symmetry axes of the crystallites relative to the fibril axis follow a distribution which, when measured along a meridian, is represented by  $\rho(\theta)$ . This distribution can be determined directly by X-ray diffraction. The fraction of crystallites in a fibril with an orientation-angle between  $\theta$  and  $\theta+d\theta$  is given by the expression

$$R(\theta)d\theta = 2\pi\rho(\theta)\sin\theta d\theta$$

with

$$\int_0^{\pi/2} R(\theta)d\theta = 1$$

The first part of the analysis will be devoted to the derivation of the relations between the change of the orientation angle  $\theta$ , the state of strain of the crystallite and the stress  $d\sigma_{33}$  along the fibril axis. Owing to the transversal isotropy of the crystallite we need to evaluate only the deformation of a small rectangular section PQRS of a crystallite lying in the plane formed by the symmetry axis along PR and the fibril axis as depicted in *Figure 1*. Omitting the pure translational part of deformation the new coordinates of the section PQRS deformed by a strain function  $(u,w)$  are

$$P'(0,0), \quad Q'\left(\frac{\partial u}{\partial z}dz, dz + \frac{\partial w}{\partial z}dz\right)$$

$$S'\left(dx + \frac{\partial u}{\partial x}dx, \frac{\partial w}{\partial x}dx\right), R'\left(dx + \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial z}dz, dz + \frac{\partial w}{\partial x}dx + \frac{\partial w}{\partial z}dz\right)$$

where  $x$  and  $z$  are orthogonal axes related to the fibril such that  $z$  is parallel to the fibril axis. The corresponding strain tensor is

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

where  $u_1 = u, u_3 = w, x_1 = x$  and  $x_3 = z$ .

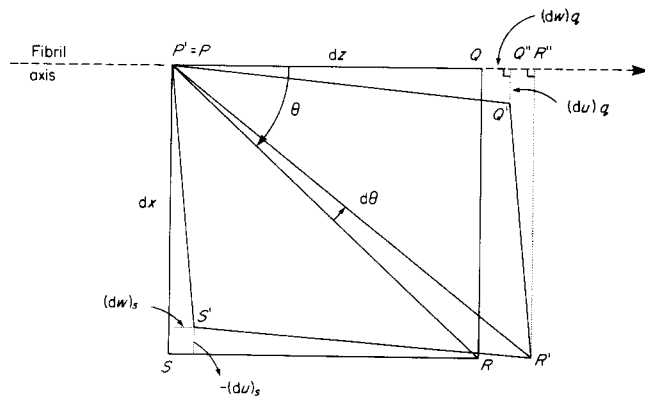
As rigid rotation of the crystallites is not considered, the displacement gradient is symmetric. Hence

$$\epsilon_{13} = \frac{\partial u}{\partial z} = \frac{\partial w}{\partial x}$$

After deformation the orientation angle of the symmetry axis is given by

$$\tan(\theta + d\theta) = \frac{R'R''}{P'R''}$$

$$= \frac{\epsilon_{13} + (\epsilon_{11} + 1)\tan\theta}{1 + \epsilon_{33} + \epsilon_{13}\tan\theta}$$



**Figure 1** Deformation of a section PQRS of a crystallite, the symmetry axis of which is parallel to PR and subtends an angle  $\theta$  with the fibril axis

from which is derived

$$d\theta = \epsilon_{13}(\cos^2\theta - \sin^2\theta) + (\epsilon_{11} - \epsilon_{33})\sin\theta\cos\theta \quad (1)$$

Relative to the axes of the crystallite the compliance tensor  $s'_{ijkl}$  with transversal isotropy is given by five independent constants

$$s'_{1111} = s'_{2222} = \frac{1}{e_1}$$

$$s'_{1313} = s'_{2323} = \frac{1}{4g}$$

$$s'_{3333} = \frac{1}{e_3}$$

$$s'_{1122} = -\frac{\nu_{12}}{e_1}$$

$$s'_{1133} = -\frac{\nu_{13}}{e_3}$$

where  $e_1$  is the modulus of elasticity normal to the symmetry axis,  $g$  the shear modulus in a plane containing the symmetry axis,  $e_3$  the chain modulus,  $\nu_{12}$  the Poisson ratio for a stress normal to the symmetry axis and  $\nu_{13}$  the Poisson ratio for a stress parallel to this axis. The strain components in equation (1) are given by

