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The viscoelastic extension of polymer fibres: creep behaviour

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Abstract

The continuous chain model developed for the description of the tensile deformation of fibres is extended to include the creep behaviour. The description of the viscoelastic extension of the fibre is based on the linear viscoelastic shear deformation of the domain. From the time dependent change of the chain orientation angle the creep strain of the fibre is derived. The proposed theory allows the prediction of the creep of poly(*p*-phenyleneterephthalamide) fibres with an arbitrary value for the modulus or orientation parameter.

Keywords: Fibres; Creep; PpPTA; Aramid

1. Introduction

Highly oriented crystalline polymer fibres are commonly applied when a high stability of shape in a construction is requested. This implies that for engineering purposes accurate values must be known for both the immediate and the long-term response of the fibre to loading. The long-term behaviour of the technical fibres is predicted from the data of extensive measurements of creep at a constant load or stress relaxation at a constant deformation. A rheological model for the prediction of the creep and stress relaxation of the fibre, based on easy measurable parameters of the microstructure of the fibre would facilitate and increase the reliability of the prediction of the long time behaviour greatly.

The elastic extension of oriented crystalline fibres has been described successfully by the model of Northolt and Van der Hout [1]. Subsequently it has been generalised by Baltussen et al. to the continuous chain model for the finite deformation of fibres of linear polymers below the glass transition temperature [2–6]. This model describes the deformation of the fibre as the sum of a linear extension and a rotation of the chains towards the fibre axis. Apart from the typical concave shape of the stress strain curve this theory describes the increase of the sonic modulus and the contraction of the orientation distribution during the fibre extension. In particular it predicts an almost linear relation between the compliance and the strain which is experimentally well established [7,8]. During creep a linear relation between the sonic compliance and the creep strain has been observed as well [9,10]. A typical example of the strain and the sonic compliance during the creep of a Twaron 1000® fibre, poly(*p*-phenylene terephthalamide) and abbreviated as PpPTA, has been depicted in Fig. 1. Because of the similar behaviour of the sonic compliance during creep, the description of the viscoelastic deformation of the fibre by a viscoelastic shear deformation of domains is a logical extension of the continuous chain model [9,10].

In this paper we present a quantitative model for the viscoelastic deformation of fibres of linear polymers. A linear viscoelastic process models the viscoelastic deformation. The creep of PpPTA fibres with an arbitrary value for the modulus or orientation parameter can be predicted by the presented equations.

As the continuous chain model holds for the elastic deformation of arbitrary fibres of linear polymers below the glass transition temperature, it is expected that the presented theory can be used for description of the creep deformation of the same group of fibres. In a subsequent paper the relation between creep, stress relaxation and the viscoelastic response to more complex loadings will be reported.

The viscoelastic deformation, like creep and stress relaxation, depends on structural parameters like the orientation of the chains and the lateral interactions between the polymer chains, and external parameters like the applied stress, the elapsed time since the beginning of the experiment, the

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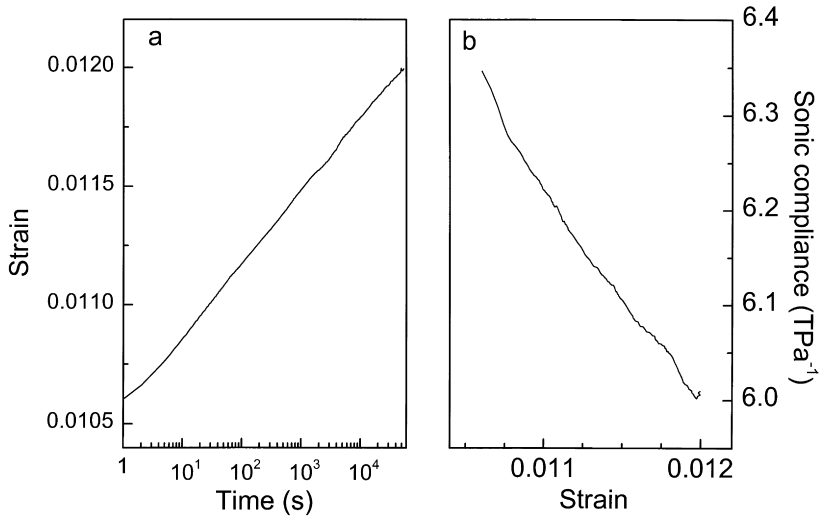

Fig. 1. The creep strain versus time (a) and the sonic compliance versus the creep strain (b).

loading history, the temperature and the moisture conditions. For the application of the theory of linear viscoelasticity the time dependence of f.e. the creep deformation should be known.

In case of PpPTA fibres the creep is proportional to the logarithm of the time. Many authors have reported the "logarithmic creep law", which holds at all values of the applied creep stress, except below the yield stress [10–12]. This property makes PpPTA fibres very suitable for a systematic study of the effect of the other parameters. The slope of the curve of the creep versus the logarithm of the time is called the logarithmic creep coefficient and it is non-linear with the applied stress. The typical convex curve of the logarithmic creep coefficient versus the applied stress is shown in Fig. 2 for three PpPTA yarns with very different values of the initial modulus. It is observed from Fig. 2 that the logarithmic creep rate is a decreasing function of the fibre modulus. The aim is to describe the stress and modulus dependence of the logarithmic creep coefficient of PpPTA fibres as shown in Fig. 2.

2. Theory

2.1. The elastic extension of a polymer fibre

It has been shown that the elastic deformation of oriented fibres should be described by the theory of elasticity for finite deformation [2,3]. The continuous chain model for the elastic extension of a polymer fibre below the glass transition temperature supposes that a fibre consists of long and continuous chains of a linear polymer with their average direction along the fibre axis. The deformation of the fibre is equal to the average deformation of a polymer

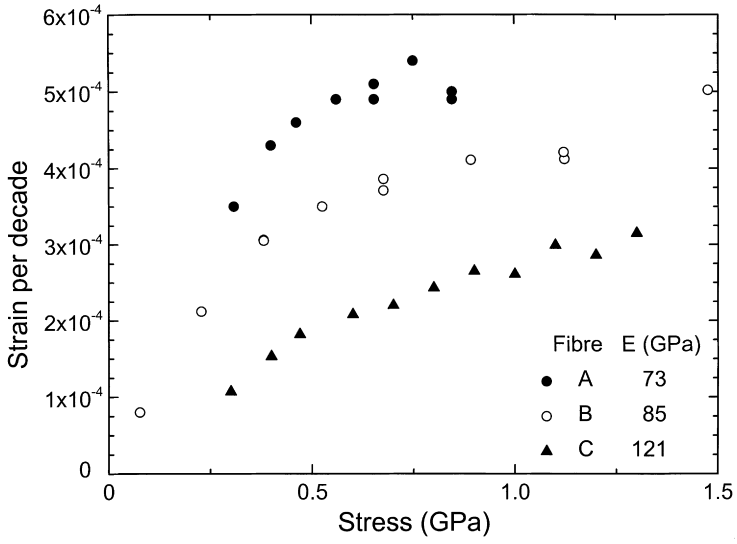

Fig. 2. The logarithmic creep coefficient of three PpPTA yarns versus the stress.

