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The viscoelastic extension of polymer fibres: complex loadings

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Abstract

The response of oriented polymer fibres to complex loading patterns is investigated. It is shown that the creep and stress relaxation is non-linear with the applied stress. The ratio of the creep rate and the stress–relaxation rate is given by the local slope of the tensile curve and not by the elastic modulus as predicted by linear viscoelastic theory. A consequence of this observation is that viscoelastic and yield deformations are coupled. By analysing the results of the step-creep and the strain–relaxation–strain experiments performed on poly(*p*-phenylene terephthalamide) fibres, it is shown that the linear superposition principle does not apply to the tensile deformation of polymer fibres above the yield point. Finally the various components of the tensile deformation that should be covered by a constitutive equation for polymer fibres are discussed.

Keywords: Fibres; Creep; Stress relaxation

1. Introduction

Oriented polymer fibres are often applied because of their high dimensional stability. Examples are fibre reinforced driving belts, tyres or optical cables. The fibres in these constructions are subjected to varying tensile forces. In order to optimise the performance of these constructions it is necessary to know the mechanical response of the fibre to complex loadings. This response is a complicated problem because most oriented fibres do not conform with the well known theory of linear viscoelasticity [1].

During the last decades, highly oriented polymer fibres, like poly(*p*-phenylene terephthalamide) or PpPTA, poly(*p*-phenylene benzobisoxazole) or PBO and poly[2,6-diimi-diazo(4,5-*b*:4′5′-*e*)pyridinylene-1,4(2,5-dihydroxy)-phenylene] or PIPD, have been developed. They are characterised by a high modulus, a high strength and low creep rates. These properties may suggest that using the principles of linear viscoelasticity the response to complex loadings can be approximated. However, like the polyamide, polyester and cellulose fibres, they show a yield in the tensile curve at a strain between about 0.005 and 0.025 indicating at least plastic behaviour. In general, yielding is considered to begin at that point in the tensile curve at which a deviation of linear elastic behaviour is observed. The yielding phenomenon has been explained by the onset of a sequential and plastic orientation mechanism brought about by the resolved shear stress [2]. A simple theory shows that the yield strain is a function of the orientation parameter. It also explains the difference between the first loading curve and the hysteresis curve of polymer fibres. Yet, as shown in this paper yielding and viscoelasticity of polymer fibres are not separate phenomena.

The theory of linear viscoelasticity distinguishes between elastic deformation, delayed elastic deformation and Newtonian flow. Elastic deformation is an immediate and reversible response to a stress. Delayed elastic deformation is a time-dependent and reversible deformation. Newtonian flow is a time-dependent and permanent deformation. Experimentally, five contributions to the tensile deformation of the polymer fibre can be distinguished: (1) an elastic contribution, (2) the yield deformation which is partly permanent and (3) partly recoverable, (4) a time-dependent reversible contribution, and (5) a time-dependent permanent contribution. The elastic deformation is practically immediate. On the time-scale of a tensile experiment, the yield deformation is

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immediate as well. The yield deformation is not a purely permanent deformation, but partly recoverable. The recoverable part of the deformation is called semi-plastic deformation. Newtonian flow occurs in fibres above the glass transition temperature [3]. In oriented fibres below the glass transition temperature Newtonian flow does not occur. These five deformations make a complete description of the deformation of polymer fibres, including the high-modulus fibres, subjected to complex loadings a difficult problem.

In a series of publications, the continuous chain model for the tensile deformation of polymer fibres in the glassy state has been presented [2,4–7]. In this series model, the parameters are the chain orientation, the average modulus for shear between the chains, the chain modulus and a simple yield criterion based on the critical resolved shear stress. Next, a model for the viscoelastic deformation of polymer fibres has been developed which is based on the linear viscoelastic shear deformation of the domain being the building block of the continuous chain model [8]. It has been shown that the creep of aramid or poly(*p*-phenylene terephthalamide) fibres, abbreviated here as PpPTA, can be described by this linear viscoelastic domain approximation. In the theory of linear viscoelasticity, the relation between different viscoelastic quantities, such as creep and stress relaxation, and the response to complex loadings, can be reduced to a single time-dependent function. In this article on complex loadings of oriented polymer fibres below the glass transition temperature, we will discuss a number of features related to the tensile deformation of real fibres which cannot be described by the linear viscoelastic domain approximation.

Because of the complexity of the deformation of oriented fibres, first the elementary relation between creep and stress relaxation will be considered for mechanically conditioned and non-mechanically conditioned fibres. It will be shown that a simple viscoelastic theory fails to describe this relation, because it appears that it is necessary to account for yield deformation as well. Subsequently it will be shown that the creep of mechanically conditioned fibres and non-mechanically conditioned fibres cannot be described by a single time-dependent creep compliance function for the domain.

The response to complex loading is commonly described by the Boltzmann superposition principle, or by modifications of this superposition principle [1,9–12]. The principle of superposition is tested in two experiments. In the step-creep experiment, the response of the fibre to a stepwise increased load is measured, in the strain–relaxation–strain experiment the strain is increased at a constant strain rate up to a certain value. At this value of the strain, the relaxation of the stress is measured during a certain time and subsequently the strain is increased at a constant strain rate up to failure. It will be shown that the deformation in these experiments is not in agreement with the principle of superposition.

2. The model for a polymer fibre with elastic, viscoelastic and plastic deformation

2.1. Elastic and viscoelastic deformation

In the continuous chain model the strain of the polymer fibre is considered to be equal to the strain of a chain with average properties, measured along the fibre axis [4–6]. The chain is divided into small straight segments, the angle between the chain segment and the fibre axis in the unloaded state is denoted by Θ. The angle Θ follows an orientation distribution $\rho(\Theta)$. The local mechanical properties are determined by a small domain around the chain segment. It is supposed that this domain has transverse isotropic symmetry with the following elastic constants: the chain elastic modulus e_c, the transverse modulus e_1, the modulus for shear parallel to the chains g and the Poisson ratios ν_{12} and ν_{13} for application of a stress normal and parallel to the chain axis, respectively. All domains have equal mechanical properties. Only the elongation and rotation of chain segments cause the extension of the fibre. Chain deformation is supposed to be perfectly elastic, because of the covalent nature of the intra-chain bonds [13]. The rotation is caused by shear deformation of the domain. Time-dependent and plastic deformation contributions to the total strain of the fibre are described by time-dependent and plastic simple shear deformations of the domain. A constitutive equation for viscoelastic polymer fibres has been derived by using the concept of a linear viscoelastic shear mechanism for the deformation of the domain.