$$\epsilon_{11} = s_{1133}d\sigma_{33}$$

$$\epsilon_{13} = s_{1333}d\sigma_{33} \quad (2)$$

$$\epsilon_{33} = s_{3333}d\sigma_{33}$$

in which the components of the compliance tensor relate to the axes  $x$  and  $z$  of the fibril (see *Figure 1*). They can be expressed in the elastic constants of the crystallite after a coordinate transformation  $s_{ijkl} = a_{im}a_{jn}a_{ko}a_{lp}s'_{mnop}$  where  $a_{im}, a_{jn}, \dots$  are given by the transformation matrix.

$$(a_{ij}) = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix}$$

This yields

$$s_{1133} = \left(\frac{1}{e_1} + \frac{1}{e_3} - \frac{1}{g}\right)\sin^2\theta\cos^2\theta - \frac{\nu_{13}}{e_3}(\cos^4\theta + \sin^4\theta) \quad (3)$$

$$s_{1333} = \sin\theta\cos\theta\left\{\frac{\cos^2\theta}{e_3} - \frac{\sin^2\theta}{e_1} + \left(\frac{\nu_{13}}{e_3} - \frac{1}{2g}\right)(\cos^2\theta - \sin^2\theta)\right\} \quad (4)$$

$$s_{3333} = \frac{1}{e_3} + A\sin^2\theta + B\sin^4\theta \quad (5)$$

with

$$A = \frac{1}{g} - \frac{2(1 + \nu_{13})}{e_3} \quad \text{and} \quad B = \frac{1}{e_1} - \frac{1}{g} + \frac{(1 + 2\nu_{13})}{e_3}$$

With the relations (2)–(5) we derive from relation (1)

$$\frac{d\theta}{\sin\theta\cos\theta} = -\frac{d\sigma_{33}}{2g} \quad (6)$$

which in integrated form becomes

$$\tan\theta = \tan\theta_0 \exp\left(-\frac{\sigma_{33}}{2g}\right) \quad (7)$$

where  $\theta_0$  is the initial orientation angle. Under the tension  $\sigma_{33}$  the crystallites with initial orientation angles between  $\theta_0$  and  $\theta_0 + d\theta_0$  will rotate to angles between  $\theta$  and  $\theta + d\theta$ . Hence the new distribution  $R'(\theta)$  and the initial distribution  $R(\theta_0)$  are related by

$$R'(\theta)d\theta = R(\theta_0)d\theta_0 \quad (8)$$

Then we may write for a distribution  $\rho(\theta)$

$$\langle \tan^2\theta \rangle = \langle \tan^2\theta_0 \rangle \exp\left(-\frac{\sigma_{33}}{g}\right) \quad (9)$$

where

$$\langle \tan^2\theta \rangle = \frac{\int_0^{\pi/2} \rho'(\theta) \tan^2\theta \sin\theta d\theta}{\int_0^{\pi/2} \rho'(\theta) \sin\theta d\theta} \quad (9a)$$

A relation similar to equation (9) was derived previously

$$\langle \sin^2\theta \rangle = \langle \sin^2\theta_0 \rangle \exp\left(-\frac{2\sigma_{33}}{g}\right)$$

and experimentally confirmed for PpPTA fibres<sup>9</sup>. For a contracted distribution of Gaussian shape the difference between both orientation parameters is small. The difference by a factor 2 in the exponential term is due to the fact that in the earlier work expression (5) was used as a starting point for the analysis.