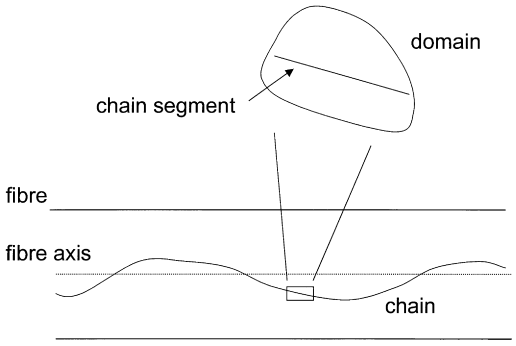

Fig. 3. A schematic picture of a chain, a chain segment and the surrounding domain. The fibre strain is determined by the projection of the chain on the fibre axis.

chain in the direction of the fibre axis. The basic element for the calculations is a small straight chain segment. The deformation of the chain segment is determined by the elastic properties of the surrounding domain. Within a domain the orientation of the polymer chain does not change and is parallel to the symmetry axis. A schematic picture of this representation is drawn in Fig. 3. It is supposed that a domain has a transverse isotropic symmetry with the following elastic constants: the chain modulus e_c, the transverse modulus e_1, the modulus for shear parallel the symmetry axis g, and the Poisson ratios ν_{12} and ν_{13} for application of a stress normal and parallel to the symmetry axis, respectively. The orientation angle Θ between the undeformed chain segment and the fibre axis follows an orientation distribution $\rho(\Theta)$. Assuming that the chain does not break during the viscoelastic extension of the fibre, the extension of the fibre by a tensile stress σ_f is equal to the change of the projection length of the chain on the fibre axis. The projection length of the chain is given by the formula

$$L = L_c\langle[1 + \varepsilon_c(\Theta, \sigma_f)] \cos\theta(\Theta, \sigma_f)\rangle \tag{1}$$

with L_c the contour length of the chain, e_c the strain of the chain segment and θ the angle between the deformed chain segment and the fibre axis. The fibre strain is equal to

$$\varepsilon_f = \frac{L - L_o}{L_o} \tag{2}$$

The quantity L_o can be calculated directly from the initial orientation distribution $\rho(\Theta)$. For the calculation of L the deformation of a chain segment subtending an angle Θ with respect to the fibre axis has to be calculated. The deformation of the domain $\wp$ has been depicted in Fig. 4. The deformation gradient denoted by $\boldsymbol{F}\cdot\boldsymbol{F}$ can be decomposed in a rotation and a symmetric tensor $\boldsymbol{I} + \boldsymbol{U}$

$$\boldsymbol{F} = \boldsymbol{R}(\boldsymbol{I} + \boldsymbol{U}) \tag{3}$$

It is supposed that no rigid rotation of the domain occurs. In that case $\boldsymbol{R} = \boldsymbol{T}$ with $\boldsymbol{T}$ a shifter who parallel transports vectors emanating from $\wp$ to vectors emanating from the deformed domain $\varphi(\wp)$. In orthogonal co-ordinates it holds that $F^i_J = (I + U)^i_J$. The angle θ between the deformed chain segment and the fibre axis is given by the angle between $\boldsymbol{T}(\hat{\boldsymbol{I}}_3)$ and $\boldsymbol{F}(\hat{\boldsymbol{I}}_3)$

$$\tan(\theta - \Theta) = \tan\delta^{(3)} = \frac{U_{13}}{1 + U_{13}} \tag{4}$$

The angle between $\boldsymbol{T}(\hat{\boldsymbol{I}}_1)$ and $\boldsymbol{F}(\hat{\boldsymbol{I}}_1)$ is denoted by $\delta^{(1)}$

$$\tan\delta^{(1)} = -\frac{U_{13}}{1 + U_{11}} \tag{5}$$

The angle θ is calculated using the elastic properties of the domain, which are defined by the stored elastic energy function

$$\boldsymbol{W} = \tfrac{1}{2}\boldsymbol{E}^{IJKL}\varepsilon_{IJ}\varepsilon_{KL} \tag{6}$$

where $\boldsymbol{E}$ the elasticity tensor of the linear theory of elasticity, and with $\varepsilon_{IJ} = \boldsymbol{U}_{IJ} + \boldsymbol{U}_{IK}\boldsymbol{U}_{KJ}$ being the Lagrangian or

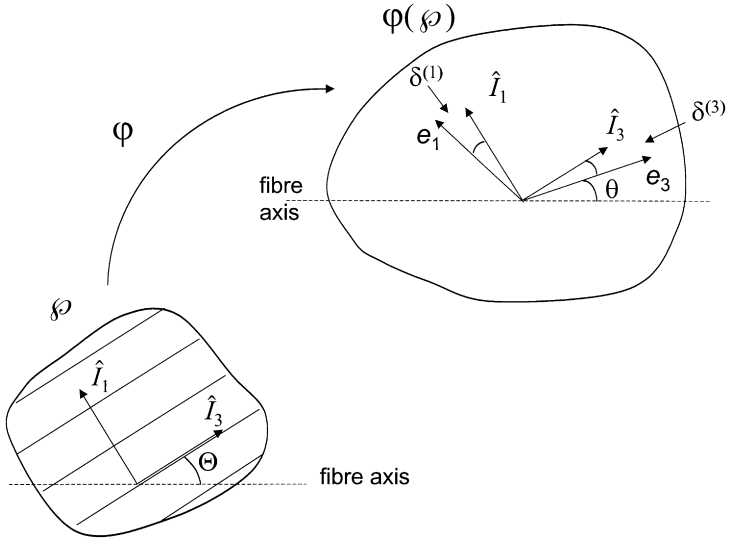

Fig. 4. Schematic drawing of the deformation of the domain $\wp$ into $\varphi(\wp)$, see for details Ref. [2].

