Polymer Bulletin 36, 125–131 (1996)

Polymer Bulletin

A model for the tensile curve with yield of a polymer fibre

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Received: 31 July 1995/Accepted: 2 September 1995

Summary

A model is presented for the tensile curve of fibres made of linear extended polymers measured below the glass transition temperature. In this series model the parameters are the chain orientation distribution, the average modulus for shear between the chains, the chain modulus and a simple yield condition based on the critical resolved shear stress. A good agreement between the experimental tensile curves of poly(p-phenylene terephthalamide) and poly(ethylene terephthalate) fibres and the theoretical curves has been obtained.

Introduction

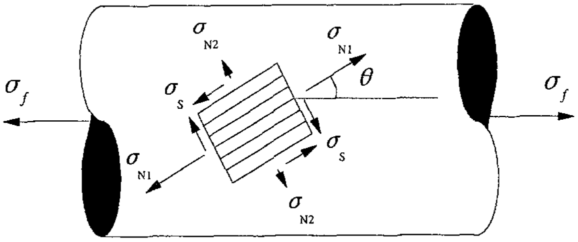
The tensile curves of fibres made of linear extended chain polymers show great similarity below the glass transition temperature. Yield is observed at a strain ε_y between 0.005 and 0.02 strain depending on the overall orientation parameter (1). Up to yielding the fibre extension is practically elastic. For larger strains the extension is composed of an elastic and a plastic contribution. As the plastic deformation does not contribute to the increase of the tensile stress, this causes the typical decrease of the slope of the stress vs. strain curve. The stress versus strain curve is also effected by the viscoelasticity of the fibre. For the fibres considered in this paper the deformation rate dependence of the stress vs. strain curve is small and thus the effect of the viscoelasticity can be neglected. Several models have been proposed for the description of the fibre tensile deformation (2-7).

A modification of the classical series aggregate model (4) was proposed by Northolt and van der Hout (8) by introducing a new strain definition which implies that the chains do not break during fibre extension. As a consequence of this model the contributions to the fibre strain are composed solely of the chain extension and the chain rotation due to shear. The parameters pertaining to the elastic extension of fibres in this model are the chain modulus e_c, the average modulus for shear between the chains g and the orientation distribution of the chains $\rho(\theta)$. The model has provided a satisfactory description for the sonic modulus vs. strain curve, as well as for the tensile curve up to fracture after mechanically conditioning of well-oriented poly(p-phenylene terephthalamide) fibres, abbreviated here as PpPTA (9). Subsequently, it was shown that this model can also be used to describe the course of the sonic modulus versus the strain of medium-oriented cellulose fibres (10). Moreover, it was demonstrated that the viscoelastic deformation of PET and PpPTA originates from a viscoelastic shearing movement of adjacent chains (9)(11). In a forthcoming paper the modified series model has been used as the basis for the description of yielding in polymer fibres (1). The critical resolved shear stress law of Schmid (12) is applied to the elementary domain of the modified series model, with the result that the yield strain as a function of the overall orientation parameter can be calculated. Good agreement with the experimental results for a large variety of fibres was obtained. A generalization of the series model for fibres with an arbitrary orientation distribution has been proposed by Baltussen; a full report of this work is in preparation (13). The equations which result from this "continuous chain model" are slightly different from those derived by Northolt and van der Hout.

In this preliminary note we show that the stress vs. strain curve of a polymer fibre can be modelled by combining the continuous chain model for the elastic extension of fibre with the yielding concept presented in our forthcoming paper on fibre yielding (1). The proposed model neglects the various kinds of structural details, such as tie molecules, alternating crystalline blocks and amorphous regions, crystalline bridges etc, which have played a prominent role in the various models proposed for drawn polymers.