The contribution of a deformed crystallite to the fibril strain can be defined in two ways. The first is based on the relative change in length of a line element oriented parallel to the fibre axis

$$\varepsilon_c^{(1)} = \frac{PQ'}{PQ} - 1 = \varepsilon_{33} \quad (10)$$

which, with relations (2) and (5), is expressed by

$$\varepsilon_c^{(1)} = s_{3333} d\sigma_{33} \quad (11)$$

with  $s_{3333}$  given by relation (5). The second definition is a consequence of the selected fibre model and is based on the relative change of the projection on the fibre axis of a line element parallel to the symmetry axis of the crystallite

$$\varepsilon_c^{(2)} = \frac{P'R''}{PQ} - 1 = \frac{\partial w}{\partial z} + \frac{\partial w}{\partial x} \frac{\partial x}{\partial z}$$

where  $x$ ,  $z$  and  $w$  are taken at  $R$ . This implies

$$\varepsilon_c^{(2)} = \varepsilon_{33} + \varepsilon_{13} \tan\theta \quad (12)$$

which yields, together with relations (2), (4) and (5)

$$\varepsilon_c^{(2)} = \left\{ \frac{1}{e_3} + \left( \frac{1}{2g} - \frac{1+\nu_{13}}{e_3} \right) \sin^2\theta \right\} d\sigma_{33} \quad (13)$$

A simple derivation of equation (13) pertaining to the fibre model is based on the consideration that the fibril resembles a zig-zag chain<sup>10</sup> as illustrated in Figure 2. The chain consists of rods each of which is capable of extension but not of bending, with a modulus  $e_3$ . The rotation of the rods is determined by a shear modulus  $g'$  of the surrounding material. Hence the rotation of a rod under action of a force  $df$  is identical to the rotation of the line element  $AB$  of a square subjected to a shear stress  $\sin\theta\cos\theta df/\Gamma$  where  $\Gamma$  is the cross-section of the chain. If the total length of the chain is given by  $L = nrc\cos\theta$  then

$$dL = n(\cos\theta dr - r\sin\theta d\theta)$$

The extension of the rod is

$$dr = \frac{r df}{e_3 \Gamma} \cos^2\theta$$

and the rotation of the rod is

$$d\theta = -\frac{df}{2g'\Gamma} \sin\theta\cos\theta$$

which yields for the compliance  $S = \frac{dL}{L} \frac{df}{\Gamma}$

$$S = \frac{1}{e_3} + \left( \frac{1}{2g'} - \frac{1}{e_3} \right) \sin^2\theta \quad (14)$$

While the first definition for  $\varepsilon_c$  implies that section  $PQRS$  remains rectangular in shape and that the strain is discontinuous at the crystallite boundaries, the second definition supposes an oblong shape of the crystallite, which may change in shape and thus in length, and takes account of the coupling of successive crystallites throughout the orientation process.

The derivation of the fibril extension under an axial stress will be based on the second definition as expressed by relation (13). In order to keep the derivation tractable, it is assumed that the mechanical properties of the crystallite are strongly anisotropic, i.e.  $e_3 \gg g$  and  $e_3 \gg e_1$ . Let  $R(\theta_0)$  be the initial distribution and  $R'(\theta)$  the distribution at a stress  $\sigma_{33} = \sigma$ , then the extension of the fibril is given by

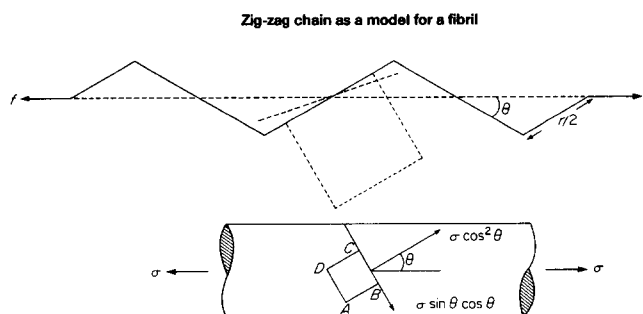


Figure 2 Schematic presentation of a simple model for a fibril. The stress diagram indicates the stresses acting on a crystallite

$$\varepsilon_f + 1 = \frac{\int_0^{\pi/2} R'(\theta)\lambda(\theta)d\theta}{\int_0^{\pi/2} R(\theta_0)\lambda_0\theta_0d\theta_0} \quad (15)$$

where  $\lambda_0\theta_0$  and  $\lambda(\theta)$  are the projected lengths of the crystallite measured along the fibril axis for stresses 0 and  $\sigma$  respectively. From relations (6) and (13) the relative extension of the crystallite at stress  $\sigma$  is derived

$$\frac{\lambda(\theta)}{\lambda_0\theta_0} - 1 = \exp\left(\frac{\sigma}{e_3}\right)\frac{\cos\theta}{\cos\theta_0} - 1 \quad (16)$$