material strain tensor. From the balance between the stored elastic energy and the work done by the external forces the stress–strain relation is derived

$$\boldsymbol{S}^{IJ} = \boldsymbol{E}^{IJKL}\varepsilon_{KL} \tag{7}$$

with $\boldsymbol{S}$ the second Piola stress tensor

$$\boldsymbol{S}^{IJ} = \boldsymbol{J}(\boldsymbol{F}^{-1})^I_i(\boldsymbol{F}^{-1})^J_j\sigma^{ij} \tag{8}$$

J is the Jacobian of $\boldsymbol{F}$, and σ the Cauchy stress on the domain. Using the stress–strain relation equation (7) the orientation of the deformed chain segment can be calculated as

$$\tan(\theta - \Theta) = \frac{\tilde{\tau}}{2g} \tag{9}$$

with

$$\tilde{\tau} = -\sigma_f \frac{1 - \dfrac{\nu_{12}\sigma_f}{e_1}\sin^2\theta}{1 + \dfrac{\sigma_f}{2e_1}\sin^2\theta + \dfrac{\sigma_f}{2g}\sin^2\theta}\sin\theta\cos\theta \tag{10}$$

The fibre strain is calculated by the combination of the strain definition given by Eqs. (2) and (9) for the orientation angle θ of the deformed chain segment, yielding

$$\varepsilon_f = \frac{\langle\varepsilon_c\cos\theta\rangle}{\langle\cos\Theta\rangle} + \frac{\langle\cos\theta\rangle - \langle\cos\Theta\rangle}{\langle\cos\Theta\rangle} \tag{11}$$

with ε_c the strain of the chain segment

$$\varepsilon_c \approx \frac{\sigma_f\cos^2\theta}{e_c} \tag{12}$$

The first term of Eq. (11) represents the strain contribution ε_c caused by the elongation of the chains, the second term represents the strain caused by the rotation of the chain segments towards the fibre axis as a result of the shear deformation of the domain. The elastic compliance E_f^{-1} during the extension of the fibre is equal to the derivative of fibre strain, Eq. (11), to the applied stress σ_f, yielding

$$\frac{1}{E_f} = \frac{1}{e_c} + \frac{1}{2g\langle\cos\theta\rangle} \times\left\langle \sin^2\theta\cos\theta\left[\frac{1 - \sigma_f\sin^2\theta\left(\dfrac{2\nu_{12}}{e_1} + \dfrac{1}{2e_1} + \dfrac{1}{g}\right)}{1 + \dfrac{\sigma_f}{2g} + \dfrac{\sigma_f}{2e_1}\sin^2\theta}\right] - \frac{2g(1+\nu_{13}) + 2\sigma_f(3-\nu_{13})\cos^2\theta}{e_c}\right\rangle \tag{13}$$

The modulus at zero stress is given by

$$\frac{1}{E_f} = \frac{1}{e_c} + \frac{\langle\sin^2\Theta\rangle_E}{2g}\left[1 - \frac{2g(1+\nu_{13})}{e_c}\right] \tag{14}$$

The subscript 'E' indicates the second moment of the orientation distribution as defined in the theory for the elastic extension of oriented crystalline polymers [1]

$$\langle\sin^2\theta\rangle_E = \frac{\langle\sin^2\theta\cos\theta\rangle}{\langle\cos\theta\rangle} \tag{15}$$

Eqs. (9) and (13) show that the modulus of the fibre increases during the extension of the fibre, due to the contraction of the orientation distribution. An approximation for the modulus of highly oriented fibres as a function of the stress is given by

$$\frac{1}{E_f} = \frac{1}{e_c} + \frac{1}{2g}\frac{\langle\sin^2\Theta\rangle_E}{\left(1 + \dfrac{\sigma_f}{2g}\right)^3} \tag{16}$$

2.2. Viscoelastic extension of a polymer fibre

Experimentally it has been shown that for various fibres the sonic modulus increases during creep deformation at a constant load [9,10]. A typical example of the compliance of a PpPTA fibre during creep is shown in Fig. 1. The increase of the sonic modulus during the elastic deformation has been explained by a rotation of the chain axis towards the fibre axis, due to the elastic shear deformation of the domain. The increase of the sonic modulus during creep suggests that the creep deformation of these fibres is caused by a similar mechanism. The elastic deformation is due to the elongation of the polymer chain and a shear displacement of adjacent chains. As covalent bonds are purely elastic, there cannot be a contribution of the chain elongation to the viscoelastic deformation of the fibre [13]. Hence, the viscoelastic deformation should be solely the result of a viscoelastic shear deformation of the domains. The continuous chain model has been developed for the description of a finite elastic deformation. The theory for finite linear viscoelasticity is a rather straightforward extension of the theory of finite elastic deformation [14]. In this theory the infinitesimal stress and strain measures σ and ε are replaced by their finite counterparts. So, in the material picture the viscoelastic relations should be developed in terms of the right Cauchy–Green tensor $\boldsymbol{C}$ and the Piola stress $\boldsymbol{S}$.

It has been argued that the yield of a polymer fibre is due to a permanent simple shear deformation of the domain, because the yield deformation is caused by a permanent displacement of adjacent chains [4]. As a similar mechanism is proposed for the viscoelastic deformation, also the viscoelastic deformation should be a simple shear deformation of the domain. The deformation of the domain consists of an elastic and a viscoelastic contribution. The elastic deformation is given by $\boldsymbol{F}_e$ and the viscoelastic deformation by $\boldsymbol{F}_v$. The reference configuration of the domain $\wp$ for the elastic deformation is the domain deformed by $\boldsymbol{F}_v$, because the stress free shape of the domain $\wp$ at a time t is given by $\boldsymbol{F}_v(\wp)$. So the total deformation of $\wp$ is given by

$$\boldsymbol{F} = \boldsymbol{F}_e\cdot\boldsymbol{F}_v \tag{17}$$

Usually the total deformation is written as the sum of the

elastic and the plastic deformation: $\boldsymbol{F} = \boldsymbol{F}_e + \boldsymbol{F}_v$ [14,15]. However, as this equation assumes a constant reference configuration for the elastic deformation, it does not describe the influence of the viscoelastic deformation on the elastic deformation. For example, for the description of the increase of the sonic modulus during creep it is necessary to use Eq. (17). This equation is similar to the commonly used equation $\boldsymbol{F} = \boldsymbol{F}_e \cdot \boldsymbol{F}_p$ for the description of plastic deformation.