The strain of the fibre ε_f is equal to the strain of a long and continuous chain with average properties that does not break during extension and given by

$$\varepsilon_f = \frac{\langle \varepsilon_c \cos\theta \rangle}{\langle \cos\Theta \rangle} + \frac{\langle \cos\theta \rangle - \langle \cos\Theta \rangle}{\langle \cos\Theta \rangle} \tag{1}$$

where θ is the angle between a deformed chain segment and the fibre axis and ε_c the strain of the chain segment. The quantity ε_c is a unique function of the momentary stress, and θ is a function of the total load history of the domain. The average is taken over the chain orientation distribution. In the case of a linear viscoelastic simple shear mechanism the simple shear deformation of the domain is given by the equation

$$\kappa_v(t) = \int_0^t j_1(t-t') \frac{\delta \tilde{\tau}(t')}{\delta t'} \mathrm{d}t' \tag{2}$$

where $j_1(t)$ is the viscoelastic shear compliance, σ_f the fibre stress and the shear stress is given by

$$\tilde{\tau} = -\sigma_f \frac{\left(1 - \frac{\nu_{12}\sigma_f}{e_1}\sin^2\theta\right)}{\left(1 + \frac{\sigma_f}{2e_1}\sin^2\theta + \frac{\sigma_f}{g}\sin^2\theta\right)} \sin\theta\cos\theta \tag{3a}$$

which for well oriented fibres can be approximated by

$$\tau = -\sigma_f \sin\theta \cos\theta \tag{3b}$$

The angle θ is given by the formula

$$\tan(\theta(t) - \Theta) = \frac{\tilde{\tau}(t)}{2g} + \frac{1}{2}\kappa_v(t) \tag{4}$$

Eqs. (2)–(4) form a constitutive equation for the viscoelastic deformation of a single domain. Together with Eq. (1) they form a constitutive equation for viscoelastic polymer fibres.

2.2. The plastic deformation

In previous papers it has been shown that the yield of a polymer fibre can be described by a permanent simple shear deformation of the domain [2,7]. It has been proposed that permanent deformation starts at a critical value κ_y of the elastic simple shear deformation κ_e/g. The 'square root' plastic shear law provides a good approximation of the stress vs. strain curve of a domain at a constant deformation rate

$$\tan(\theta(t) - \Theta) = \frac{\tilde{\tau}(t)}{2g} + \frac{1}{2}\kappa_p(t) \tag{5}$$

with

$$\begin{cases} \kappa_p = 0 & |\kappa_e| < \kappa_y \\ \kappa_p = \frac{1}{2}p\sqrt{|\kappa_e| - \kappa_y} & |\kappa_e| > \kappa_y \end{cases} \tag{6}$$

The parameter p, which determines the amount of plastic deformation, has the same sign as $\tilde{\tau}$. Experiments have shown that not all yield deformation is permanent, part of the yield deformation recovers after the load has been removed. This reversible and immediate yield deformation is called semi-plastic deformation.

2.3. The creep of aramid fibres

For PpPTA fibres, it has been observed that the time-dependent strain is proportional to the logarithm of the time

$$\varepsilon_f = \varepsilon_0 + C_{creep}\log(t) \tag{7a}$$

By extension of the continuous chain model to viscoelastic extensions we have derived previously that the creep of PpPTA fibres can be written as

$$\varepsilon_f = \varepsilon_0 + \frac{1}{2}j_1 \log(t)\langle\sigma\rangle_N \tag{7b}$$

where the normalised creep stress $\langle\sigma\rangle_N$ of the fibre is given by

$$\langle\sigma\rangle_N = \frac{\sigma_f\langle\sin^2\Theta\rangle_E}{\left(1 + \frac{\sigma_f}{2g}\right)^3} \tag{8}$$

Eqs. (7b) and (8) were confirmed by the creep experiments [8]. The shear compliance function

$$j_1(t) = j_1 \log(t) \tag{9}$$

has a single value for the domain shear creep constant j_1. Part of the creep strain is recoverable and part is permanent. The recoverable part is called primary creep and the permanent part secondary creep. A schematic picture is shown in Fig. 1. Experimentally it has been shown that the secondary creep can be removed by application of a short pre-load to the fibre [11,14]. The application of a pre-load is called mechanical conditioning of the fibre. For the conditioning, the pre-load should be higher than the load during the deformation experiment. After the pre-load has been removed, the fibre should recover for a certain time in order to start the deformation experiment from a new equilibrium state. The creep of the unconditioned fibre is a combination of primary and secondary creep. It is remarkable that the creep of both mechanically conditioned and unconditioned fibres can be described with the linear viscoelastic domain approximation [8]. The creep of mechanically conditioned fibres satisfies the same equations using another value for the domain creep coefficient j_1. Various authors have proposed that the creep of a mechanically conditioned fibre is purely viscoelastic, and therefore more appropriate for theoretical analysis [11,14]. This suggests that time-dependent deformation can be described by a viscoelastic equation like Eq. (2). It will be shown here that this picture is a simplification in case of the creep of aramid fibres (Table 1).