This results in the following formula for the fibril extension

$$\varepsilon_f + 1 = \exp\left(\frac{\sigma}{e_3}\right) \frac{\int_0^{\pi/2} R(\theta_0)\cos\theta_0(e^{-\sigma/g}\sin^2\theta_0 + \cos^2\theta_0)^{-1/2}d\theta_0}{\int_0^{\pi/2} R(\theta_0)\cos\theta_0d\theta_0} \quad (17)$$

and for the compliance  $S_{33} = \frac{d\varepsilon_f}{d\sigma}$  we get

$$S_{33} = \exp\left(\frac{\sigma}{e_3}\right) \frac{\int_0^{\pi/2} R'(\theta)\cos\theta\left(\frac{1}{e_3} + \frac{\sin^2\theta}{2g}\right)d\theta}{\int_0^{\pi/2} R(\theta_0)\cos\theta_0d\theta_0} \quad (18)$$

where  $R'(\theta)$  is given by

$$R'(\theta) = \frac{\exp\left(\frac{\sigma}{2g}\right)R(\theta_0)}{\cos^2\theta + \exp\left(\frac{\sigma}{g}\right)\sin^2\theta} \quad (19)$$

and where by relation (7)  $\theta_0 = \arctan\{\exp(\sigma/2g)\tan\theta\}$ .

The elastic tensile deformation of a fibril made up of a series arrangement of oblong crystallites, being transversely isotropic and having an initial distribution of the symmetry axes  $R(\theta_0)$ , is completely described by formulae (17), (18) and (19). Since a fibre in our model is made up of identical fibrils arranged parallel and subjected to the same stress, these formulas define the elastic extension of the fibre.

For a contracted distribution  $\rho(\theta_0)$  and for  $\sigma/e_3 \ll 1$  the expression for the fibril strain relation (17) becomes

$$\varepsilon_f = \frac{\int_0^{\pi/2} R(\theta_0)\cos\theta_0\left\{\frac{\sigma}{e_3} + \frac{1}{2}\sin^2\theta_0(1 - e^{-\sigma/g})\right\}d\theta_0}{\int_0^{\pi/2} R(\theta_0)\cos\theta_0d\theta_0} \quad (20)$$

If for the orientation parameter  $\langle \sin^2\theta \rangle$  the following

unusual definition is taken

$$\langle \sin^2\theta \rangle = \frac{\int_0^{\pi/2} R'(\theta)\sin^2\theta\cos\theta d\theta}{\int_0^{\pi/2} R(\theta_0)\cos\theta_0 d\theta_0} \quad (21)$$

then it follows from relation (20) that for a contracted distribution the tensile strain of the fibre is

$$\varepsilon_f \approx \frac{\sigma}{e_3} + \frac{\langle \sin^2\theta_0 \rangle}{2} \{1 - \exp(-\sigma/g)\} \quad (22)$$

Likewise we find that the expression for the compliance relation (18) for  $\sigma/e_3 \ll 1$  becomes

$$S_{33} \approx \frac{1}{e_3} + \frac{\langle \sin^2\theta \rangle}{2g} \quad (23)$$

Formula (22) for the fibril strain was derived previously in a less rigorous manner<sup>9</sup>, with the distinction that the exponential term contained the expression  $2\sigma/g$  instead of  $\sigma/g$ . This resulted from an incorrect derivation of relation (7). Furthermore the cofactor of  $\langle \sin^2\theta \rangle$  in relation (23) is  $(2g)^{-1}$  whereas in the relation for the compliance derived for the classical aggregate theory represented by relation (5) this factor is approximately  $g^{-1}$ . This is a consequence of the different strain definitions (10) and (12).

