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The Eyring reduced time model for viscoelastic and yield deformation of polymer fibres

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Abstract

A model is proposed for the description of the viscoelastic and yield behaviour of polymer fibres. It involves the introduction of activated transitions with relaxation times that are a function of the stress. This is analogous to the introduction of an Eyring reduced time. These transitions govern the shear deformation of a domain, being the building block of the continuous chain model for the tensile deformation of polymer fibres. The main features of the viscoelastic behaviour of fibres have been derived. They are the rate dependence of the yield stress, the transition from a concave creep curve for a stress below the yield stress to the logarithmic behaviour for stresses above the yield stress, the creep rate of a fibre, the disappearance of the yield for increasing temperatures and the response to complex loadings.

Keywords: Fibres; Viscoelasticity; Yield

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1. Introduction

In a series of publications, the continuous chain model for the tensile deformation of polymer fibres in the glassy state has been proposed [1–4]. Subsequently, a model for the viscoelastic deformation of the fibre has been developed, which is based on the linear viscoelastic deformation of a perfectly oriented domain [5–7]. It has been shown that the creep of aramid fibres can be described by this linear viscoelastic domain approximation.

A characteristic phenomenon in the tensile curve of a polymer fibre is the yield. In our first investigation of the yield we observed that the yield strain varies from 0.005 for highly oriented fibres to about 0.025 for isotropic specimens. This strain range is explained by assuming that the yield is caused by an immediate and permanent or plastic deformation [1]. By postulating a critical shear stress, τ_y, we have demonstrated that due to a sequential orientation process the yield strain of a fibre is a function of the degree of chain orientation in the fibre. Furthermore it was shown that $\tau_y = fg$, with $0.04 \le f \le 0.05$ and g being the modulus for shear parallel to the chains.

In Fig. 1, the stress versus strain curve of the PET fibre Diolen® 174S and the PpPTA fibre Twaron® 1000 have been depicted for several values of the strain rate. It is observed that the yield deformation is a function of the strain rate. In the first elastic part all the stress vs. strain curves are identical, whereas above the yield point the stress versus the strain follows parallel curves. The level of these curves is an increasing function of the strain rate. Also for isotropic polymers a temperature and strain rate dependence of the yield deformation has been observed [8]. This has lead to the proposal that the yield and viscoelastic deformations of isotropic polymers are due to the same deformation processes [9,10].

In recent studies, the relation between creep and stress relaxation, and the response to complex loading schemes for PpPTA and PET fibres have been studied [6,7]. From the results of these investigations it has been concluded that the yield and the viscoelastic deformation of a polymer fibre are also strongly related. For example, it has been observed that after a period of stress relaxation the initial response of the fibre to a subsequent tensile deformation at a constant strain rate is almost elastic. Thus initially no yield deformation occurs. Because this behaviour cannot be explained from

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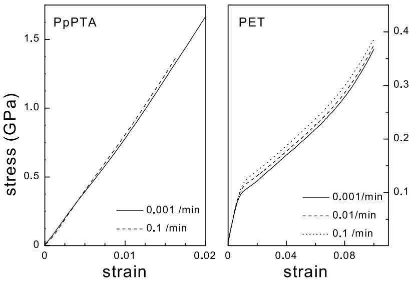

Fig. 1. The stress vs. strain curves of the PpPTA fibre Twaron® 1000 and the PET fibre Diolen® 174S as a function of the strain rate.

the classical theories of viscoelasticity or plasticity, it is necessary for the understanding of the relation between creep and stress relaxation in polymer fibres that the relation between viscoelasticity and yield has to be considered [7,11,12].

The first attempt to describe the non-linear viscoelastic behaviour of isotropic polymers and fibres was presented by Tobolsky and Eyring [13,14,15]. They introduced a stress-dependent relaxation time associated with an activated process of movements of chain segments. In subsequent developments this so-called Eyring dashpot has been applied in various modifications. Bauwens used a stress activated element to model the strain rate dependence of the yield point [8]. Shay assumed that the yield of isotropic polymers is caused by an acceleration of the viscoelastic processes due to a volume increase. This acceleration is modelled by a reduced time, t_u, which is a function of the volume [9]. In later models, the reduced time can be a general function of the deformation. Boyce, Parks and Argon extended the stress activated models for three dimensional deformations [16]. Hasan and Boyce proposed a range of activation energies to describe the distributed nature of local plastic transitions [17]. Tervoort et al. formulated a phenomenological constitutive model in which a discrete spectrum of relaxation times with a single activation energy is applied [18]. All these models refer to isotropic glassy polymers and are characterized by plastic flow.

In an attempt to model the creep of aramid fibres by Rogozinsky and Bazhenov the elongation of the fibre is considered to be the result of transitions from a kinked to a straightened conformation [19]. This conformational transition is described again by a thermoactivated process. In order to account for the fact that the activation energy of the transition is not constant for all chain fragments, they introduced a range of activation energies. Plastic flow is eliminated by assuming a limited number of transitions.

In this paper, a reduced time model, similar to the model of Rogozinsky and Bazhenov and based on a simple Eyring process, will be proposed for the description of the viscoelastic and yield deformation of polymer fibres in the glassy state. In the continuous chain model the shear deformation of the domain involves the debonding and reformation of secondary bonds between adjacent chains. Due to the disorder in the microstructure the activation energies for these mechanical transitions will be distributed. Because of the fundamental physical relation between relaxation times and activation energies, this results in a range of stress activated relaxation times. This model not only predicts the rate dependence of the yield behaviour, but also explains the most important features of the sometimes curious mechanical behaviour described recently [7]. It is believed that the proposed model provides a framework for the description of the viscoelastic and yield deformation of polymer fibres in the glassy state, including the response to complex loading schemes. A brief introduction to this Eyring reduced time model has been published recently [20].

2. A summary of the continuous chain model

The continuous chain model for the tensile deformation of polymer fibres in the glassy state is a series model and assumes that the deformation of the fibre is equal to the average deformation of a polymer chain in the direction of the fibre axis. The basic element for the calculations is a small straight chain segment. The deformation of this chain segment is determined by the elastic properties of the surrounding domain. It is supposed that this 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 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. In this series model the tensile deformation of the fibre is brought about by the combined effect of the elongation of the polymer chains and the change of the orientation of the chains in the direction of the fibre axis as exemplified by the formula for the fibre strain ϵ_f

$$\epsilon_f = \frac{\langle \epsilon_c \cos\theta \rangle}{\langle \cos\Theta \rangle} + \frac{\langle \cos\theta \rangle - \langle \cos\Theta \rangle}{\langle \cos\Theta \rangle} \tag{1}$$

where Θ is the initial angle between the axis of a chain segment and the fibre axis in the unloaded state, θ is the angle between a deformed chain segment and the fibre axis and ϵ_c the tensile strain of the chain segment. The quantity ϵ_c is a unique function of the momentary fibre tensile stress, and θ is a function of the total load history of the domain. The average is taken over the chain orientation distribution. The change of the orientation of a chain segment in the direction of the fibre axis is caused by the shear deformation of a small domain containing this chain segment. The yield in the tensile curve of polymer fibres has been modelled by introduction of a critical shear yield strain of the domain and a plastic shear law. An example is given in Fig. 2. Using this model the stress vs. strain curve of the fibre has been calculated [5].