Both the creep of mechanically conditioned and of non-mechanically conditioned fibres are influenced by the yield deformation. The influence of the yield on the viscoelastic deformation is rather typical for the deformation of polymer fibres. In addition to the effect of semi-plastic deformation, the non-linearity of the elastic deformation must be taken into account. Thus, for understanding the relations between different deformations and for the description of the response to complex loadings it is necessary to consider carefully the effects of the non-linear elastic, viscoelastic, plastic and semi-plastic deformation. Because of the

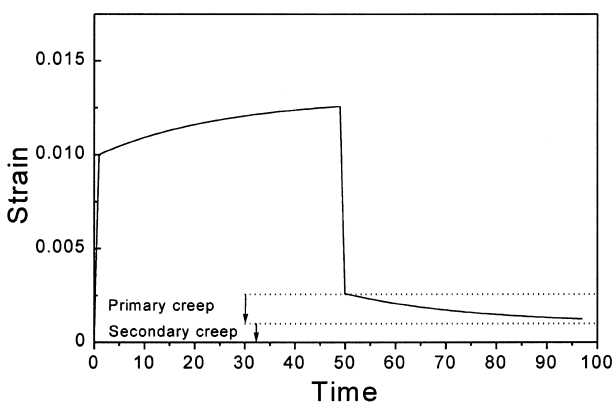

Fig. 1. Primary and secondary creep as proposed by Leaderman [11].

Table 1
The yield parameters of the conditioned and unconditioned PpPTA fibre A

	κ_y	P
Fibre A unconditioned	0.0653 ± 0.0008	0.91 ± 0.08
Fibre A conditioned	0.058 ± 0.001	0.62 ± 0.06

complex interactions between different deformation types, very simple deformations will be investigated. In the Section 3, the relation between creep and stress relaxation will be analysed.

3. The relation between creep and stress relaxation

Assuming that creep and stress relaxation are due to the same processes in the fibre, a relation might be expected between these two quantities. It will be shown that a simple consideration based on the theory of linear viscoelasticity is not confirmed experimentally. Within the theory of linear viscoelasticity the relations between the viscoelastic quantities are determined by the Boltzmann superposition principle [1]. In one dimension, the creep compliance $D(t)$ and the modulus $E(t)$ are related by

$$\int_0^t D(\tau)E(t-\tau)\mathrm{d}\tau = t \tag{10}$$

For a creep, respectively, a stress relaxation experiment the initial values of the strain and the stress are $(\varepsilon_0, \sigma_0)$. After a time t the creep strain is equal to $\Delta\varepsilon_t = \varepsilon(t) - \varepsilon_0$ and the relaxation of the stress is given by $\Delta\sigma_t = \sigma(t) - \sigma_0$. Let the creep compliance be $D(t) = \varepsilon(t)/\sigma_0$ and the stress relaxation modulus $E(t) = \sigma(t)/\varepsilon_0$, it can then be derived from Eq. (10) that for a small time-dependent deformation superimposed on a relatively large elastic deformation, i.e. for $\Delta\varepsilon/\varepsilon_0 \ll 1$ or $\Delta\sigma/\sigma_0 \ll 1$, it holds that

$$D_e + D_1(t) \approx \frac{1}{E_e + E_1(t)} \tag{11}$$

with D_e and E_e the elastic compliance and the modulus, respectively. Eq. (11) is equivalent to

$$-\frac{\Delta\sigma(\varepsilon_0, t)}{\Delta\varepsilon(\sigma_0, t)} = E_e(\varepsilon_0, \sigma_0) \tag{12}$$

For a sufficiently small time-dependent deformation, this equation should hold for non-linear viscoelastic materials as well. This can be easily understood by the following 'Gedanken' experiment. A creep experiment at a constant stress σ_0 is approximated by the following two-step procedure: (1) a period of stress relaxation during a time t_1 with an initial stress of σ_0 at $t = 0$. During this period, the stress decreases with a value $\Delta\sigma$. Next (2), at t_1 the stress is increased by $\Delta\sigma$ up to the initial value σ_0. This brings about a deformation $\Delta\varepsilon$. As this small deformation is purely elastic the relation between $\Delta\sigma$ and $\Delta\varepsilon$ is given by $\Delta\sigma/\Delta\varepsilon = E_e$. Provided the variation of the stress during the stress relaxation period is sufficiently small, the difference from a normal creep experiment is negligibly small. Recalling the logarithmic creep law, Eq. (12) implies for PpPTA fibres that stress relaxation is proportional to the logarithm of the time as well: $\sigma(t) = \sigma_0 - C_{relax}\log(t)$. It follows that the ratio of the logarithmic creep coefficient and the logarithmic relaxation coefficient, C_{relax}/C_{creep}, should be equal to the pure elastic modulus E_e at the beginning of the experiments. In Fig. 2 the creep and the stress relaxation of the PpPTA fibre A have been plotted for an initial stress of 0.65 GPa. The logarithmic dependence of the creep strain and the relaxation stress on the time holds very well over the time of the measurements. In Fig. 3a the relation C_{relax}/C_{creep} has been plotted for the PpPTA fibres A and B at several values for $(\varepsilon_0, \sigma_0)$. The values for C_{relax}/C_{creep} are compared to the elastic modulus determined from the velocity of a fast sonic pulse, which is considered to be equal to the elastic modulus E_e. It is observed in this figure that the sonic modulus of the fibre is much higher than the ratio C_{relax}/C_{creep}. This discrepancy can be understood by considering the plastic deformation of the fibre. Therefore, the Gedanken experiment above is analysed including the effect of plastic or semi-plastic deformation. Again the creep experiment is approximated by a stress relaxation experiment during a time t_1 increasing the stress at t_1 by $\Delta\sigma$ up to the initial value σ_0. The small deformation $\Delta\varepsilon$ which is necessary to increase the stress with $\Delta\sigma$ is a 'normal' mechanical deformation of the fibre and thus the deformation will follow the normal stress vs. strain curve.