A simple shear deformation is given by the tensor

$$\begin{pmatrix} 1 & 0 \\ \kappa & 1 \end{pmatrix} \tag{18}$$

As rotations are excluded, $\boldsymbol{F}_v$ should be equal to the symmetric decomposition of the simple shear tensor

$$\boldsymbol{F}_v = \begin{pmatrix} \dfrac{1 + \sin^2 \alpha_v}{\cos \alpha_v} & \sin \alpha_v \\ \sin \alpha_v & \cos \alpha_v \end{pmatrix} \tag{19}$$

with $2\tan \alpha_v = \kappa_v$. The orientation of the chain segment in the viscoelastic deformed domain is given by Θ_v

$$\tan(\Theta_v - \Theta) = \tan \alpha_v = \tfrac{1}{2} \kappa_v \tag{20}$$

The elastic deformation is defined with respect to the viscoelastic deformed domain, hence the orientation angle θ of the domain is given by

$$\tan(\theta - \Theta_v) = \frac{\tilde{\tau}}{2g} \tag{21}$$

The viscoelastic parameter κ_v is related to the load history of the Piola stress $\boldsymbol{S}$ on the domain. It is supposed that κ_v is related to the same stress which causes the elastic simple shear deformation. Therefore the elastic deformation

$$\boldsymbol{I} + \boldsymbol{U} = \begin{pmatrix} 1 + U_{11} & U_{13} \\ U_{31} & 1 + U_{33} \end{pmatrix} \tag{22}$$

is considered. The elastic simple shear parameter κ_e has been defined in Ref. [6] by the tangent of the angle between the deformed chain segment and the deformed unit vector perpendicular to the chain segment

$$\kappa_e = \tan \beta = \tan(\delta^{(3)} - \delta^{(1)}) = \frac{\tan \delta^{(3)} - \tan \delta^{(1)}}{1 + \tan \delta^{(1)} \tan \delta^{(3)}} \tag{23}$$

See Fig. 4 for the definitions of $\delta^{(1)}$ and $\delta^{(3)}$. For a purely elastic simple shear deformation the parameter κ_e is equal to the simple shear κ, see Eq. (18). The parameter κ_e can be expressed in the components of $\boldsymbol{C}$

$$\kappa_e = \sqrt{C_{22}} \frac{C_{13}}{J} \tag{24}$$

As the components of $\boldsymbol{C}$ are related to the components of $\boldsymbol{S}$ by Eq. (7), κ_e is a function $\kappa_e(\boldsymbol{S})$. In second order of the components of $\boldsymbol{U}$, κ_e can be approximated by

$$\kappa_e = 2U_{13} \tag{25}$$

Using the formulas of the elastic theory κ_e can be expressed in the fibre stress

$$\kappa_e(\boldsymbol{S}) \approx \frac{\tilde{\tau}}{g} \tag{26}$$

Suppose that the viscoelastic simple shear deformation depends on the same stress as the elastic shear deformation, then the viscoelastic shear deformation κ_v is a functional of the load history $\tilde{\tau}(t)$. Assuming that κ_v and $\tilde{\tau}(t)$ are related by a linear viscoelastic relation, the viscoelastic simple shear deformation of a domain is given by

$$\kappa_v(t) = \int_0^t j(t - t') \left(\frac{\mathrm{d}\tilde{\tau}}{\mathrm{d}t'} \right) \mathrm{d}t' \tag{27}$$

with $j(t)$ the viscoelastic shear compliance. Combination of Eqs. (21) and (22) yields the elastic plus viscoelastic deformation

$$\tan(\theta(t) - \Theta) = \frac{\tilde{\tau}(t)}{2g} + \frac{\kappa_v(t)}{2} \tag{28}$$

The tensile strain of the viscoelastic deformed fibre is given by Eq. (11) in combination with the viscoelastic Eq. (28) for θ. These equations form the constitutive equations for the viscoelastic deformation of a polymer fibre of which the viscoelastic part of the deformation is only due to a time dependent simple shear deformation of the domains. The first term on the right-hand side of Eq. (28) represents the elastic deformation, the second term represents the time dependent part of the deformation. Eq. (28) can be rather complicated because both $\tau(t)$ and $\kappa_v(t)$ are functions of θ. In the next section Eq. (28) will be analysed for a creep deformation in the limit of small creep strains.

2.3. Creep at a constant load

In a creep experiment on a fibre the elongation of the fibre is measured at a constant load. It is assumed that a load σ_f is applied at $t = 0$. As the time dependent deformation changes the load free shape of the domain is not constant. Therefore the stress on the domain and its elastic deformation change, in particular the shear deformation and the shear stress $\tilde{\tau}$. Eq. (28) for a creep experiment reads

$$\tan(\theta(t) - \Theta) = \frac{\tilde{\tau}(t)}{2g} + \frac{j(t)}{2} \tilde{\tau}(0) + \frac{1}{2} \int_{t>0}^{t} j(t - t') \frac{\mathrm{d}\tilde{\tau}}{\mathrm{d}t'} \mathrm{d}t' \tag{29}$$

In Eq. (29) the elastic deformation is analysed at t and the contribution of the integral at $t = 0$, $j(t)\tau(0)$, has been separated. This equation can be used for arbitrary orientation angle Θ, creep compliance $j(t)$ and finite strain. The creep compliance is an increasing function of t. The absolute value of the integral in the right hand side of Eq. (29) is always smaller than $|j(t)(\tau(t) - \tau(0))|$.

For highly oriented fibres, like PpPTA fibres, the viscoelastic change of θ will be small. For the example in Fig. 1 the decrease of the angle θ during the creep is equal to 10%

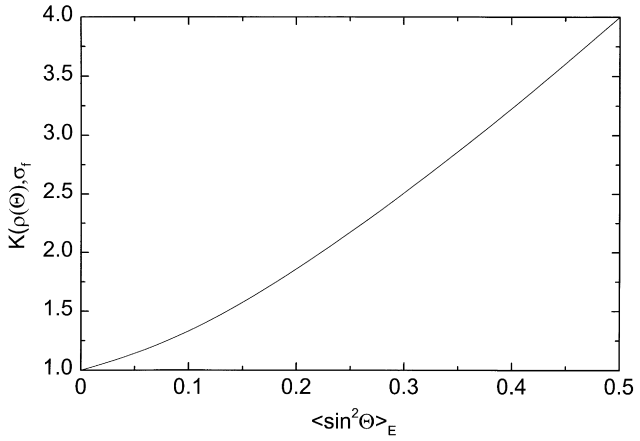

Fig. 5. The function $K(\rho(\Theta), \sigma_f)$ versus the orientation parameter $\langle \sin^2 \Theta \rangle_E$ for a Gaussian orientation distribution.