In the case of a linear viscoelastic simple shear mechanism the deformation, κ_ν, of the domain is given by

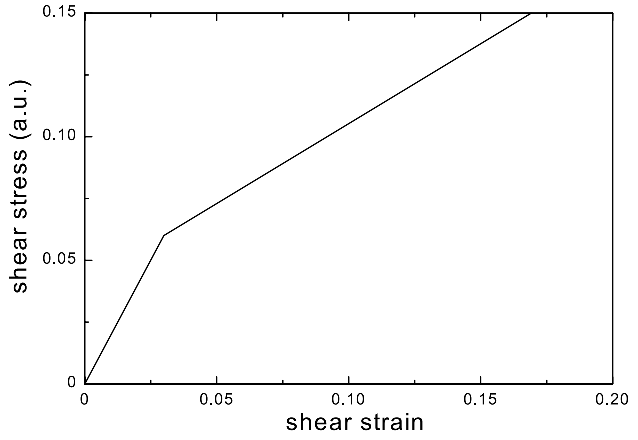

Fig. 2. The assumed shear stress vs. strain curve for the shear deformation of an oriented domain.

the equation

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

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

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

where σ_f the fibre stress. For oriented fibres expression (3) is well approximated by

$$\tau = -\sigma_\mathrm{f}\sin\theta\cos\theta \tag{3a}$$

The angle θ is a function of the time and given by the formula for the shear strain of the domain

$$\epsilon_{13} = \tan(\theta(t) - \Theta) = \frac{\tilde{\tau}(t)}{2g} + \frac{1}{2}\kappa_\nu(t) \tag{4}$$

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. The viscoelastic and yield deformation of the polymer fibre has been described by the viscoelastic and plastic shear deformation of the domain [5–7]. This mechanism explains the almost linear curves of the sonic compliance vs. strain and of the orientation parameter $\langle\sin^2\theta\rangle_\mathrm{E}$ of the polymer chains vs. strain during elastic, viscoelastic and yield deformation. As the creep of many oriented fibres is approximately proportional to the logarithm of time, a logarithmic creep law is assumed for shear deformation of the domain. By using this creep law it was possible to quantitatively model the stress and modulus dependence of the creep of PpPTA fibres [6].

The newly proposed Eyring reduced time model provides a mechanical element for the description of the elastic, viscoelastic and yield deformation of the domain, reducing the viscoelastic and yield deformation to a single activated process. The analysis will be limited to the response of a single domain to a shear stress. The extension to the deformation of a fibre is straightforward. It will be shown that the observed tensile behaviour of polymer fibres as summarised in Section 3 can be reproduced. It has not been tried to fit the model numerically to a particular fibre. For reasons of simplicity the responses to unloading and dynamic loadings will not be considered here. These can be incorporated in the future.

3. The observed tensile behaviour of polymer fibres in the glassy state

In our previous reports on the tensile deformation of fibres, the following observations have been made:

(1) The yield deformation of the fibre is dependent on the strain rate. This was observed for oriented PET and PpPTA fibres. Above the yield point the stress vs. the strain follows parallel curves of which the levels depend on the strain rate. This implies a similar behaviour for the shear deformation of a single domain. A schematic picture of the corresponding shear deformation curves for a domain has been drawn in Fig. 3.

(2) The creep and the stress relaxation of oriented fibres is often approximately linear versus the logarithm of the time The fibre creep can be described by $\epsilon(t) = \epsilon_0 + C_\mathrm{creep}\log(t)$ and the stress relaxation by $\sigma(t) = \sigma_0 - C_\mathrm{relax}\log(t)$. It has been shown that this logarithmic law holds particularly well for oriented PpPTA fibres [6,7].

(3) The ratio of the logarithmic creep rate C_creep and the logarithmic relaxation rate C_relax, when starting both experiments at the same initial stress σ_0 and initial strain ϵ_0, is given by $C_\mathrm{relax}/C_\mathrm{creep} = E_\mathrm{m}$ with E_m the derivative of the stress vs. strain curve, $d\sigma/d\epsilon$, in the point (ϵ_0, σ_0). This behaviour was observed for PpPTA

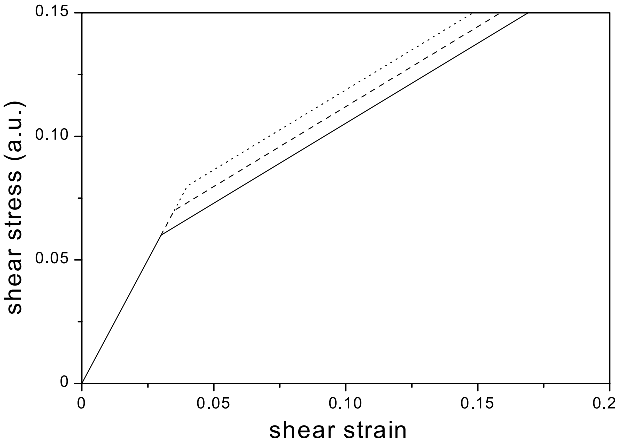

Fig. 3. The shear stress vs. strain for the shear deformation of an oriented domain at several values of the strain rate.

fibres [7]. As the mechanical modulus E_m depends on the amount of yield deformation, the viscoelastic and yield deformation are related.

(4) At a stress below the yield point the creep strain of a polymer fibre follows a concave curve prior to the logarithmic behaviour, as shown for PpPTA in Fig. 4. The same can be observed for the creep of PET fibres.

(5) Stepwise increasing the creep stress, it is found that the creep at each step is equal or even larger than the normal creep measured at that stress, see Fig. 5. So, increasing the stress by steps of σ_0, the creep due to the third step, at a total stress of $3\sigma_0$, is equal or larger than the creep measured in a normal creep experiment at a stress $3\sigma_0$. This behaviour was observed for PpPTA fibres and is contradictory to a superposition principle [7].

(6) In a strain–relaxation–strain experiment the strain is firstly increased at a constant strain rate; at a stress σ_0 the deformation is stopped and a relaxation experiment is performed during a certain time t_1, subsequently the strain is increased at a constant strain rate up to failure. The response of a Diolen 174S PET fibre to this sequence has been plotted in Fig. 6.