Theory

A brief outline of the theory is presented here. The fibre is regarded to consist of long and continuous chains which do not fracture during deformation. Along the chain small linear segments of equal length are considered. The angle between the chain segment and the fibre axis is denoted by θ, its value at zero stress by θ_0, and the orientation distribution by $\rho(\theta)$. The immediate surroundings of a segment, which include the segment itself, are considered to be a domain. The chain segment is the axis of symmetry of the domain. It is assumed that the domain has a transverse isotropic symmetry around the chain axis. The mechanical properties of the domain are characterized by the chain modulus e_c and the average modulus g for shear between the chains. As the elastic constants of the domain are known in the symmetry coordinate system of the domain, the applied tensile stress σ_f



NORMAL STRESSES: $\sigma_{N1} = \sigma_f \cos^2\theta$

$\sigma_{N2} = \sigma_f \sin^2\theta$

SHEAR STRESS: $\sigma_S = \sigma_f \sin\theta \cos\theta$

Figure 1 The stresses acting on a single domain at an angle θ with the applied tension.

is analyzed in this coordinate system

$$\sigma = \sigma_f \begin{bmatrix} \cos^2\theta & -\sin\theta\cos\theta \\ -\sin\theta\cos\theta & \sin^2\theta \end{bmatrix} \tag{1}$$

The stresses acting on a domain are depicted in figure 1. Application of a tensile stress σ_f on the fibre results in a strain in the direction of the chain

$$\varepsilon_{33} = \frac{\sigma_f}{e_c}\cos^2\theta \tag{2}$$

and a shear deformation

$$\varepsilon_{13} = -\frac{\sigma_f}{2g}\sin\theta\cos\theta \tag{3}$$

In ref. 13 it will be shown that, due to the elastic shear deformation of the domain, the orientation angle θ of the chain segment decreases according to the relation

$$\tan(\theta - \theta_0) = -\frac{\sigma_f}{2g}\sin\theta\cos\theta \tag{4}$$

Assuming that the elastic fibre strain equals the relative change of the projected length of the chain on the fibre axis, it follows that

$$\varepsilon_f = \frac{\sigma_f}{e_c} + \frac{\langle\cos\theta\rangle - \langle\cos\theta_0\rangle}{\langle\cos\theta_0\rangle} \tag{5}$$

According to the model, the sonic modulus of the fiber is given by

$$\frac{1}{E_f} = \frac{1}{e_c} + \frac{\langle\sin^2\theta\rangle_E}{2g} \tag{6}$$

with $<\sin^2\theta>_E$ the strain orientation parameter of the chains (8).

Schmid's law states that for an anisotropic material plastic deformation starts at a critical value of the resolved shear stress σ_y along a slip plane. As the shear yield strain of a domain has been shown to be approximately constant for a

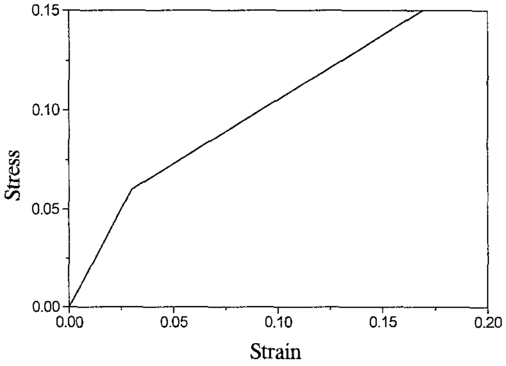


Figure 2 The stress strain curve of a single domain.

large number of polymers (1), a critical shear yield strain, $\gamma_y \simeq 0.025$, is postulated instead of a shear yield stress. Above the critical shear yield strain the plastic shear deformation satisfies a plastic shear law. From the comparison with the experimental curves it appears to be necessary to introduce an effect of strain hardening due to the increasing plastic deformation. This causes an increase of the elastic deformation beyond the yield point. It is proposed that above the yield point the plastic shear deformation $\varepsilon_{13}^{(p)}$ is proportional to the difference between the elastic shear strain ε_{13} and the critical shear strain

$$\begin{cases} \varepsilon_{13}^{(p)} = 0 & |\varepsilon_{13}| \leq \gamma_y \\ \varepsilon_{13}^{(p)} = p(|\varepsilon_{13}| - \gamma_y) & |\varepsilon_{13}| > \gamma_y \end{cases} \tag{7}$$

whereby the parameter determining the amount of plastic deformation p and the shear strain ε_{13} have equal signs. The stress vs. strain curve of the domain is depicted in figure 2. The direction of the chain segment in the elastically and plastically deformed domain is given by

$$\begin{cases} \tan(\theta - \theta_0) = \varepsilon_{13} + \varepsilon_{13}^{(p)} \\ \varepsilon_{13} = -\dfrac{\sigma_f}{2g}\sin\theta\cos\theta \end{cases} \tag{8}$$

The stress vs. strain curve of a fibre including yield is now computed by combining equation (7) and (8) for the orientation angle θ of the deformed chain segment, and equation (5) for the fibre strain.