Due to plastic deformation of the fibre the derivative of the stress vs. strain curve is much lower than the elastic modulus. From this argument it is predicted that $\Delta\sigma$ will be related to $\Delta\varepsilon$, not by the pure elastic modulus E_e, but by the mechanical modulus E_{mech} in the point $(\varepsilon_0, \sigma_0)$ being the derivative of the stress vs. strain curve of the fibre in this point. Thus, separating the normal viscoelastic contribution $\Delta\varepsilon_v = \Delta\sigma/E_e$ and the yield contribution $\Delta\varepsilon_p$, the total deformation can be written as $\Delta\varepsilon = \Delta\sigma/E_{mech} = \Delta\varepsilon_v + \Delta\varepsilon_p$. Using the logarithmic creep and relaxation laws, the logarithmic creep rate should be related to the logarithmic

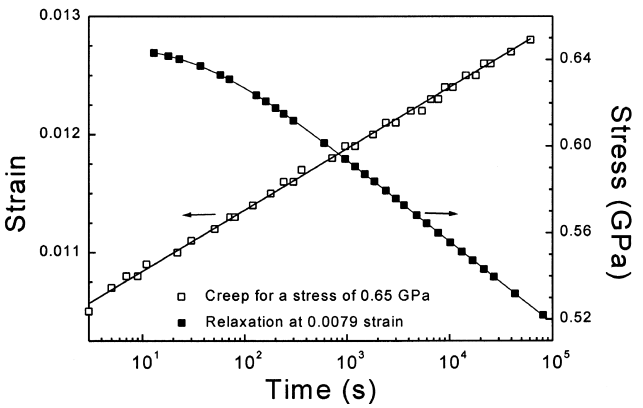

Fig. 2. Creep and stress relaxation of a PpPTA yarn at a stress of 0.65 GPa.

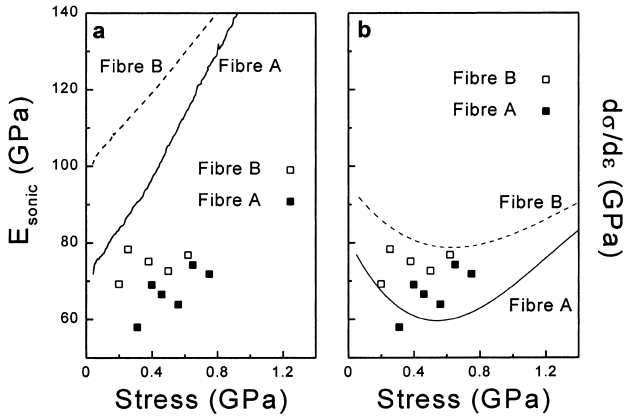

Fig. 3. (a) Comparison of the ratio of the logarithmic stress relaxation coefficient and the logarithmic creep coefficient C_{relax}/C_{creep} (represented by symbols) and the sonic modulus (drawn curves), and (b) comparison of the ratio C_{relax}/C_{creep} with the derivative of the stress vs. strain curve (drawn curves) as a function of the stress for the PpPTA fibres A and B.

relaxation rate by the relation

$$\frac{C_{relax}}{C_{creep}} = E_{mech} \tag{13}$$

In Fig. 3b the values of C_{relax}/C_{creep} have been plotted together with the derivatives of the stress vs. strain curves. It is observed that the values of C_{relax}/C_{creep} are close to the mechanical modulus of the fibre at the initial deformation $(\varepsilon_0, \sigma_0)$. As the viscoelastic and yield deformation are caused by the viscoelastic and the yield shear deformation of the domains respectively, the equation $\Delta\varepsilon = \Delta\varepsilon_v + \Delta\varepsilon_p$ should hold for the shear deformation of a simple domain: $\Delta\kappa = \Delta\kappa_v + \Delta\kappa_p$. Recalling the Gedanken experiment, the normal viscoelastic contribution $\Delta\kappa_v$ can be approximated by the elastic deformation $\Delta\kappa_e$ after the period of stress relaxation. However, in that case, the contribution of plastic deformation $\Delta\kappa_p$ should be related to $\Delta\kappa_e$ by the yield function $P(\kappa_e)$. Therefore, it is proposed that the value of the yield deformation is a function of the sum of the elastic simple shear κ_e and the viscoelastic shear deformation κ_v. Using the square root plastic shear law this yields the equation

$$\tan(\theta(t) - \Theta) = \frac{\tilde{\tau}(t)}{2g} + \frac{1}{2}\kappa_v(t) + \frac{1}{2}\kappa_p(t) \tag{14}$$

with

$$\begin{cases} \kappa_p = \frac{1}{2}p\sqrt{|\kappa_e + \kappa_v| - \kappa_y} & |\kappa_e + \kappa_v| > \kappa_y \\ \kappa_p = 0 & |\kappa_e + \kappa_v| < \kappa_y \end{cases} \tag{15}$$

The yield parameter p and $\tilde{\tau}$ have equal signs.

The relation between the creep rate and the stress relaxation rate shows that yield deformation occurs during creep. Thus, in order to understand even the simplest relations between viscoelastic properties, the complex character of the tensile deformation of a polymer fibre, comprising elastic, semi-plastic and viscoelastic contributions, should be considered. Apparently, the occurrence of yield during immediate and time-dependent deformation is due to the same yield phenomena and can therefore be derived from a single principle.

The difference between the time-dependent deformation of mechanically conditioned and mechanical unconditioned fibres is a very characteristic property of polymer fibres. In previous studies it has been supposed that the creep of mechanically conditioned fibres is a viscoelastic deformation, which can be described by an equation similar to Eq. (2), while the secondary viscoelastic deformation is influenced by plastic deformation or yield [11]. Using the terminology of this paper, this suggests that no plastic or semi-plastic deformation occurs during the creep of mechanically conditioned fibres. In the case no yield deformation occurs during the viscoelastic deformation, the relation between the stress relaxation rate and the creep rate is given by the elastic modulus E_e. Thus the time-dependent deformation of mechanically conditioned fibres can be characterized by the ratio of their creep and stress relaxation rate. The creep and the stress relaxation of two PpPTA fibres A and B with different initial moduli, after mechanical conditioning, have been measured at several values for the initial stress, see Fig. 4a and b. For the mechanically conditioned fibres the values for the creep and stress relaxation rate have been compared in a slightly different way, as the creep and stress relaxation experiments were not performed at exactly the same value for the initial stress. The experimental points for C_{creep} and C_{relax} have been fitted by a smooth function over the experimentally investigated stress interval. The ratio between the stress relaxation rate and the creep rate has been calculated by using these functions. The results for the PpPTA fibres A and B have been plotted in Fig. 5a and b. For comparison the sonic modulus and the derivative of the stress vs. strain curve of the mechanically conditioned fibre have been drawn. The derivative of the stress vs. strain curve has been approximated by a smooth function as well. These two figures clearly show that the ratio of the stress relaxation rate and the creep rate is close to the derivative of the stress

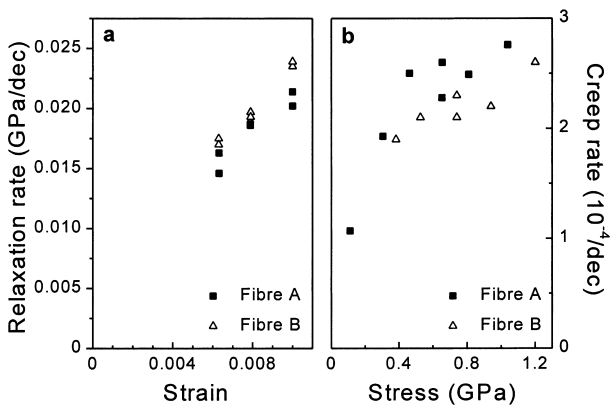

Fig. 4. (a) Stress relaxation rate and (b) creep rate of the PpPTA fibres A and B after mechanically conditioning.