Surprisingly, immediately after the relaxation period, no yield occurs during the second period of deformation at a constant strain rate. At a somewhat larger strain the stress vs. strain curve continues along the normal stress vs. strain curve of the fibre. Also this experiment shows a strong relation between yield and viscoelastic deformation [7].

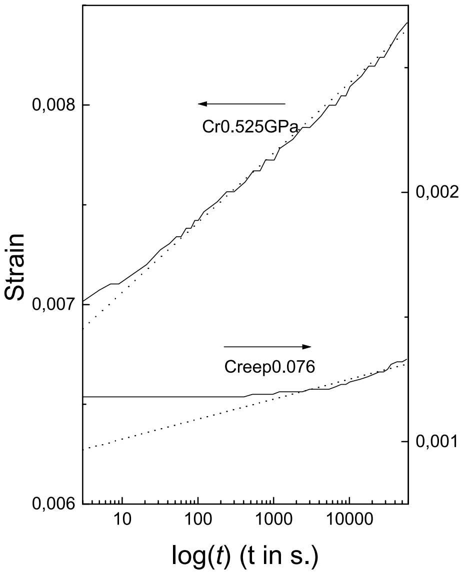

Fig. 4. Below the yield point, at a tensile stress of 0.076 GPa, the initial part of the creep strain vs. the time curve of a PpPTA fibre Twaron® follows a concave curve.

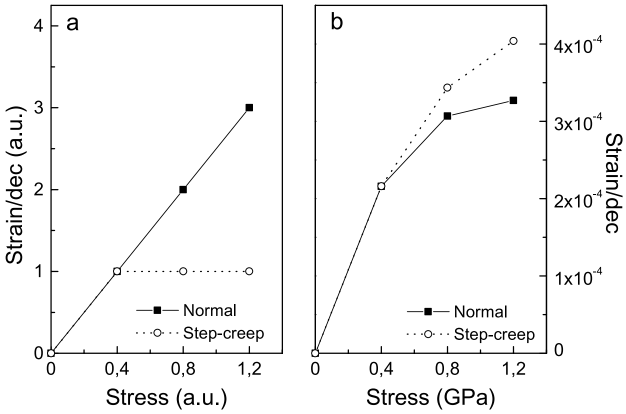

Fig. 5. The creep rate of (a) a linear viscoelastic solid compared to (b) a PpPTA fibre Twaron® 1000 in the step-creep experiment and in a normal creep experiment.

4. The Eyring reduced time model

The plastic deformation of an ideal plastic material starts at a critical stress and is independent of the deformation rate or temperature. Although for isotropic polymers a, rather small, dependence on the deformation rate and the temperature has been observed, the classical theory of plasticity can be applied very well to the yield deformation of polymer fibres in the glassy state [12]. It has been shown that the yield in the tensile curves of polymer fibres can be described by a simple yield criterion and a plastic deformation law for the shear deformation of the domains [5]. The plastic deformation is independent of the time scale of the deformation, thus it can be regarded as an immediate process. Once the stress has arrived at the critical stress the plastic deformation occurs immediately, the amount of plastic strain being independent of the deformation rate. From the experiments of Bauwens it is known that the deformation rate and temperature dependence of the yield stress of poly(methyl methacrylate) or PMMA can be described by a simple Eyring process [8]. It will be shown

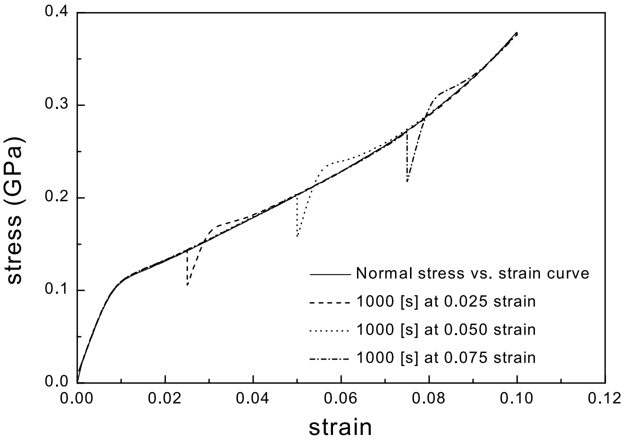

Fig. 6. The stress vs. strain curve of a PET fibre Diolen® 174S in the strain–relaxation–strain experiment compared with the normal stress vs. strain curve of the fibre.

that an Eyring process is also very suitable for the description of the transition of ideal plastic, to a viscoelastic or time dependent behaviour.

The shear deformation of a domain brings about a mutual displacement of adjacent chains, the amount of which is determined by the secondary bonding between the chains. The straining of this bonding is now modelled as an activated shear transition between two states separated by an energy barrier U as depicted in Fig. 7a and b. In a perfect crystal there is only a single value for U, but in semi-crystalline and paracrystalline fibres a distribution of U may be expected which can be associated with the energies of the various conformations of the secondary bonds between the chains. The occupation of state 1 is equal to N_1, the occupation of state 2 is equal to N_2 and the total occupation is equal to $N_1 + N_2 = N$. The plastic shear strain is proportional to the decrease of the occupation of state 1 or proportional to the increase of the occupation of state 2. Without external stress the probability for transition from state 1 to state 2 (ν^+) is proportional to the Boltzmann factor $N_1\exp[-U/kT]$, and for the inverse transition $2 \rightarrow 1(\nu-)$ the probability is proportional to $N_2\exp[-U/kT]$. Suppose a shear stress τ causes a linear shift $|\tau|\Omega$ of the energy of the first state and a shift $-|\tau|\Omega$ of the second state, Ω being the activation volume. Then, the differential equation for the occupation of state 1 is given by

$$\frac{dN_1}{dt} = -N_1\nu\exp\left[-\frac{(U-|\tau|\Omega)}{kT}\right] + (N-N_1)\nu \exp\left[-\frac{(U+|\tau|\Omega)}{kT}\right] \tag{5}$$

where ν is the frequency associated with the motions of chain segments at a temperature T. We assume that at $t=0$ $N_1 = N_2 = N/2$. The relaxation time δ associated with the transition is given by

$$\frac{1}{\delta} = \nu\left\{\exp\left[-\frac{(U-|\tau|\Omega)}{kT}\right] + \exp\left[-\frac{(U-|\tau|\Omega)}{kT}\right]\right\} \tag{6}$$