Results and discussion

The stress strain curves of three PpPTA and two semicrystalline poly(ethylene terephthalate) (PET) fibres were measured at a test length of 100 mm and a strain rate of 10 %/min. The calculated curves were obtained by using a fitting procedure based on the equations presented above. In case of PpPTA fibres the orientation of the chains was described by a Gaussian distribution function, a value of 220 GPa was used for the chain modulus and 2 GPa for the shear modulus (8)(9). In the fitting procedure the critical shear strain γ_y and the "depth" of the yield characterized by the parameter p were varied, see equations (7) and (8). The results for the PpPTA fibres are shown in Figure 3. For the calculation of the tensile curves of the PET fibres an affine orientation function was applied, and for the domain properties the values e_c = 125 GPa and g = 1.1 GPa.

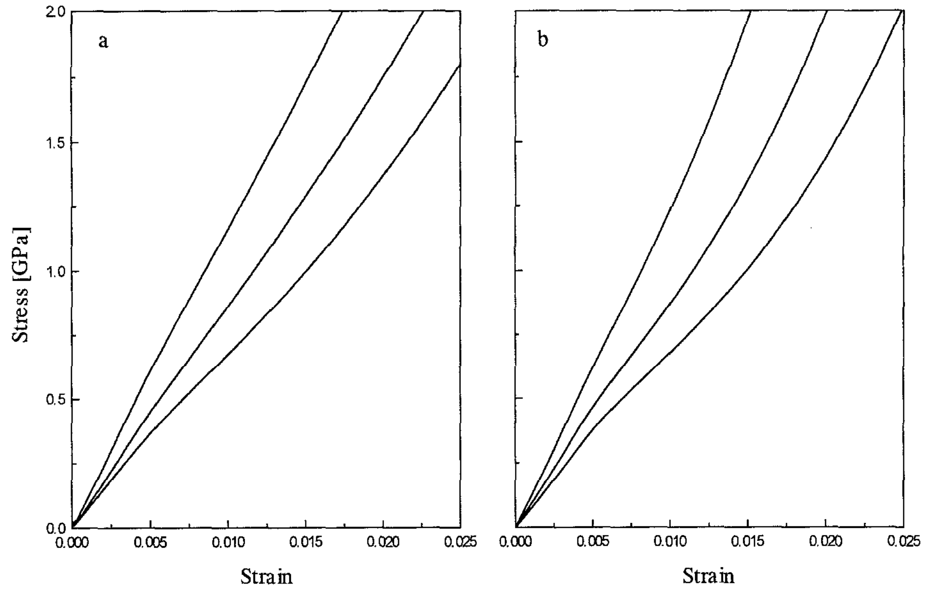


Figure 3 The observed stress strain curves (a) of three PpPTA fibres compared to the calculated curves (b).