## RESULTS AND DISCUSSION

The formulas derived for the elastic extension (relation (17)) and the compliance of the fibril (relation (18)) contain the crystallite orientation distribution  $\rho(\theta)$  in an unspecified form. They enable us to follow the change of the shape of the distribution during tensile deformation and to investigate the effect of the kind of initial distribution on the tensile curve of the fibre. The distributions selected for this analysis are a Cauchy distribution

$$\rho_c(\theta_0) = \frac{\rho_c(0)}{1 + p \tan^2\theta_0} \quad (24)$$

and a Gaussian distribution

$$\rho_g(\theta_0) = \rho_g(0)\exp(-q \tan^2\theta_0) \quad (25)$$

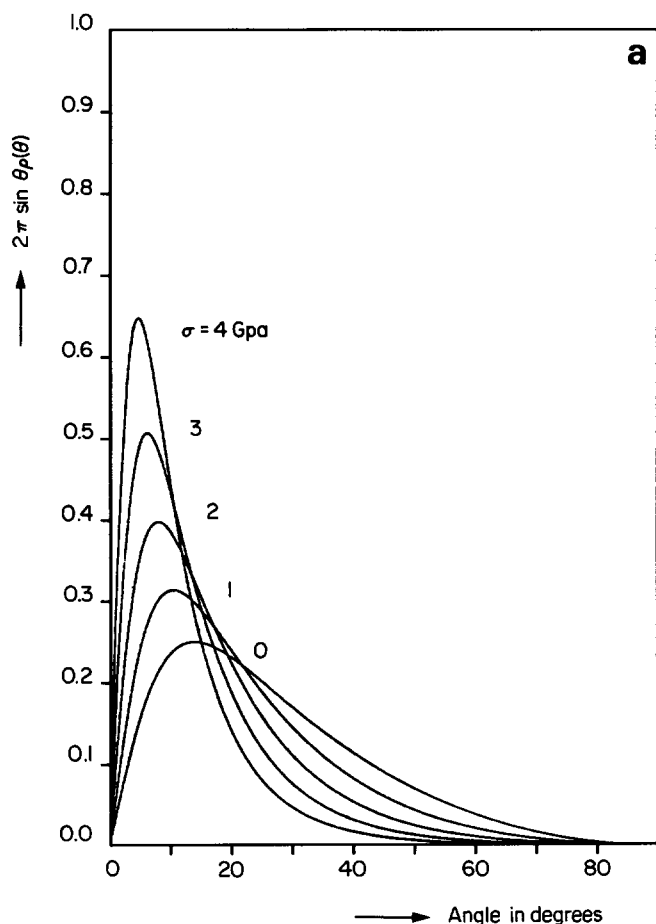
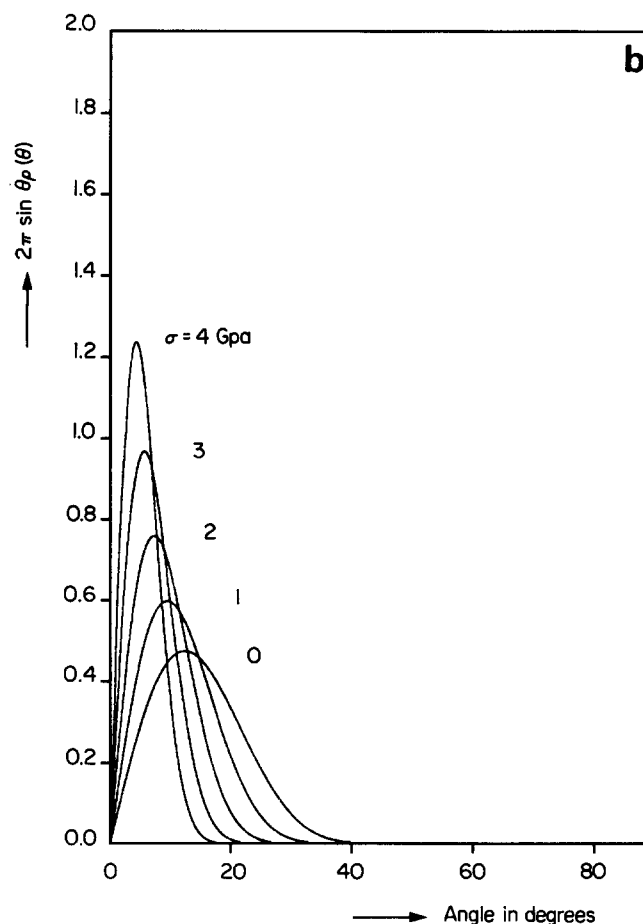
The shape of a symmetrical distribution profile is described by the ratio  $2w/\beta$ , where  $2w$  is the width at half of the peak height  $\rho(0)$  and  $\beta$  is the integral breadth defined by

$$\beta = \frac{\int_{-\pi/2}^{\pi/2} \rho(\theta)d\theta}{\rho(0)}$$

Using relation (19) the distributions at increasing stress values were calculated for Cauchy and Gaussian initial distribution. Table 1 lists the shape parameter  $2w/\beta$  as a function of the applied stress. Apparently the shape