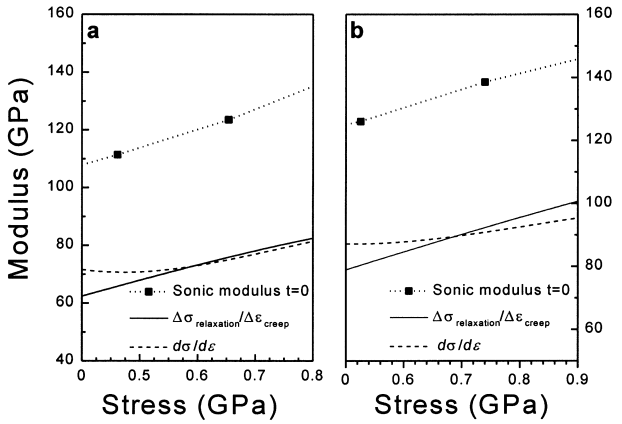

Fig. 5. The ratio between the stress relaxation and the creep for the mechanically conditioned PpPTA fibres between 0 and 0.8 GPa: (a) fibre A and (b) fibre B. For comparison the sonic modulus and the derivative of the stress vs. strain curves of the mechanically conditioned fibres have been drawn. Tensile curves have been measured at a strain rate of 10%/min using a test length of 10 cm.

vs. strain curve of the fibres, see Eq. (12), which is considerably lower than the sonic or the elastic modulus of the fibre. This experimental relation implies that also for mechanically conditioned fibres yield occurs during the time-dependent deformation, similar to the time-dependent deformation of non-mechanically conditioned fibres. As the ratio between the creep rate and the stress relaxation rate is equal to the mechanical modulus, the creep and stress relaxation of mechanically conditioned aramid fibres satisfy Eqs. (14) and (15).

In Fig. 6 the derivatives of the entire stress vs. strain curves of the PpPTA fibres A and B are shown. In these curves, the start of the yield deformation at about 0.005 strain is observed clearly. In addition to the yield point a change of the slope of the stress vs. strain curve is observed at the value of the strain that has been applied during the mechanical conditioning of the fibre. This effect is predicted by the sequential orientation mechanism [3].

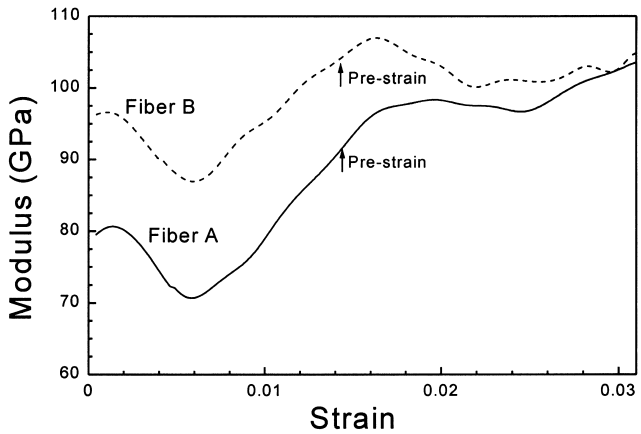

Fig. 6. The derivative of the stress vs. strain curves of representative filaments of the PpPTA fibres A and B after mechanically conditioning. Tensile curves have been measured at a strain rate of 10%/min using a test length of 10 cm.

4. Complex loadings

In Section 3 creep and stress relaxation have been analysed. In this section, the response of the fibre to two different complex loadings will be studied. The experiments were chosen in order to test the possibility of some kind of superposition principle for the description of time-dependent deformation. Essential to linear superposition is the principle that the effect of subsequent deformations can be obtained by summing the effects of the individual deformations. For example the response to a stress step $\Delta\sigma_1$ at time t_1 is determined by a function of the time: $\varepsilon(t) = D(t - t_1)\Delta\sigma_1$. The additional response to a subsequent stress step at time t_2 is independent of the stress step at t_1. The total response of the fibre after the second stress step $\Delta\sigma_2$ is the sum of the two individual responses: $\varepsilon(t) = D(t - t_1)\Delta\sigma_1 + D(t - t_2)\Delta\sigma_2$. This superposition principle is tested by the step-creep experiment. In this experiment, the stress is increased step-wise. At each stress level, the creep is measured.

In the step-creep experiment of the PpPTA fibre the stress steps amounted to 0.4 GPa and the creep was measured during 1000 s. The result has been plotted in Fig. 7. At each step the additional creep due to a load step relative to the base line of the creep curve due to previous steps obeys the logarithmic creep law. For a linear viscoelastic material following a logarithmic creep law, $D(t) = C\log(t - t_0)$, the logarithmic creep rates for a normal creep experiment and for the step-creep experiment have been plotted in Fig. 8a. Fig. 8b shows the experimental results for the PpPTA Twaron® 1000 fibre. The logarithmic creep coefficient of the additional creep measured in the step-creep experiment is compared to the logarithmic creep coefficient of the total creep strain in a normal creep measurement at the same stress.