In the exponential function, the absolute value of τ is introduced, because the energy shift $\tau\Omega$ is defined to be a positive quantity. The activated transition will now be described in its simplest form, viz. for $U/kT \gg 1$. This implies that at low temperatures even for a small stress the backward transition rate $\nu-$ can be neglected with respect to $\nu^+$and the relaxation time can be approximated by

$$\frac{1}{\delta} = \nu\exp\left[-\frac{(U-|\tau|\Omega)}{kT}\right] \tag{7}$$

Hence, Eq. (5) becomes

$$\frac{dN_1}{dt} = -\frac{N_1}{\delta} \tag{8}$$

For constant $|\tau|$ the solution of this equation is given by

$$N_1 = \frac{N}{2}\exp\left(-\frac{t}{\delta}\right) \tag{9}$$

As for the derivation of Eqs. (7)–(9) only the transitions $1 \rightarrow 2$ have been counted, these equations do not describe recovery processes, where the transitions $2 \rightarrow 1$ are important as well. These approximations have been made for convenience's sake, but neither imply a limitation for the model, nor are essential to the results of the calculations. Eq. (7) is the well known formula for the relaxation time of an Eyring process. In Fig. 8 the relaxation time for this plastic shear transition has been plotted versus the stress for two temperature values. It can be observed from this figure that in the limit of low temperatures, the relaxation time changes very abruptly at the shear yield stress $|\tau_y| = U/\Omega$. Below this stress the relaxation time is very long, which corresponds with an approximation of elastic behaviour. At the shear yield stress the relaxation time becomes suddenly very short. Thus in an experiment at a constant stress rate all transitions occur almost immediately at the shear yield stress. This critical behaviour closely resembles the ideal plastic behaviour. This can be expected for a polymer far below the glass transition temperature where the mobility of the chains is low. At a high temperature the transition is a smoother function of the applied stress. This behaviour may be expected for a polymer close to the glass transition temperature. In this case the backward transitions should

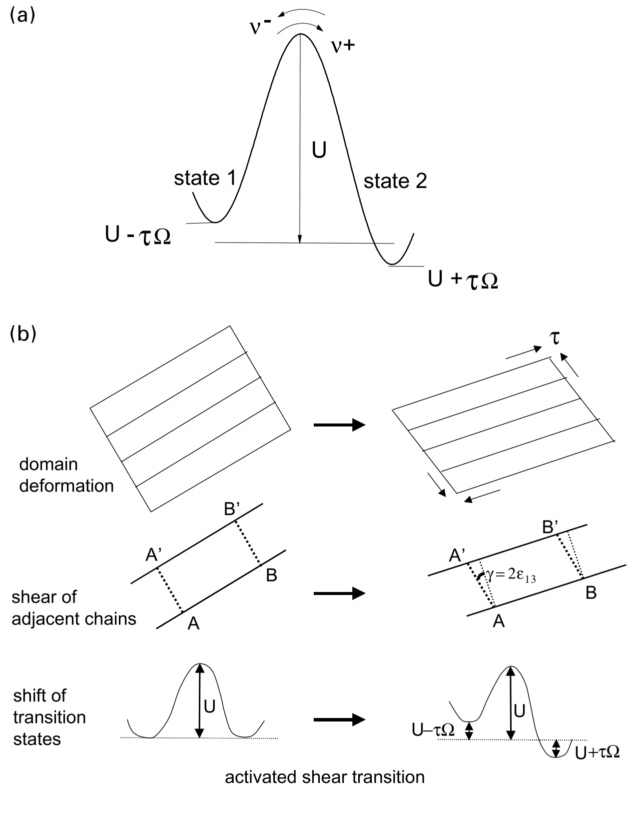

Fig. 7. (a) The Eyring reduced time model involves the activated site model for plastic and viscoelastic shear deformation of adjacent chains ($\tau > 0$). (b) The activated shear transition for the modelling of the viscoelastic and plastic shear deformation of a domain consisting of parallel aligned chain segments.

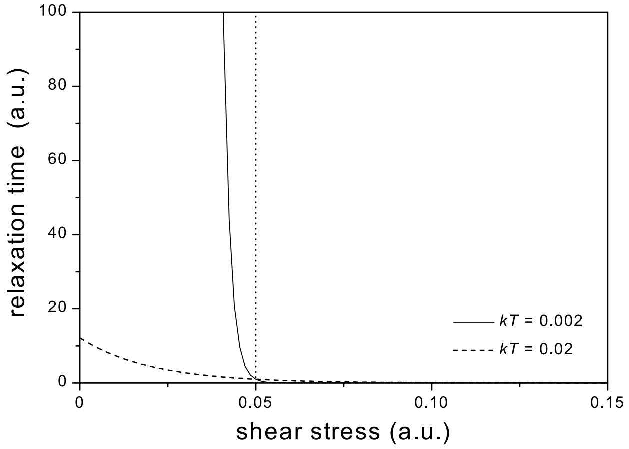

Fig. 8. The relaxation time of an Eyring process as a function of the stress, for a low and a high temperature.

also be taken into account. This different character in the two temperature limits renders the Eyring process very suitable for modelling the coupled yield and viscoelastic deformation of fibres in the glassy state.

If the applied shear stress varies during the experiment, e.g. a tensile test at a constant strain rate, the relaxation time of the activated transitions changes during the test. This is analogous to the idea of a reduced time, which has been introduced to model the acceleration of the relaxation processes due to the deformation. It is proposed that the reduced time is related to the transition rate of an Eyring process [13–15]. The differential Eq. (8) for the transition rate is rewritten as

$$\frac{\mathrm{d}N_1}{\mathrm{d}t_\mathrm{u}} = -N_1 \tag{10}$$

with the reduced time t_u

$$\mathrm{d}t_\mathrm{u} = \frac{\mathrm{d}t}{\delta} \tag{11}$$

Thus

$$t_\mathrm{u} = \int_0^t \nu \exp\left[-\frac{(U - |\tau(t')|\Omega)}{kT}\right]\mathrm{d}t' \tag{12}$$

As the viscoelastic and plastic shear strain, $\epsilon_\mathrm{p} = |\tan(\theta_\mathrm{p} - \Theta)|$, is assumed to be proportional to $N/2 - N_1$ it follows from Eqs. (10) and (11) that

$$\epsilon_\mathrm{p} = \tfrac{1}{2}I[1 - \exp(-t_\mathrm{u})] \tag{13}$$

The magnitude of the activated transition is denoted by I, where $I = cN$and c an arbitrary constant. At temperatures far below the glass transition temperature the transitions with an energy U will relax suddenly and almost completely at a tensile shear stress $|\tau_\mathrm{y}| = U/\Omega$. In order to describe a shear stress vs. strain curve as drawn in Fig. 3, it is proposed to describe the viscoelastic and plastic shear deformation of a domain by a transition density function $I(U)$. Hence, following Eq. (4) the total shear strain of a domain is given by

$$|\epsilon_{13}(t)| = |\tan(\theta(t) - \Theta)| = \frac{|\tau(t)|}{2g} + \frac{1}{2}\int_0^\infty I(U)[1 - \exp(-t_\mathrm{u})]\mathrm{d}U \tag{14}$$

with t_u calculated from the loading history with Eq. (12). In this formula, the elastic shear deformation is described by a linear relation.