of the value at $t = 0$. Therefore $\tau(t) - \tau(0)$ can be neglected with respect to $\tau(0)$ and thus the integral in the right hand side of Eq. (29) can be neglected with respect to the other terms. The orientation angle of the only elastically deformed domain at $t = 0$ is denoted by θ_o. Owing to the viscoelastic deformation the orientation angle θ decreases during the creep experiment, therefore the shear stress on the domain slightly decreases and the elastic shear strain decreases as well. The change $\Delta\theta = \theta(t) - \theta_o$ of the orientation angle during creep is calculated by considering the contributions of both the viscoelastic increase and the elastic decrease of the shear deformation. For the small creep strains which occur during the creep of highly oriented fibres $\Delta\theta$ is very small, so the terms $\tan(\theta(t) - \Theta) = \tan(\Delta\theta + (\theta_o - \Theta))$ and $\tau(t) = \tau(\theta(t)) = \tau(\Delta\theta + \theta_o)$ can be developed up to the linear term in $\Delta\theta$. Using Eq. (21) for elastic deformation at $t = 0$ the equation

$$\Delta\theta = -\frac{j(t)\sigma_f}{2}\left[\frac{1 - \dfrac{2\nu_{12}\sigma_f}{e_1}\sin^2\theta_o}{1 + \dfrac{\sigma_f}{2g} + \dfrac{\sigma_f}{2e_1}\sin^2\theta_o}\right]\sin\theta_o\cos\theta_o \tag{30}$$

results for the change of the orientation angle during creep. The term $2\Delta\theta/j(t)$ is almost equal to $\tau(\theta_o)$. It is remarked that $\Theta - \theta_o$ is not equal to the elastic change of the orientation angle during the creep deformation, because the shear stress on the domain decreases due to the viscoelastic deformation.

At a constant load σ_f, due to the viscoelastic rotation of the chain segment, also the contribution of the chain elongation ε_c to the fibre strain changes slightly. For highly oriented rigid chain polymers this contribution can be neglected because the chain elongation is very small and the value of $\langle \cos\theta \rangle$ changes only very little during creep. Neglecting the contribution of the chain elongation, the time dependent deformation of the fibre is given by

$$\varepsilon_f(t) = \frac{\langle \cos\theta(t) \rangle - \langle \cos\theta_o \rangle}{\langle \cos\Theta \rangle} \tag{31}$$

The creep strain is developed in first-order of $\Delta\theta$ as well

$$\varepsilon_f(t) = -\frac{\langle \sin\theta_o \Delta\theta \rangle}{\langle \cos\Theta \rangle} \tag{32}$$

Substitution of Eq. (30) yields

$$\varepsilon_f(t) = \frac{j(t)}{2}\langle\sigma\rangle_N \tag{33}$$

with the normalised creep stress $\langle\sigma\rangle_N$ given by

$$\langle\sigma\rangle_N = \frac{\sigma_f}{\langle \cos\Theta \rangle}\left\langle \frac{1 - \dfrac{2\nu_{12}\sigma_f}{e_1}\sin^2\theta_o}{1 + \dfrac{\sigma_f}{2g} + \dfrac{\sigma_f}{2e_1}\sin^2\theta_o}\sin^2\theta_o\cos\theta_o \right\rangle \tag{34}$$

Eq. (33) predicts the creep strain as a function of the applied stress and the orientation distribution. This equation can be used if (1) the integral in Eq. (29) can be neglected; and (2) if the first-order approximations in $\Delta\theta$ are allowed. For most technical fibres these equations can be used as their creep is rather small.

The time dependence of the shear compliance $j(t)$ should be determined empirically. A good approximation for the normalised stress can be calculated from the fibre modulus E_f at $t = 0$ immediately after loading

$$\langle\sigma\rangle_N \approx 2\sigma_f g\left(\frac{1}{E_f} - \frac{1}{e_c}\right) \tag{35}$$

Using the equations of the modified series model Northolt has shown that the experimentally observed relation between the compliance $D_f = E_f^{-1}$ of the fibre and the creep strain can be described by

$$\frac{\Delta\varepsilon_f}{\Delta D_f} = -g \tag{36}$$

For highly oriented fibres, when all terms with $\sin^2\theta$ within the square brackets in Eq. (13) can be neglected, a similar relation can be calculated by making a first order development in $\Delta\theta$ of the equations for the fibre strain (11) and the modulus (13). The result is given by the equation

$$\frac{\Delta\varepsilon_f}{\Delta D_f} = -\frac{g}{\left(1 + \dfrac{\sigma_f}{2g}\right)}K(\rho(\Theta), \sigma_f) \tag{37}$$

K is a function of the orientation distribution at the beginning of the creep experiment. In Fig. 5 K has been drawn versus $\langle \sin^2\theta \rangle_E$ for a Gaussian orientation distribution.

2.4. The creep of PpPTA fibres

The time dependence of the creep compliance j is experimentally determined. For PpPTA fibres the logarithmic

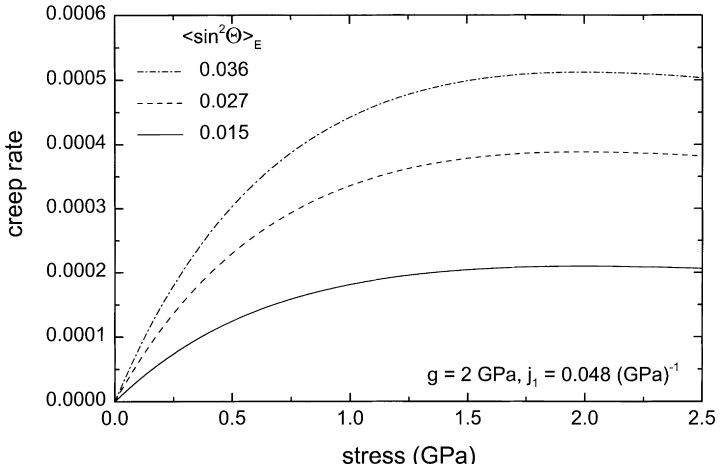

Fig. 6. The creep per decade as a function of the fibre stress according to Eq. (41) for PpPTA fibers with different orientation parameters.

creep law $j(t) = j_1 \log(t)$ is experimentally well established. Substitution of the logarithmic creep law in Eq. (33) yields

$$\varepsilon_f(t) = \tfrac{1}{2} j_1 \log(t) \langle\sigma\rangle_N \tag{38}$$

Eq. (38) predicts that the logarithmic creep coefficient of the creep is proportional to the normalised creep stress. The constant of proportionality j_1 is a material constant describing the creep of PpPTA fibres. The constant j_1 will be called the domain shear creep constant. For purely elastic deformation equation (28) reads

$$\tan(\theta - \Theta) = -\frac{\sigma_f}{2g} \sin\theta \cos\theta \tag{39}$$

In Ref. [3] it has been shown that an analytical approximation for this equation is

$$\tan\theta = \frac{\tan\Theta}{\left(1 + \dfrac{\sigma_f}{2g}\right)} \tag{40}$$