The logarithmic creep rate of the additional creep in the step-creep experiment is equal or even larger than the logarithmic creep rate of the total creep in a normal creep

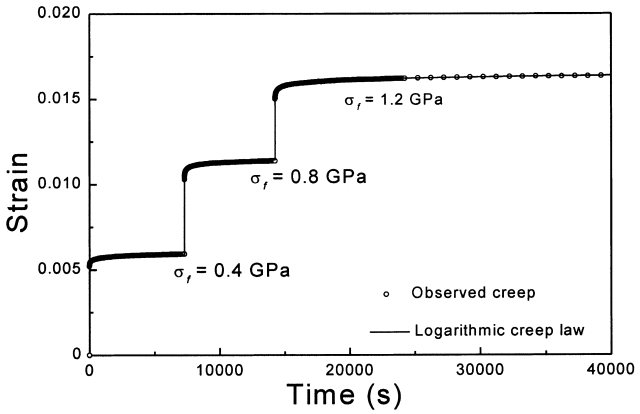

Fig. 7. The strain vs. the time of the PpPTA fibre Twaron® 1000 in a step-creep experiment. The drawn lines represent for each step the superposed curves due to the logarithmic creep law, $D(t) = C\log(t)$, applied at each step.

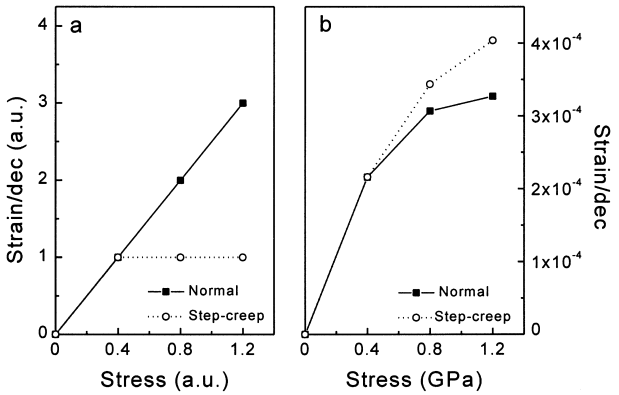

Fig. 8. The additional logarithmic creep rate in a step-creep experiment and the total logarithmic creep rate in a normal creep experiment of (a) a linear viscoelastic solid following a logarithmic creep law and (b) the PpPTA Twaron® 1000 fibre.

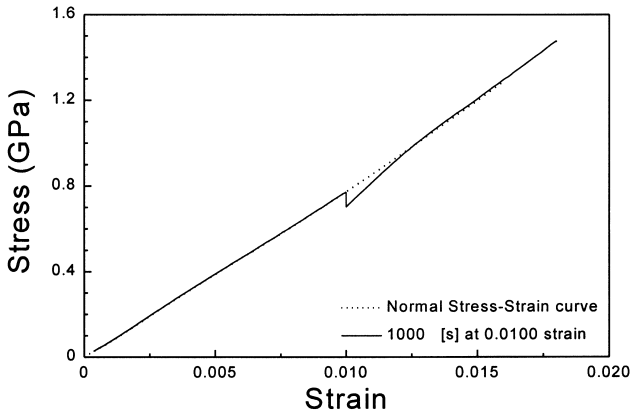

Fig. 9. The stress vs. strain curve for a PpPTA Twaron® 1000 fibre in a strain–relaxation experiment compared to the normal stress vs. strain curve.

experiment at the same stress level. This result is rather surprising because the increase of the stress in the step-creep experiment is much less than in a normal creep experiment. For example, the logarithmic creep rate of the additional creep due to the step 0.8–1.2 GPa, is even somewhat larger than the logarithmic creep rate of the total creep due to the step 0.0–1.2 GPa. Obviously, this result cannot be described by a traditional superposition principle, because such a principle predicts that the creep rate due to a small step is smaller than the creep rate due to a large step. The result of this experiment suggests that the load history until the second step is erased by the second step and the load history until the third step is erased by the third step. Thus, e.g. little difference exists between the state of the fibre at the beginning of the third step and a fibre at the beginning of a creep experiment at 1.2 GPa.

This idea has been investigated by the strain–relaxation–strain experiment. In this experiment the strain is increased at a constant strain rate of 10%/min up to a strain ε_0, than a stress relaxation is performed for 1000 s, and finally the strain is increased at a constant strain rate up to failure. The stress vs. strain curve of a Twaron® 1000 fibre during the strain–relaxation–strain measurement is depicted in Fig. 9. For comparison, the normal stress vs. strain curve at a constant strain rate has been depicted as well. In the strain–relaxation–strain experiment the stress follows the normal stress vs. strain curve up to the strain ε_0. During the period of relaxation the stress decreases by an amount of $\Delta\sigma$. It is worth noting that in the second period of deformation at a constant strain rate, the stress vs. strain curve approaches the normal stress vs. strain curve again. Apparently the stress–relaxation results in a decrease of yield deformation in the subsequent deformation of the fibre at a constant strain rate. Once the relaxed stress has been compensated for, the deformation continues along the normal stress vs. strain curve. Thus, the initial yield deformation in the second period is very low due to the stress relaxation in the preceding period. This implies a strong interaction between the viscoelastic and the yield deformation.

The stress–relaxation–stress experiment was repeated for Twaron® 1000 fibres, performing the relaxation at several values for ε_0. At $\varepsilon_0 = 0.01$ the effect of a relaxation of 50.000 s was measured as well, the results are shown in Fig. 10. All the observed curves have the same shape. In the second period of deformation at a constant strain rate, after the period of stress relaxation, the initial yield deformation is very low, until the stress vs. strain curve approaches the normal stress vs. strain curve. The response of a poly-(ethylene terephthalate) or PET fibre, viz. Diolen® 174S, in the strain–relaxation–strain experiment is plotted in Fig. 11. The stress vs. deformation curve shows the same characteristic shape. As can be seen in Fig. 11, in the case of the PET fibre a small overshoot for the stress has been found after the relaxation period. At certain values of the strain, the stress in the strain–relaxation–strain experiment is even larger than the stress in the normal stress vs. strain curve. The results of the strain–relaxation–strain experiments are in agreement with the interpretation given above. After of a