For the analysis of formula (14) a shape for the transition density function should be assumed. This function determines the details of the viscoelastic and yield behaviour. First it will be assumed that $I(U)$ has the simple flat shape shown in Fig. 9. A flat shape is a realistic approach for oriented crystalline or semicrystalline polymers such as Nylon-6 and PpPTA, and is very suitable to illustrate the qualities of Eq. (14) [21,22]. The step at $U = U_0$ causes a yield point in the shear stress vs. shear strain curve. The density function has been cut off at an energy U_m, which has been chosen such that it does not influence the results of the calculations. Hence, the integration range effectively is $[U_0, U_\mathrm{m}]$.

5. Extension at a constant rate of stress

Most tensile tests are performed at a constant rate of strain. For mathematical convenience, Eq. (14) will be analysed for a constant rate of stress. For the shear stress vs. shear strain curves of polymer fibres in the glassy state this does not make much difference. Eq. (14) has been analysed for three values of the stress rate $\alpha = 0.01$, 0.05 and 0.25 GPa s^{-1} and the parameter values: $kT = 0.4 \times 10^{-20}$ J ($T = 17$ °C), $\Omega = 250 \times 10^{-30}$ m^3, $[U_0, U_\mathrm{m}] = [2, 20] \times 10^{-20}$ J, $g = 2$ GPa, $\tau_\mathrm{y} = 0.08$ GPa and $I_0 = 0.02 \times 10^{20} \times$ J^{-1}. The results have been plotted in Fig. 10. Above the yield point the shear stress vs. shear strain curves follow parallel curves. Due to the particular choice for $I(U)$ a straight line is obtained. Using the equations of the continuous chain model and Eq. (14) for the shear deformation of the domains, the typical parallel shear stress

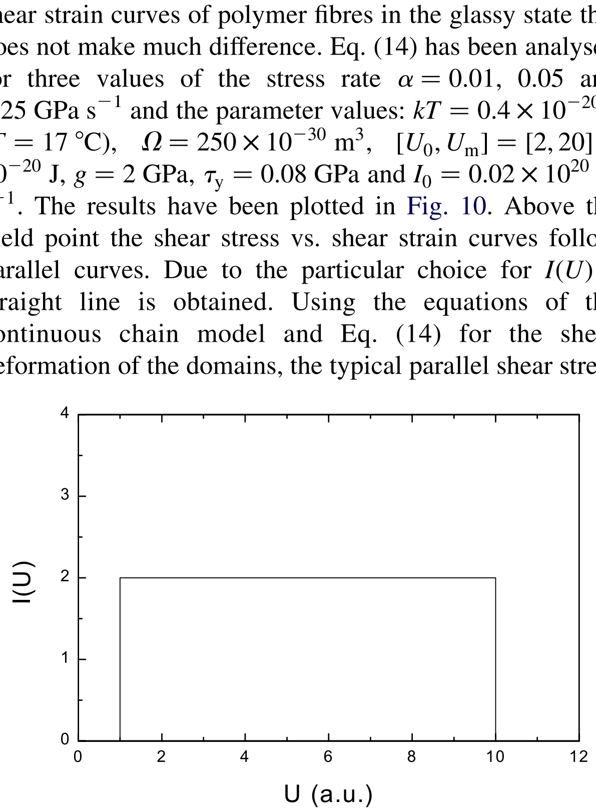

Fig. 9. The energy density function $I(U) = I_0$.

vs. shear strain curves as shown in Fig. 3 can be reproduced. It is noted that at the moderately low temperature used for the calculation the onset of the calculated yield is rather smooth. This is much like the experimentally observed yield behaviour, whereas a critical yield stress as has been previously used in the calculation of the tensile curve of a fibre, gives rise to a rather sharp transition at the yield strain [5]. The temperature dependence of the stress vs. strain curves calculated with Eq. (14) has been shown in Fig. 11. At low temperature a yield point is predicted which disappears with increasing temperatures. Presumably, by including also backwards transitions the disappearance of the yield will proceed more rapidly. This behaviour is very similar to the behaviour of polymer fibres. Below the glass temperature a pronounced yield point can be observed, which disappears at the glass transition temperature.

The slope of the shear stress vs. shear strain curve above the yield point, $2g_{\mathrm{m}}$, calculated with Eq. (14) is given by

$$2g_{\mathrm{m}} = \frac{2g}{1 + gI_0\Omega} \tag{15}$$

The yield point can be defined by the intersection of the elastic line with slope $2g$ below the yield point and the straight line with slope $2g_{\mathrm{m}}$ above the yield point. Using this definition it can be derived from Eq. (14) that the yield point is given by

$$\tau_{\mathrm{y}} = \frac{U_0}{\Omega} + \frac{kT}{\Omega}\left[-\chi + \log\left(\frac{|\dot{\tau}|\Omega}{\nu kT}\right)\right] \tag{16}$$

with $\chi \approx 0.57722$ the Euler constant and $\dot{\tau}$ the stress rate. This formula holds only for $U/kT \gg 1$ and $|\tau|\Omega/(\nu kT) < \exp(\chi)$. Eq. (16) is similar to the formula for the strain and temperature dependence of the yield point calculated with the thermally activated viscosity proposed by Bauwens and Eyring [8,13,14]. It has been shown by Bauwens and many other workers that the strain rate and temperature dependence of the yield stress of many polymers follow the Eyring equation [8,12].

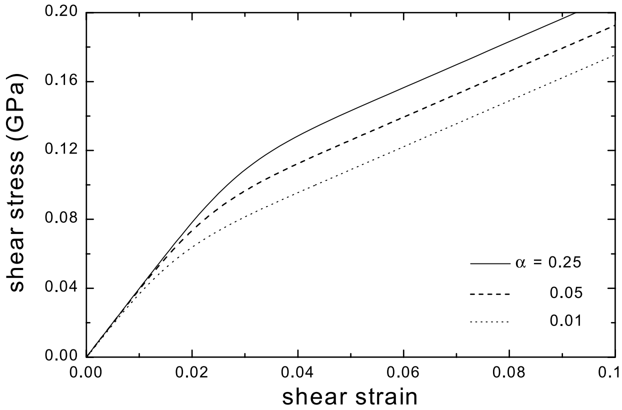

Fig. 10. The calculated shear stress vs. strain curve as a function of the stress rate. Above the yield point the curves follow parallel lines. The values of the parameters used in the calculations are $kT = 0.4 \times 10^{-20}$ J, $\Omega = 250 \times 10^{-30}$ m^3, $[U_0, U_{\mathrm{m}}] = [2, 20] \times 10^{-20}$ J, $g = 2$ GPa, $\tau_{\mathrm{y}} = 0.08$ GPa, $I_0 = 0.02 \times 10^{20}$ J^{-1}, $\alpha = 0.01$, 0.05 and 0.25 GPa s^{-1}.