**Table 1** Width at half-height,  $2w$ , and the shape parameter,  $2w/\beta$ , as a function of the stress. The initial distributions are of Cauchy and Gaussian type with  $2w = 30^\circ$ . The value for  $g$  in the calculations was 2 GPa)

$\sigma$ (GPa)	Cauchy		Gauss	
	$2w$ (degrees)	$2w/\beta$	$2w$ (degrees)	$2w/\beta$
0	30	0.789	30	0.962
1	22.7	0.784	23.0	0.952
2	17.4	0.783	17.7	0.946
3	13.5	0.783	13.7	0.943
4	10.4	0.783	10.6	0.921

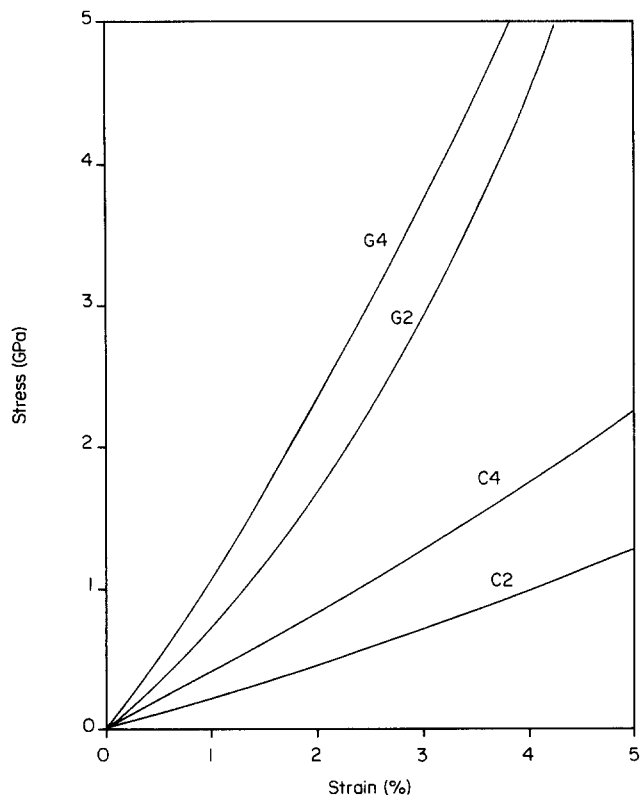
**Figure 3a** Plots of  $R(\theta) = 2\pi\rho(\theta)\sin\theta$  for increasing stress. The initial distribution  $\rho(\theta_0)$  is of the Cauchy type with  $2w = 30^\circ$ . The shear modulus  $g$  is 2 GPa**Figure 3b** Plots of  $R(\theta) = 2\pi\rho(\theta)\sin\theta$  for increasing stress. The initial distribution  $\rho(\theta_0)$  is of the Gaussian type with  $2w = 30^\circ$ . The shear modulus  $g$  is 2 GPa

parameter of  $\rho(\theta)$  changes very little, only a progressive contraction occurs. A different result is obtained for the non-symmetrical distribution function  $R(\theta)d\theta = 2\pi\rho(\theta)\sin\theta d\theta$  representing the fraction of crystallites having orientation angles between  $\theta$  and  $\theta + d\theta$ . Figures 3a and 3b depict the change of this function at increasing stress and show the decreasing number of crystallites with orientation angles in the tail of the distribution, particularly in case that the distribution is of the Cauchy type. The effect of the type of the initial distribution and the shear modulus  $g$  on the shape of the tensile curve of the fibre is shown in Figure 4.