Using Eqs. (34) and (40), together with the approximation $\tan\Theta \approx \sin\Theta$ for well-oriented fibres, Eq. (38) can be written as

$$\varepsilon_f(t) = \frac{j_1 \log(t)}{2} \langle\sin^2\Theta\rangle_E \frac{\sigma_f}{\left(1 + \dfrac{\sigma_f}{2g}\right)^3} \tag{41}$$

In this equation the factor containing the fibre stress has a maximum value for $\sigma_f = g$. Fig. 6 shows the creep per decade for fibres with different values of the orientation parameter. If the sonic modulus at the beginning of the experiment is known, Eq. (35) can be used

$$\varepsilon_f(t) = \frac{j_1 \log(t) \sigma_f}{2} \left[\frac{1}{E_f} - \frac{1}{e_c}\right] 2g \tag{42}$$

Since Eq. (41) does not account for the plastic deformation during loading of the fibre the second method yields a more accurate prediction for the creep strain. Both equations will be compared with the results of the experiments.

Table 1
The sonic modulus of the fibres used for the creep measurements

Fibre	Sonic modulus (GPa)	Sonic modulus after m.c. (GPa)[a]
A	73	84
B	88	100
C	121	–
D	84	–
E	132	134

[a] The abbreviation m.c. indicates a mechanically conditioned fibre.

3. Experimental

Experiments have been performed on a selection of PpPTA fibres with very different values for the orientation parameter and initial modulus. During the experiments on fibres A, B and E, the sonic modulus has been monitored during creep. The sonic moduli of the fibres have been listed in Table 1.

The viscoelastic response of a fibre to a static load decreases considerably after the fibre has been pre-loaded up to a stress higher than the stress during the creep experiment. Leaderman explains this phenomenon by the absence of plastic deformation in the second deformation [16]. The plastic deformation has been removed by the first higher load. The short pre-loading of the fibre is called mechanical conditioning. The non-recoverable creep is called secondary creep and the recoverable creep is called primary creep [16]

The response of a PpPTA fibre to a short loading has been depicted in Fig. 7. As the load has been applied only a few seconds, the viscoelastic deformation should be very small. However, it is observed from Fig. 7 that the fibre slowly recovers to a new equilibrium length. This implies that the non-elastic deformation is not completely permanent.

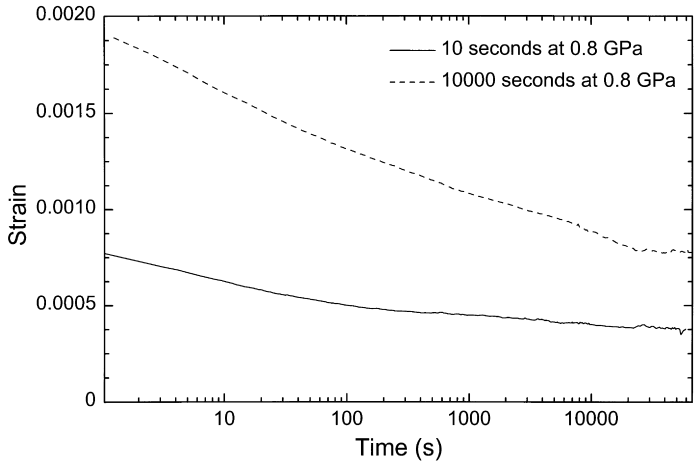

Fig. 7. The recovery of a PpPTA fibre after being loaded at 0.8 GPa during 10 seconds. For comparison the recovery has been plotted after being loaded at 0.8 GPa during 10^4 seconds.

The same effect can be observed in the yield behaviour of the pre-loaded fibre. If the fibre is loaded shortly after the application of the pre-load, the yield point has disappeared. After a longer waiting time the yield, and thus non-elastic deformation, reappears [4]. These observations indicate that division in primary and secondary creep, and in mechanically conditioned and not mechanically conditioned yarns, might be too simple for the complete description of the viscoelastic phenomena of polymer fibres. Nevertheless the fibres change due to a pre-load which results in a higher initial modulus and a lower creep rate. It may be assumed that, apart from a permanent contraction of the orientation distribution, an eventual chain slip component in the deformation will be reduced by the mechanical conditioning. Creep experiments after a mechanical conditioning have been performed on three of the tested fibres.

3.1. The relation between the sonic compliance and the creep strain

According to Eq. (37) the variation of the compliance during creep is related to the creep strain by the shear modulus g. In Fig. 8 the experimental values have been compared to the values predicted by the theory. The experimental values and the predicted value are in the same order of magnitude, which supports the assumption that the main mechanism of creep is a viscoelastic shear deformation of the domains. Because the variations of both the strain and the sonic modulus during creep are very small the value of $\Delta\varepsilon/\Delta D_f$ is sensitive to small disturbances, which may cause the discrepancy between the experimental and the calculated values. A contribution of chain slip to the creep strain would cause a too high value for $\Delta\varepsilon/\Delta D_f$. The continuing process of breaking and reformation of secondary bonds

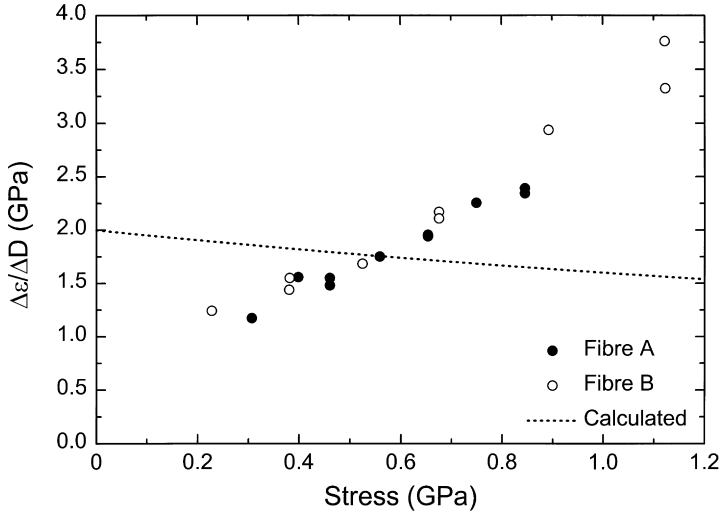

Fig. 8. The quantity $\Delta\varepsilon_f/\Delta D$ versus the creep stress. The dotted line has been calculated with Eq. (37).