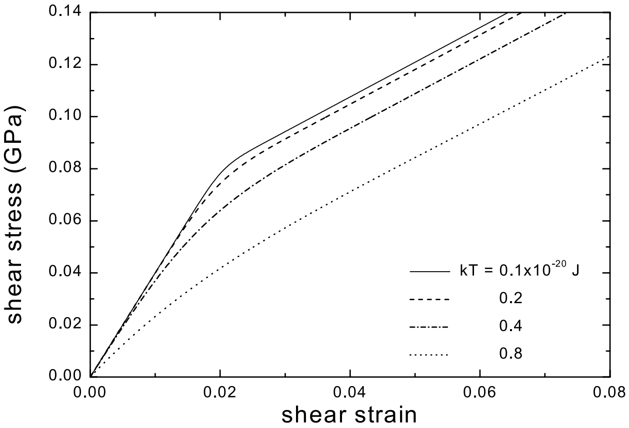

Fig. 11. The calculated shear stress vs. strain curve as a function of the temperature calculated with $\Omega = 250 \times 10^{-30}$ m^3, $[U_0, U_{\mathrm{m}}] = [2, 20] \times 10^{-20}$ J, $g = 2$ GPa, $I_0 = 0.02 \times 10^{-20}$ J^{-1}, $\alpha = 0.01$, $kT = 0.1$, 0.2, 0.4 and 0.8×10^{20} J.

6. Creep and stress relaxation

Because during a creep experiment the orientation distribution of the chains progressively contracts, the shear stress $\tau = -\sigma_{\mathrm{f}} \sin\theta \cos\theta$ is in principle a function of time. However, usually the change of angle is very small, allowing the approximation

$$\tau = -\sigma_{\mathrm{f}} \sin\theta_0 \cos\theta_0 \tag{17}$$

where θ_0 is the orientation angle of the only elastically deformed domain at $t = 0$. Thus the shear stress acting on the domain is assumed to be constant during creep [6]. Using Eq. (14) an expression for the creep will be derived for a creep shear stress above the creep shear yield stress and for large t. Furthermore, a flat transition density function is used or $I(U) = I_0$ on the interval $[U_0, U_{\mathrm{m}}]$ and $I(U) = 0$ elsewhere. This yields the following equations for the total creep shear strain including the elastic contribution

$$|\epsilon_{13}(t)| = \frac{|\tau|}{2g} + \frac{I_0}{2}\int_{U_0}^{U_{\mathrm{m}}} [1 - \exp(-t_{\mathrm{u}})]\mathrm{d}U \tag{18}$$

with

$$t_{\mathrm{u}} = \nu t \exp\left(-\frac{U}{kT}\right)\exp\left(\frac{|\tau|\Omega}{kT}\right) \tag{19}$$

The calculation involves the integral

$$f_1(t) = \int_{U_0}^{U_{\mathrm{m}}} \exp(-t_{\mathrm{u}})\mathrm{d}U \tag{20}$$

which after the transformation $x = t_{\mathrm{u}}$ and $\mathrm{d}U = -kT\mathrm{d}$

$[\log(x)]$ becomes

$$f_1(t) = -kT\int_{x_1}^{x_2}\exp(-x)\mathrm{d}[\log(x)]$$
$$= -kT\left\{\int_{x_1}^{x_2}\mathrm{d}[\exp(-x)\log(x)] + \int_{x_1}^{x_2}\log(x)\exp(-x)\mathrm{d}x\right\} \tag{21}$$

with the boundaries

$$x_1 = \nu t\,\exp\left(\frac{|\tau|\Omega}{kT}\right)\exp\left(-\frac{U_0}{kT}\right) \text{ and } x_2 = \nu t\,\exp\left(\frac{|\tau|\Omega}{kT}\right)\exp\left(-\frac{U_\mathrm{m}}{kT}\right) \tag{22}$$

For large t and finite U_0 the term of the first integral on the right-hand side of Eq. (21) $\exp(-x_1)\ln(x_1) \rightarrow 0$, while for large U_m of this integral the term $\exp(-x_2) \rightarrow 1$. With these assumptions the second integral on the right-hand side can be approximated by

$$kT\int_{x_1}^{x_2}\log(x)\exp(-x)\mathrm{d}x \approx -kT\int_0^\infty \log(x)\exp(-x)\mathrm{d}x = kT\chi \tag{23}$$

where $\chi \approx 0.57722...$ is the Euler constant. Expression (21) now becomes

$$f_1(t) = -kT\left[\chi + \log(\nu t) + \frac{(|\tau|\Omega - U_\mathrm{m})}{kT}\right] \tag{24}$$

so that we find from Eqs. (18), (20), (23) and (24) for the total shear creep strain

$$|\epsilon_{13}(t)| = \frac{|\tau|}{2g} + \frac{1}{2}kTI_0\left[\chi + \log(\nu t) + \frac{(|\tau|\Omega - U_0)}{kT}\right] \tag{25}$$

The true shear creep strain can be written as

$$|\epsilon_\mathrm{v}(t)| = |\epsilon_{13}(t)| - \frac{|\tau|}{2g} = \epsilon_0 + \frac{1}{2}kTI_0\log(t) \tag{26}$$

with

$$\epsilon_0 = \frac{1}{2}kTI_0\left[\chi + \log(\nu) + \frac{|\tau|\Omega - U_0}{kT}\right] \tag{27}$$

Thus for a flat transition density function the calculated shear creep strain is proportional to the logarithm of the time, which corresponds with the creep behaviour of most polymer fibres in the glassy state.

At low shear strain and small creep times deviations from the logarithmic creep law have been observed as shown in Fig. 4. In order to analyse the creep for small values of t and τ the shear creep strain is calculated by the numerical integration of Eq. (18) with a constant value for the applied shear stress τ. The result has been plotted in Fig. 12a. For a shear stress below the yield point the creep strain follows a concave curve versus the time, which agrees with the creep of PpPTA and PET below the yield point, see Fig. 4. As shown by Eq. (25) and by Fig. 12a the creep shear strain for a flat transition density function is calculated to be independent of the shear stress, which is not in agreement with the observations [6].