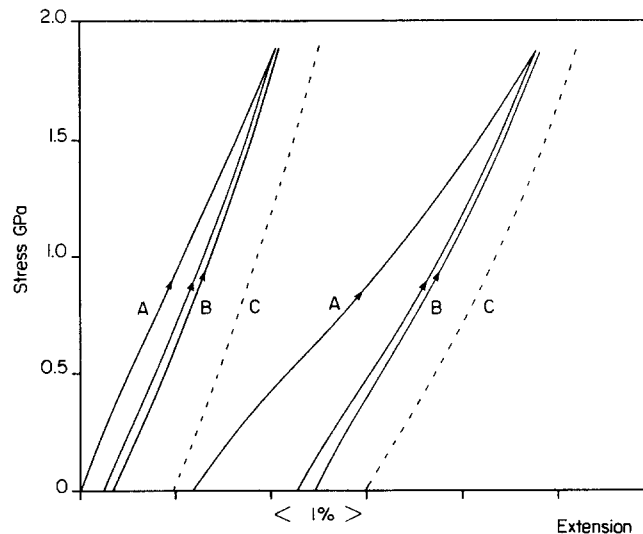
Tensile curves have been calculated for a Cauchy as well as for a Gaussian initial distribution with the same width  $2w$  and for  $g$  values of 2 and 4 GPa, while for all curves  $e_3 = 240$  GPa. The initial moduli,  $E_0 = S_{33}^{-1}$ , for the Cauchy distribution are 22.4 and 41 GPa and for the

Gaussian distribution 66.5 and 104.1 GPa respectively, for the lower and higher value of  $g$ . Evidently, according to this fibre model the initial distribution and the crystallite shear modulus are important factors determining the stress build-up, i.e. they affect the brittleness of the fibre. Figure 5 shows the effect of the distribution in a different way. Tensile curves are computed for Gauss and Cauchy distributions with  $2w = 2.5^\circ$  and  $26.5^\circ$ . The initial slope,  $E_0 = 43.5$  GPa, of the curve for a Gauss distribution of  $2w = 26.5^\circ$  equals the initial slope of the curve for a Cauchy distribution of  $2w = 2.5^\circ$ .

In the actual tensile curve of PpPTA fibres the extension is made up of elastic, visco-elastic and plastic deformation. Figure 6 depicts the first and repeated extensions of a low and high modulus PpPTA fibre, and the theoretical curves computed for  $e_3 = 240$  GPa and  $g = 2$  GPa. The orientation parameters  $\langle \sin^2\theta_0 \rangle$  were



**Figure 4** Calculated tensile curves for a Gaussian (G) and Cauchy (C) distribution of  $\rho(\theta_0)$ , both with  $2w=20^\circ$  and for  $e_3=240$  GPa. Two values for the shear modulus,  $g=2$  and 4 GPa, have been used



**Figure 6** Comparison of the experimental elastic extension with the computed curve for a low and a high modulus PpPTA fibre. Curves (A) are the first extensions, (B) are the repeated extensions and (C) are the computed curves with origin displaced to the right for the sake of clearness

derived with relation (23) from the sonic moduli measured before the second extension. The absence of any appreciable hysteresis between the repeated extensions shows that the deformation is practically elastic. Comparison of the repeated extensions with the computed curves, proves that the simple relation (22) provides a good approximation for the elastic extension of this fibre.

It should be noted that the formula for the extensional compliance  $S_{33}$  for this fibre model does not contain the fourth moment  $\langle \sin^4 \theta \rangle$  of the orientation distribution  $\rho(\theta)$ . The formula for the classical series aggregate model