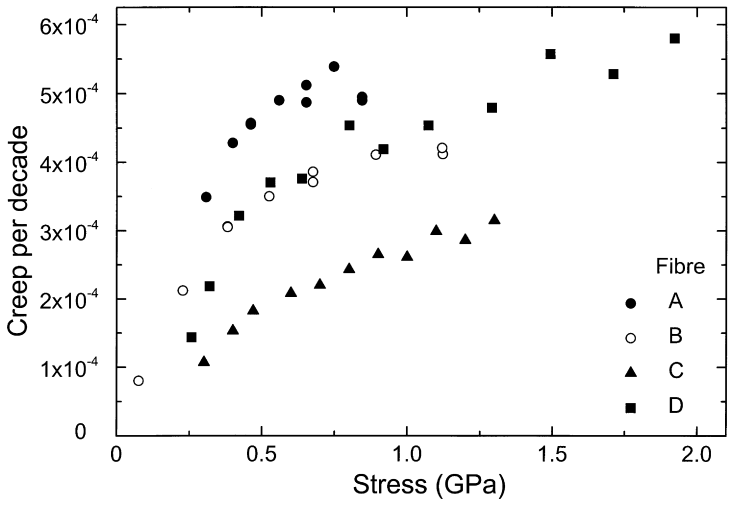

Fig. 9. The logarithmic creep coefficient versus the creep stress for a selection of PpPTA fibres.

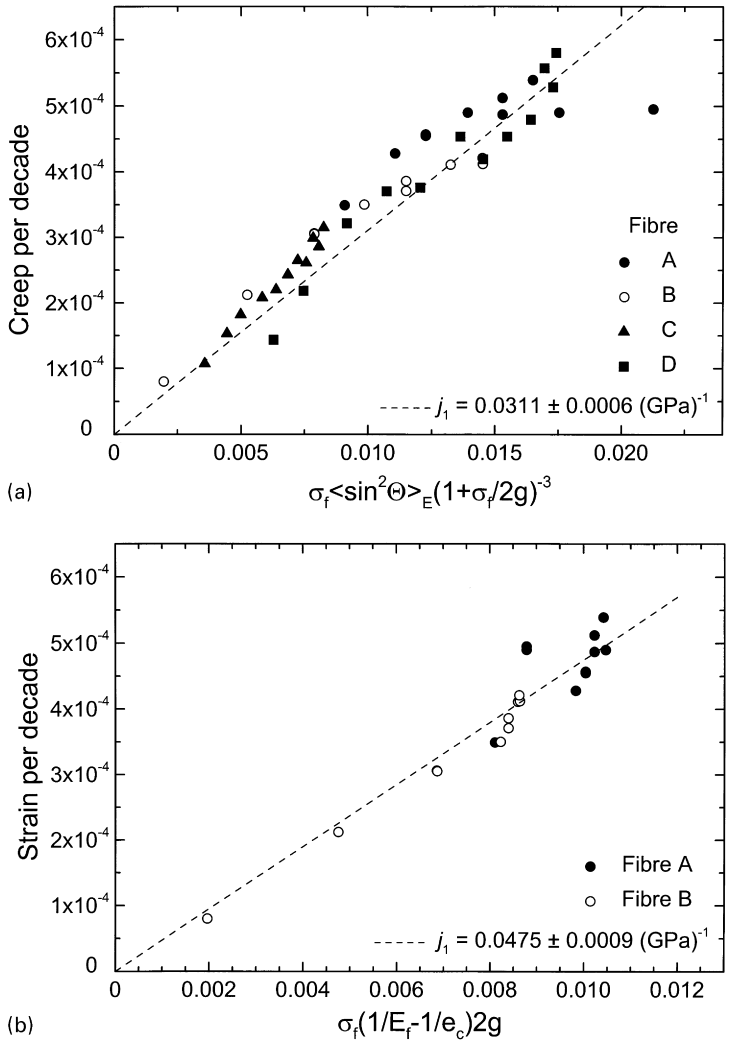

Fig. 10. The logarithmic creep coefficient for a selection of PpPTA fibres versus: (a) the normalised stress calculated with formula (41); and (b) calculated with formula (42).

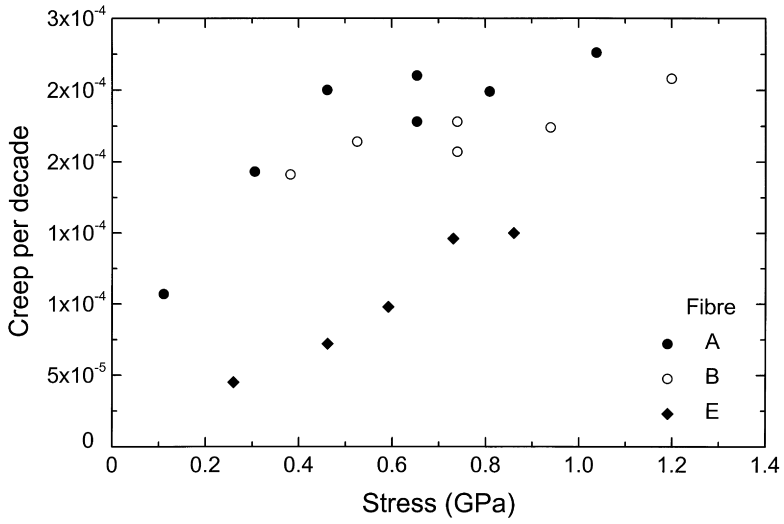

Fig. 11. The logarithmic creep coefficient versus the stress for a selection of mechanical conditioned PpPTA fibres.