As has been shown in Ref. [6] that the time dependent part of the fibre strain is obtained from the time dependent contribution of the shear strain of the domain according to

$$\epsilon_\mathrm{f}(t) = -\frac{\sin\theta_0}{\cos\Theta}\epsilon_\mathrm{v}(t) \tag{28}$$

For well-oriented fibres $\sin\theta_0 \approx \tan\theta_0$ and as shown in Ref. [3] the orientation angle immediately after loading is well approximated by the analytical function

$$\tan\theta_0 = \frac{\tan\Theta}{\left(1 + \frac{\sigma_\mathrm{f}}{2g}\right)} \tag{29}$$

Hence, from Eqs. (26), (28) and (29) it follows that the calculated stress dependence of the logarithmic creep

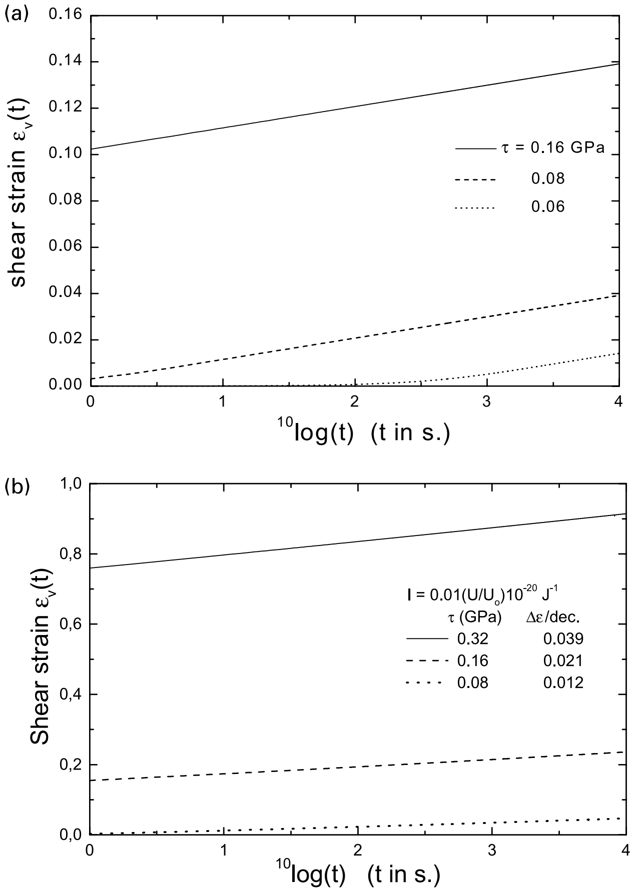

Fig. 12. (a) The calculated creep shear strain of a domain for $kT = 0.4\times10^{-20}$ J, $\Omega = 1250\times10^{-30}$ m^3, $[U_0, U_\mathrm{m}] = [10, 100]\times10^{-20}$ J, $I(U) = I_0 = 0.01\times10^{20}$ J^{-1}, for $\tau = 0.06$, 0.08 and 0.16 GPa, $\tau_\mathrm{y} = 0.08$ GPa. (b) The calculated shear creep strain of a domain for $kT = 0.4\times10^{-20}$ J, $\Omega = 1250\times10^{-30}$ m^3, $[U_0, U_\mathrm{m}] = [10, 100]\times10^{-20}$ J, $I(U) = 0.01(U/U_0)\times10^{20}$ J^{-1}, for $\tau = 0.08$, 0.16 and 0.32 GPa, $\tau_\mathrm{y} = 0.08$ GPa.

coefficient of a fibre for a flat transition density function, $I(U) = I_0$, is given by the factor $(1 + \sigma_f/2g)^{-1}$. This is different from the result derived and experimentally confirmed in a previous paper [6]. There it was derived that assuming a linear viscoelastic simple shear mechanism according to Eq. (12), the logarithmic creep rate of the fibre is given by

$$\frac{d\epsilon_f(t)}{d[\log(t)]} = \frac{j_1}{2} \frac{\sigma_f \sin^2 \Theta}{\left(1 + \frac{\sigma_f}{2g}\right)^3} \tag{30}$$

However, a flat density transition function is not the only function that yields a logarithmic time dependence of the creep. Fig. 12b presents the creep shear strain numerically calculated with Eq. (18) for the transition density function $I(U) = 0.01U/U_0$. For three values of the shear stress 0.08, 0.16, 0.32 GPa the shear creep rate is 0.012, 0.021 and 0.039 per decade, respectively. Calculation of the fibre creep rate using Eq. (28) yields then approximately the same stress dependence as given by Eq. (30). A similar result can also be derived analytically as shown in the Appendix. Thus the exact form of the logarithmic creep coefficient depends on the shape of the plastic transition density function $I(U)$. This can be demonstrated by analysis of the retardation spectrum. In the theory of linear viscoelasticity the time dependent shear compliance $j(t)$ is written in terms of a continuous retardation spectrum $L(\delta)$

$$j(t) = j_0 + \int_0^\infty \frac{L(\delta)}{\delta}\left[1 - \exp\left(-\frac{t}{\delta}\right)\right] d\delta \tag{31}$$

For a logarithmic creep behaviour $L(\delta)$ should be constant. Using Eq. (7) for the relaxation time δ in combination with Eq. (14), it is easily shown that for a stress step function at $t = 0$ the retardation spectrum for a density function $I(U)$ is given by

$$L(\delta) = kTI(U) \text{ with } U = kT\log(\nu\delta) + |\tau|\Omega \tag{32}$$

So, the transition density function $I(U) = I_0$ yields a constant retardation spectrum and thus a logarithmic creep behaviour versus the time. The creep behaviour during a time interval t is determined by $L(\delta)$ on the interval $[0, t]$. Hence, it can be concluded from Eq. (32) that the creep behaviour on an interval $[0, t]$ is determined by the shape of $I(U)$ on the interval $\Delta U = [|\tau|\Omega, kT\log(\nu t) + |\tau|\Omega]$. A logarithmic creep law can be expected when $I(U)$ is constant over this interval. As ΔU is proportional to kT, this implies that at low temperatures a logarithmic creep law can be expected, which is independent of the shape of $I(U)$. At higher temperatures the time dependence of the creep can be dependent on the shape of $I(U)$ yielding concave or convex creep curves versus the logarithm of the time.

The calculation of the stress relaxation rate is somewhat tiresome because $\epsilon(t)$ has been expressed as a function of $\tau(t)$. It can be shown that for a flat transition density function the relaxation is given by

$$|\tau(t)| = \tau_0 - \frac{kTgI_0}{1 + gI_0\Omega}\log(t) \tag{33}$$

for a shear stress larger than the shear yield stress. It is easily seen from Eqs. (15), (26), (27) and (33) that the ratio between the logarithmic relaxation coefficient and the logarithmic creep coefficient is given by the mechanical modulus g_m. This surprising result agrees with the experimental results presented in Ref. [7] and it is an indication that indeed the viscoelastic and yield deformation are due to a single mechanism of activated shear transitions.