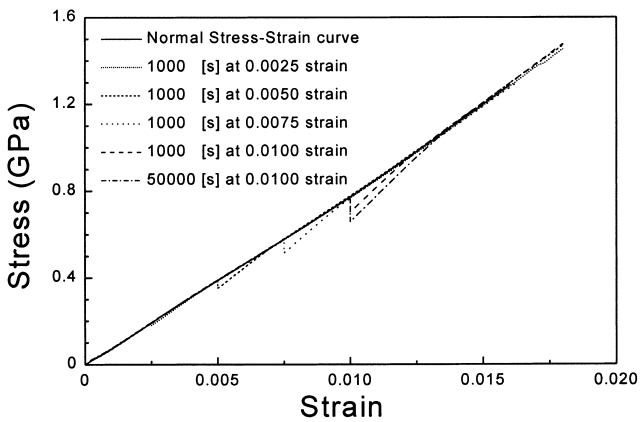

Fig. 10. The stress vs. strain curve of the PpPTA Twaron® 1000 fibre in the strain–relaxation experiment with 1000 s relaxation at several values of the strain. At a strain of 0.01 a relaxation of 1000 and 50,000 s have been investigated.

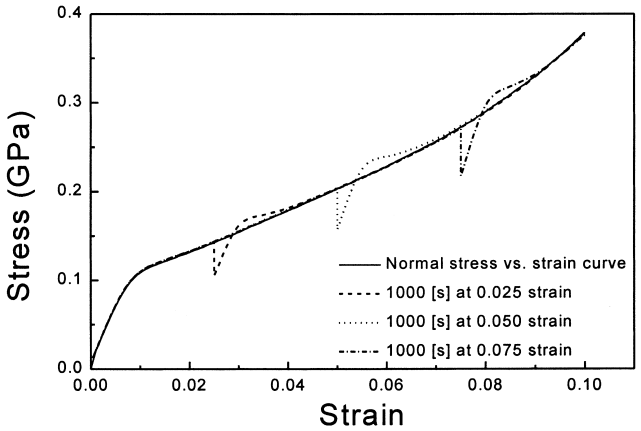

Fig. 11. The stress vs. strain for the PET fibre Diolen® 174S in the strain–relaxation experiment compared to the normal stress vs. strain curve of the fibre.

period of creep or stress relaxation, and presumably after an arbitrary complex loading, the yield deformation is much lower initially, until the stress vs. strain curve approaches the original stress vs. strain curve. Thereupon deformation follows the normal stress vs. strain curve of the fibre. Hence, at a certain value of the strain, say ε_1, no difference exists between a fibre which has been extended continuously and a fibre which has been subjected to a complex loading with a maximum strain $\varepsilon_0 < \varepsilon_1$. At least the creep rate and the deformation at constant rate, at ε_1, do not depend on the loading history in these experiments. This observation is very similar to the difference between the first loading curve and the hysteresis curves of a polymer fibre and has been explained by the sequential orientation mechanism that provides the structural description of the tensile deformation of a polymer fibre [2]. Apparently, this typical behaviour is due to a strong interaction between the yield and the viscoelastic deformation and it indicates that the distinction between yield and viscoelasticity is probably artificial. As shown below it cannot be explained by the standard model for the linear viscoelasticity of a solid consisting of a Maxwell element parallel to a spring [9].

It is interesting to compare the response of the fibres in these two experiments with the predictions of linear superposition. The response of a linear viscoelastic material to a step-creep experiment is given by $\varepsilon(t) = D(t - t_1)\Delta\sigma_1 + D(t - t_{2)}\Delta\sigma_2$. There is no relation between the response to the first and the second load. The response to a step $\Delta\sigma_i$ is only a function of $\Delta\sigma_i$. In case of a real fibre the effect of the first step $\varepsilon(t) = D(t - t_1, \Delta\sigma_1)$ is erased by the immediate response to the subsequent step $\Delta\sigma_2$. The creep due to the second step is equal to the creep due to the step $\Delta\sigma_1 + \Delta\sigma_2 : \sigma(t) = D(t - t_2, \Delta\sigma_1 + \Delta\sigma_2)$. The response to the second step is not a function of $\Delta\sigma_2$ but a function of $\Delta\sigma_1 + \Delta\sigma_2$. This is a violation of the superposition principle.

A typical response of the standard linear viscoelastic solid to the strain–relaxation–strain experiment is shown in Fig. 12a. The relaxation time in this example is long with respect to the time of deformation at a constant strain rate. This implies a material with a low creep rate as is usually observed in technical polymer fibres below the glass transition temperature. For the standard linear viscoelastic solid, the response after a period of relaxation is independent of the previous part. The third part of the curve is the elastic deformation translated downwards. In case of a real polymer fibre the stress vs. strain curve after a period of relaxation is very different from the normal stress–strain curve. Allen showed in similar experiments that after a period of relaxation the stress vs. strain curve almost follows the original curve [15]. In order to model this behaviour using the standard linear viscoelastic solid a very short relaxation time is required as shown in Fig. 12b. However, this yields a solid with a high creep rate, which is not observed in technical fibres below T_g.