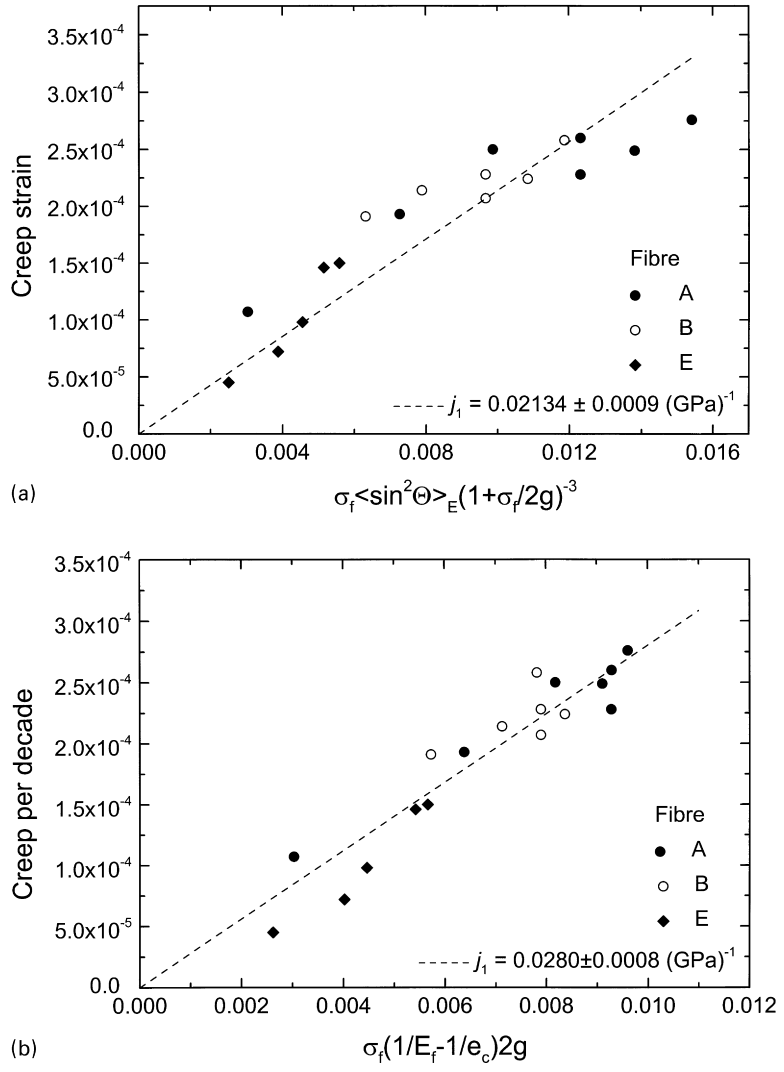

Fig. 12. The logarithmic creep coefficient for a selection of mechanical conditioned PpPTA fibres versus the normalised stress calculated (a) with formula (41) and (b) with formula (42).

may influence the value of the shear modulus, and therefore the value of the sonic modulus during creep. This would cause a too low value for $\Delta\varepsilon/\Delta D_f$.

3.2. The normalised creep stress

Creep experiments as a function of the stress have been performed on the five PpPTA fibres listed in Table 1. The creep of the fibres A to D has been measured without mechanical conditioning and the creep of the fibres A and B have been measured after mechanical conditioning as well. The creep of the fibre E has been measured only after mechanical conditioning. In Fig. 9 the logarithmic creep rate has been plotted versus the creep stress. For all fibres the logarithmic creep rate follows the typical convex curve similar to the curves presented in Fig. 2, the low modulus fibres showing the highest creep rate. For several fibres the creep has been measured at the same stress twice. These measurements give an indication of the reproducibility of the creep measurement. The variation on the logarithmic creep coefficient is estimated to be smaller than 3%. By plotting the data of Fig. 9 versus the normalized stress according to the expressions given by Eqs. (41) and (42), we can investigate whether the creep of the PpPTA yarns is described by a single compliance constant j_1. For all fibres a shear modulus of 2 GPa has been assumed. In Fig. 10a the logarithmic creep rate has been plotted versus the normalised creep stress calculated by Eq. (41). The dashed line has been determined by linear regression only varying its slope. All data points of the creep of all fibres lay close to the theoretical line. From the regression line a value of $j_1 = 0.0311 \pm 0.0006\ (\mathrm{GPa})^{-1}$ has been calculated for the domain shear creep constant. The standard deviation for the individual point from the theoretical line is equal to $4.9 \times 10^{-5}\ (\mathrm{GPa})^{-1}$. In Fig. 10b the logarithmic creep rate has been plotted versus the normalised creep stress calculated using the sonic modulus at the beginning of the creep experiment with Eq. (42). The agreement of the experimental logarithmic creep rates with the theoretical curve is somewhat better. From the slope of the regression line in Fig. 10a value of $j_1 = 0.0475 \pm 0.0009\ (\mathrm{GPa})^{-1}$ results for the domain shear creep constant of primary creep. The standard deviation for the individual data points is equal to $3.4 \times 10^{-5}\ (\mathrm{GPa})^{-1}$. Although both formulas show a fair agreement with the experimental data the latter should be preferred because it accounts for the effect of plastic deformation on the initial value of the normalised creep stress.

The results of the experiments on the mechanically conditioned yarns are presented in Figs. 11 and 12. In Fig. 11 the raw data has been plotted. Fig. 12a and b show the logarithmic creep rate versus the normalised creep stress. In Fig. 12a the logarithmic creep rate has been plotted versus the normalised stress calculated by Eq. (41). The regression line yields for the domain shear creep constant of the mechanically conditioned fibres $j_1 = 0.0214 \pm 0.0009\ (\mathrm{GPa})^{-1}$. The standard deviation for the individual point is equal to $3.4 \times 10^{-5}\ (\mathrm{GPa})^{-1}$. In Fig. 12b the logarithmic creep rate has been plotted versus the normalised stress calculated by Eq. (42). The regression line yields for the domain shear creep constant of the mechanically conditioned fibres the value $0.0280 \pm 0.0008\ (\mathrm{GPa})^{-1}$. The standard deviation for the individual point is equal to $2.3 \times 10^{-5}\ (\mathrm{GPa})^{-1}$, thus also for the creep of mechanically conditioned fibres the best description of the logarithmic creep rate is obtained using the normalised shear stress estimated from the sonic modulus at the beginning of the creep experiment.

As shown by Eq. (42) the creep rate has a maximum value for $\sigma_f = g$. Though the data of Figs. 2, 9 and 11 show the creep rate to level off for increasing stress, the number of data in the high stress region is not sufficient to confirm this theoretical result.

4. Conclusions

The continuous chain model for the description of the tensile curve of a polymer fibre below the glass transition temperature has been extended to include viscoelastic deformation. Similar to the description of the yield behaviour of a polymer fibre, the viscoelastic deformation is caused by the viscoelastic simple shear displacement of adjacent chains in the domains of the fibre. This allows the calculation of the time dependent change of chain orientation angle, which yields the viscoelastic extension of the fibre. For small creep strains the relation for the stress dependence of the creep rate of polymer fibres has been derived. It shows that the creep rate has a maximum value for a fibre stress equal to the value of the internal shear modulus. By the introduction of a normalised shear stress a simple relation has been derived which allows the determination of the creep compliance constant.

As an example of the application we have shown that the creep behaviour of PpPTA fibres can be well described by the proposed theory. The results of the experiments show that PpPTA fibres having different moduli still have the same value of the creep compliance constant. Mechanical conditioning of the fibres lowers this constant.

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