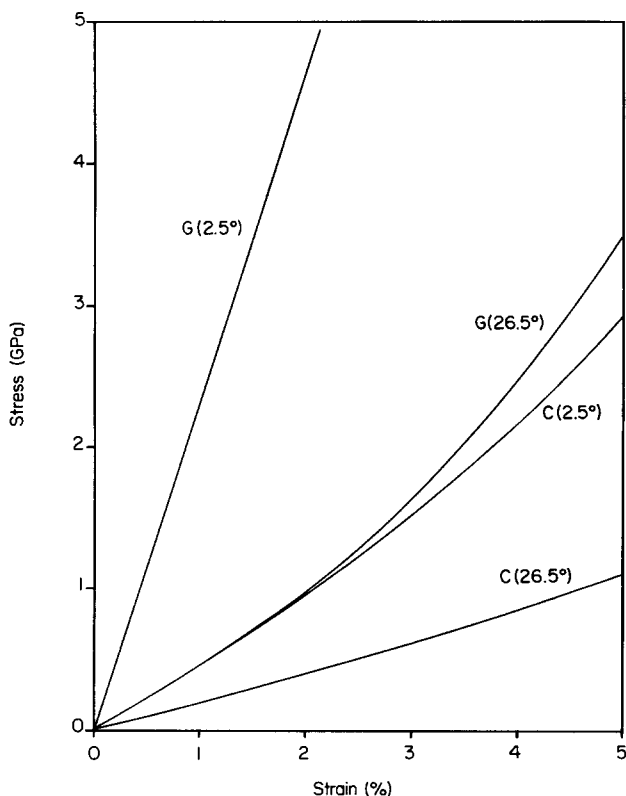
$$S_{33} = \frac{1}{e_3} + A \langle \sin^2 \theta \rangle + B \langle \sin^4 \theta \rangle \quad (26)$$

is derived by averaging relation (5) and is based on the assumption that the crystallites do not distort under the applied stress. For orientation distributions commonly found in high-modulus fibres  $\langle \sin^4 \theta \rangle \approx 0$ , which implies that the difference between relations (23) and (26) reduces to a factor of 2 in the second term of both relations. The linear relation between  $S_{33}$  and  $\langle \sin^2 \theta \rangle$  has been observed during tensile deformation of PpPTA fibres<sup>9</sup>. The slope has a value of  $0.26 \text{ (GPa)}^{-1}$ , which, according to relation (23) results in a value  $g = 1.9$  GPa. Extrapolation for  $\langle \sin^2 \theta \rangle \rightarrow 0$  gave  $e_3 = 240$  GPa. From relations (9) and (12), or (26) with  $\langle \sin^4 \theta \rangle \rightarrow 0$ , we invariably derive independently of the kind of model

$$\ln \left[ \frac{\frac{1}{E_0} \frac{1}{e_3}}{\frac{1}{E} \frac{1}{e_3}} \right] = \frac{\sigma}{g} \quad (27)$$

which provides a method for the determination of  $g$ . By measuring the sonic modulus for increasing load, relation (27) gave  $g = 2$  GPa<sup>9</sup>. We believe that this confirmation of  $g$  underlines the correctness of the presented fibre model for describing the elastic extension of PpPTA fibres.

Finally, it seems likely to us that the fibre model is also



**Figure 5** Tensile curves for a Gaussian (G) and a Cauchy (C) distribution of  $\rho(\theta_0)$ , both calculated for  $2w=2.5^\circ$  as well as for  $2w=26.5^\circ$ . Note the same initial modulus of 43.5 GPa for the narrow Cauchy and the broader Gauss distribution

suit to describe the elastic extension of carbon fibres. Preliminary calculations show that in the expression for the compliance (relation (23)) the factor  $(2g)^{-1}$  must be replaced by

$$\left( \frac{1}{2g} - \frac{\nu_{13}}{e_3} - \frac{1}{e_1} \right)$$

where  $e_1$  is the modulus in the graphite planes,  $e_3$  the modulus normal to these planes and  $g$  the modulus for the shearing deformation of these planes. A detailed account will be published later.

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#### REFERENCES

- 1 Kratky, O. *Kolloid Z.* 1933, **64**, 213
- 2 Kratky, O. and Mark, H. *Z. Phys. Chem.* 1937, **B36**, 129
- 3 Hermans, P. H. 'Physics and Chemistry of Cellulose Fibres', Elsevier, Amsterdam, 1949
- 4 Hermans, J. J. *Kolloid Z.* 1943, **103**, 210
- 5 Kuhn, W. and Grün, F. *Kolloid Z.* 1942, **101**, 248
- 6 Crawford, S. M. and Kolsky, H. *Proc. Phys. Soc.* 1951, **B64**, 119
- 7 Ward, I. M. *Proc. Phys. Soc.* 1962, **80**, 1176
- 8 Ward, I. M. 'Mechanical Properties of Solid Polymers', Wiley Interscience, New York, 1971
- 9 Northolt, M. G. *Polymer* 1980, **21**, 1199
- 10 Treloar, L. R. G. *Polymer* 1960, **1**, 95

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