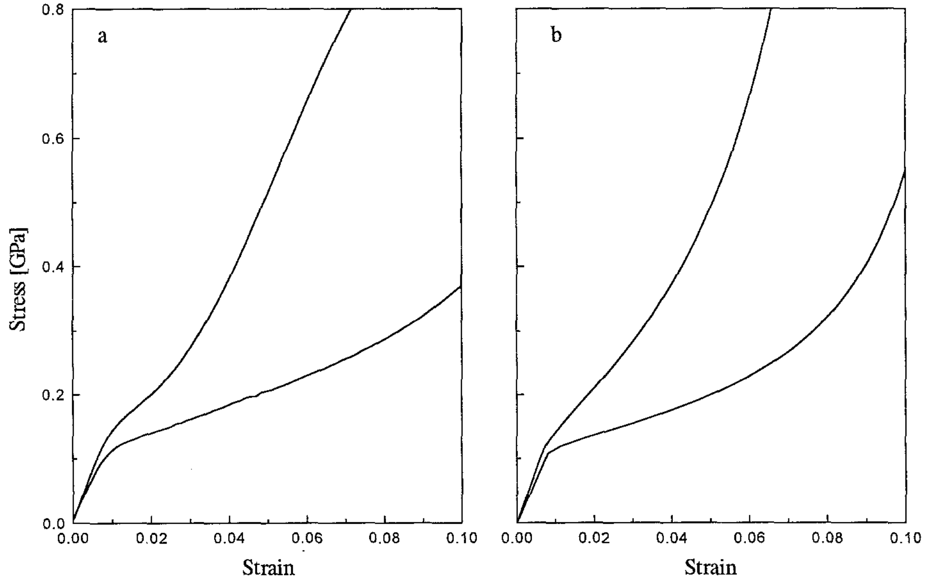


Figure 4 The observed stress vs. strain curves (a) of two PET fibres compared to the calculated curves (b).

The affine orientation distribution is given by[15,16]

$$\rho(\Theta) = \left[\frac{\lambda^2}{\cos^2\theta + \lambda^3 \sin^2\theta}\right]^{3/2} \qquad \textbf{(9)}$$

Figure 4 shows the results and Table 1 lists the values for the parameters which furnished the best fit with the experimental curves of the PpPTA and the PET fibres. Good agreement for both kinds of polymers is obtained. The essential features of the experimental tensile curves, viz. an initial straight part up to yielding followed by a decrease of the slope and subsequently a curve with increasing slope, are also displayed by the theoretical curves. In case of the PET fibres it should be reminded that the used equations are approximations for highly oriented fibres. This causes some minor differences with respect to a more rigorous calculation (14). At high stresses near the maximum of the slope the observed strain tends to be larger than the calculated strain for which presumably slip and fracture of chains are responsible. In case of PET fibres, flow processes are initiated during tensile extension at stresses near this maximum. In addition to these effects the response of the domain to the applied stress may become nonlinear.

Fibre	E_0	γ_y	p
PpPTA	71	0.03	3
"	89	0.03	3
"	124	0.03	3
PET Diolen 1125T	13	0.025	3.5
PET Diolen 174S	16	0.025	20

Table 1 The parameters which have been used for the calculation of the theoretical stress strain curves.

It is remarkable that the proposed model describes the tensile curves rather well both for PpPTA and PET fibres despite the large differences in structure, morphology and orientation parameter. In the case of semicrystalline polymers such as PET the relevant part of the orientation distribution is determined by the amorphous phase as the highly oriented crystalline phase in these fibres can hardly contribute to the fibre extension.

In conclusion, it has been demonstrated that the essential features of the fibre tensile curve up to the maximum of the slope can be described by the continuous chain model, in conjunction with a simple model for plastic deformation of the domain.

References

1. Northolt MG, Baltussen JJM, Schaffers-Korff B (1995) Polymer, in press.
2. Porter RS, Wang LH (1995) Macromol Sci Rev Macromol Chem Phys C35:63.
3. Takayanagi M, Imada K, Kajiyama T (1966) J Polym Sci Pt C 15:263.
4. Ward IM (1962) Proc Phys Soc 80:1176.
5. Hadley DW, Pinnock PR, Ward IM (1969) J Mat Sci 4:152.
6. Prevorsek DC, Sharma RK (1974) Polym Eng Sci 14:778.
7. Peterlin A (1979) Polym Eng Sci 19:118.
8. Northolt MG, van der Hout R (1985) Polymer 26:230.

9 Northolt MG, Sikkema D (1990) Advances in Polymer Sci 98:115.

10. Northolt MG, de Vries H (1985) Die Angew Makromol Chem 133:183.
11. Northolt MG, Roos A, Kampschreur J (1989) J Polym Sci Phys Ed 27:1107.
12. A.H. Cottrell, "Dislocations and Plastic Flow in Crystals", Clarendon Press, Oxford, 1953, p4.
13. Baltussen JJM, To be published.
14. Baltussen JJM, To be published.
15. W.Kuhn and F.Grün (1942), Kolloid Zeitschr.101:248.
16. S.J.Picken, S. van der Zwaag and M.G.Northolt (1992), Polymer 33:2998.