Obviously the response of a real fibre is very different

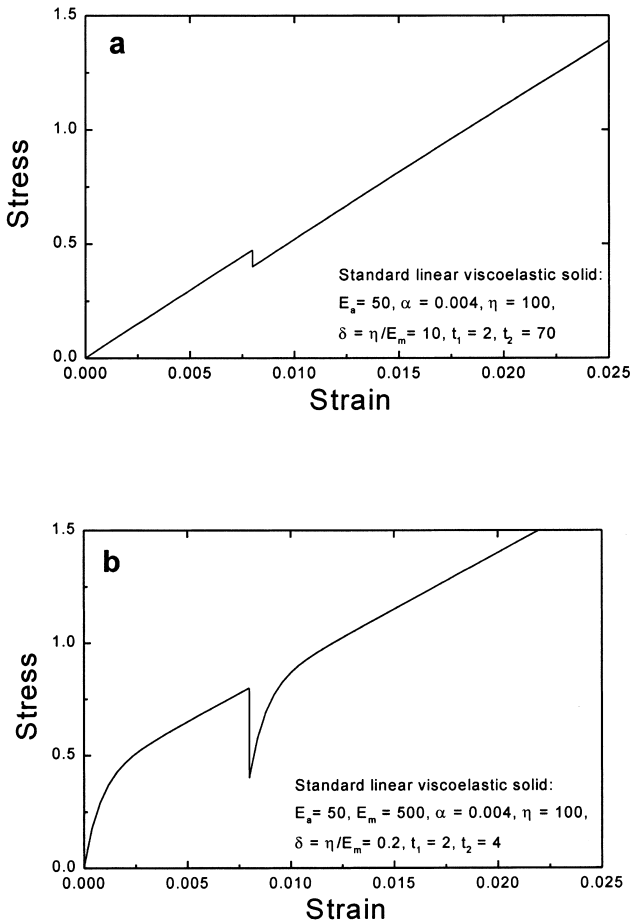

Fig. 12. Application of the superposition principle in the calculation of the stress vs. strain curve of a standard linear viscoelastic solid in the strain–relaxation–strain experiment. The model consists of a spring E_a parallel to a Maxwell element consisting of a spring E_m, a dashpot η and a relaxation time $\delta = \eta/E_m$. The strain rate is α. (a) $\delta = 10$ s, a stress relaxation between $t_1 = 2$ and $t_2 = 70$ s. (b) $\delta = 0.2$ s, a stress relaxation between $t_1 = 2$ and $t_2 = 4$ s.

from the response of the standard linear viscoelastic solid. The time of relaxation strongly influences the subsequent deformation at a constant strain rate of the fibre. In some respect, the behaviour of the fibres in these experiments is even contrary to the principle of superposition. It has been observed that the creep due to a small increment of the stress can be equal to the creep due to a three times larger stress increase and in the second and third period of the strain–relaxation–strain experiment the response of the fibre is only determined by the total value of the stress. Therefore, it is concluded that a superposition principle is not suitable for the description of the response of polymer fibres to complex loadings.

Reviews of the non-linear viscoelastic behaviour of polymer fibres have been given by Hadley and Ward [9] [12]. A mathematically rigorous description of non-linear viscoelasticity is given by the multiple integral representation [16]. This representation describes the interaction between subsequent deformations by higher order terms of the type: $E_2(t-t_1, t-t_2)\varepsilon_1(t_1)\varepsilon_2(t_2)$. It can be shown that an arbitrary non-linear response can be described by a multiple integral. Hadley and Ward have attempted to describe the creep of polypropylene fibres using a multiple integral representation [9,17]. Most of these models assume a certain kind of superposition.

Ward remarks about the status of the models for non-linear viscoelasticity that, "…at the present stage none of these approaches are entirely satisfactory" [9]. The experimental evidence for a strong link between the yield and viscoelastic properties of the polymer fibres, as results from the above experiments, is a new element with respect to Ward's discussion. Given the type of interaction between yield and viscoelastic deformation, in particular the fact that the loading history can be erased by a subsequent deformation, the multiple integral representation does not seem to be a practical formalism for the description of the response of polymer fibres to complex loadings. Probably, a better understanding of the relation between the yield and the time-dependent deformation is necessary in order to find a satisfactory representation for the response of a polymer fibre to complex loadings. For isotropic polymers a coupling of the yield and the viscoelastic deformation has been proposed and studied by several authors [18,19].

5. Discussion and conclusions

In the previous sections several aspects of the response of polymer fibres to complex loadings and the relation between different loading programs have been studied. It may be clear from the complex, confusing behaviour of the fibre in the various experiments that a formal representation of the mechanical behaviour of the fibre will be very complicated. The major conclusions resulting from this research have been listed below. A constitutive equation for polymer fibres below the glass transition temperature should describe the following phenomena.

1. The non-linear elastic deformation.
2. The yield being an immediate plastic and semi-plastic deformation. An immediate plastic deformation is a permanent deformation which is immediate on the time scale of the deformation, a semi-plastic deformation is an immediate 'plastic' deformation which recovers as a function of the time elapsed after the load has been removed. Initially, after the load of a fibre has been removed, the yield point in the range of 0.005–0.02 strain has disappeared. During the recovery process the yield at the beginning of the stress–strain curve slowly increases as a function of the recovery time. After very long recovery times the yield point becomes almost equal to the yield point of the fibre before the loading. Above the maximum load value of the preceding load cycles the stress–strain curve follows the stress vs. strain curve of the unloaded fibre.
3. Delayed elastic deformation and delayed permanent deformation. The time-dependent deformation is partly reversible (delayed elastic), and partly permanent (delayed permanent).
   - The creep and stress relaxation of oriented polymer fibres is non-linear with the applied stress.
   - Creep and stress relaxation are related by the mechanical modulus of the fibre. This implies that the viscoelastic and yield deformation are coupled.
   - The creep and stress relaxation of mechanically conditioned fibres is lower than the creep of mechanical unconditioned fibres.
4. The linear superposition principle does not apply to the deformation of polymer fibres above the yield point. A strong interaction between yield and viscoelastic deformation has been observed. Viscoelastic relaxation results in a lower yield deformation in a subsequent extension of the fibre. Independently from the preceding loading program, above the maximum foregoing stress, the deformation of the fibre returns to the normal stress vs. strain curve. The loading history seems to be erased by the subsequent deformation.

Important aspects of the tensile deformation of polymer fibres can be understood from the continuous chain model as has been described in this and previous papers. The continuous chain model is based on simple, elementary deformation principles for the domain. The non-linear elastic deformation has been described satisfactorily by the inclusion of the geometrical effects of the deformation on the domain. The tensile curve of a real fibre with yield has been modelled assuming a simple shear yield law for the domain. The creep of PpPTA fibres could be described by a linear creep law for the shear creep of the domain. The relation between creep and stress relaxation has been explained by the effect of yield during the viscoelastic

deformation of the fibre. However, the strong interaction between yield and viscoelastic deformation indicates that the distinction between these phenomena is probably artificial. In a following paper, a new model for the time-dependent and yield deformation will be presented. It involves the introduction of activated transitions for the description of the shear deformation with relaxation times that are a function of the stress, thereby removing the distinction between yield and viscoelasticity. It is believed that this model provides a framework for the interpretation of the response of a polymer fibre to complex loadings and the link between the yield and viscoelastic properties of polymer fibres.

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