7. The response to complex loading schemes

Eq. (14) explains the response of the fibre to a stepwise increased stress as well. The creep at a certain stress τ_1 is caused by the transitions with an activation energy approximately in the interval $[\tau_1\Omega, \tau_1\Omega + kT\log(\nu t)]$, where t is the total creep time. During the creep, the transitions with these energies relax, but the transitions with an energy much higher are not effected at all. The creep due to a next step, increasing the stress to τ_2 is caused by transitions with an activation energy of about $U = \tau_2\Omega$, with $\tau_2 > \tau_1$. If $\tau_2\Omega > \tau_1\Omega + kT\log(\nu t)$, the transitions at an energy $U = \tau_2\Omega$ are still unrelaxed after the period of creep at τ_1. In that case, the creep behaviour at the second level is independent of the creep at the previous step. Thus, provided that $\tau_2\Omega - \tau_1\Omega > kT\log(\nu t)$, Eq. (14) predicts that at each step the creep will be equal to the creep in a normal creep experiment at that stress level. This behaviour, which is in disagreement with superposition, was observed for PpPTA fibres, see Fig. 5.

The response of polymer fibres to a strain–relaxation–strain experiment can be explained by a similar argument. In this experiment, the strain is first increased at a constant strain rate, at a stress σ_0 the deformation is stopped and a relaxation experiment is performed during a time t_1, after which the strain is increased at a constant strain rate up to failure. During the first period of constant strain rate a dynamic equilibrium is created between the deformation and the activated transitions. At the moment that the deformation is stopped the fibre is out of equilibrium, there are many activated transitions with a rather short relaxation time, which have not relaxed yet. During the relaxation period, these transitions take place and a new equilibrium is developed. At the end of the relaxation period only very slow transitions with a large relaxation time occur. This implies that at the beginning of the second period of deformation at a constant strain rate the fibre is almost elastic. Increasing the stress, activated transitions with higher energy begin to relax, which cause a kind of yield point. After the initial, almost elastic, part the stress vs. strain curve continues along the original stress vs. strain curve of the fibre. This experiment has been simulated numerically substituting the period of a constant strain, by a period of constant stress, which is much easier for the calculation. The result has been presented in Fig. 13. The calculated behaviour shown in this figure is very similar to the observed curves presented in Fig. 6.

Eq. (14) has been derived for shear transitions in only one direction. For the calculation of the response to more complicated loading schemes, such as the recovery after the load has been removed, shear transitions in both directions should be considered. In addition it is necessary to specify the density function I as a function of the activation energies U_f for the forward transition $1 \rightarrow 2$ and the activation energies U_m for the backward transition $2 \rightarrow 1$. With a proper choice of the density function $I(U_f, U_m)$ it will be possible to give detailed predictions of the response of polymer fibres to complex loading schemes. It has been observed that the yield deformation is not completely permanent, but partly recoverable [7]. It has also been shown that after the fibre has been unloaded, initially the stress vs. strain curve shows no yield, but after a longer waiting time the yield point slowly reappears [1]. This semi-plastic deformation can be understood, supposing that the activation energy of the second state of a shear transition U_2 is in the order of kT. In that case, the second state is only stable for the loaded fibre. Unloading the fibre this state becomes unstable again and the shear transition will be reversed, resulting in the recovery of the yield deformation. As during this recovery the occupation of state 1 increases it can be understood that due to the activation energy U_f for the transition $1 \rightarrow 2$, the yield point slowly returns after the fibre has been unloaded.

In an earlier paper, we presented the continuous chain model for the description of the stress versus strain curve of polymer fibres with yield [5]. In this model, the plastic behaviour of the fibre is realised by adding a plastic component to the shear deformation of the domain, being the basic element of the model. As Eq. (14) describes the viscoelastic as well as the plastic properties of the domain, the continuous chain model allows in a similar fashion the calculation of the response of a polymer fibre to complex loading patterns.

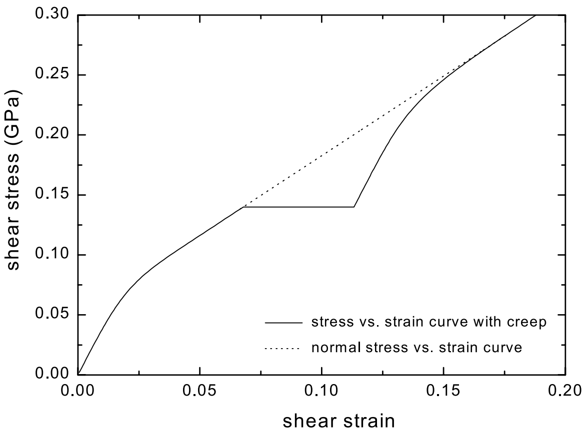

Fig. 13. The calculated response to an alternating period of a constant strain rate and constant stress. Also the calculated curve returns to the normal stress vs. strain curve. The values of the parameters are $kT = 0.4 \times 10^{-20}$ J, $\Omega = 250 \times 10^{-30}$ m^3, $[U_0, U_m] = [2, 100] \times 10^{-20}$ J, $g = 2$ GPa, $I_0 = 0.02 \times 10^{20}$ J^{-1}, $\alpha = 0.02$ GPa s^{-1}, for $0.0 < t < 7$ s $\tau = \alpha t$, for $7 \le t \le 240$ s $\tau = 0.14$ GPa, for $240 \le t \le 250$ s $\tau = \alpha t$.

8. Conclusions

It has been shown that the viscoelastic and yield deformation of a polymer fibre can be described by a process of activated shear transitions with a distribution for the activation energies. These shear transitions govern the time dependent and plastic displacement of the chains. The proposed model gives a correct description of the experimentally observed strain rate dependence of the yield deformation. The relation between creep and stress relaxation, and the response to the more complex loadings has been reproduced. It has been shown that at a constant strain rate, above the maximum preceding stress, the deformation of the fibre returns to the normal stress vs. strain curve. It is concluded that the main features of the time dependent and yield behaviour of polymer fibres in the glassy state can be described by the proposed theory. This model in conjunction with the continuous chain model may provide a basis for a constitutive equation for the deformation of polymer fibres, which describes the deformation of the fibre due to arbitrary loading patterns.

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Appendix A

The calculation of the fibre creep rate for the transition density function $I(U) = I_0 U$ begins with the derivation of the shear creep strain

$$|\epsilon_{13}(t)| = \frac{|\tau|}{2g} + \frac{I_0}{2}\int_{U_0}^{U_m} U[1 - \exp(-t_u)]\mathrm{d}U \tag{34}$$

with

$$t_u = \nu t \exp\left(-\frac{U}{kT}\right)\exp\left(\frac{|\tau|\Omega}{kT}\right) = q\exp\left(-\frac{U}{kT}\right) \tag{35}$$

The calculation of Eq. (34) involves the integral

$$f(t) = \int_{U_0}^{U_m} U[\exp(-t_u)]\mathrm{d}U \tag{36}$$

After transformation $t_{\mathrm{u}} = x$ and $\mathrm{d}U = -kT\mathrm{d}[\log(x)]$ Eq. (36) becomes

$$f(t) = -(kT)^2 \int_{x_1}^{x_2} \exp(-x)[\log(q) - \log(x)]\mathrm{d}[\log(x)] \quad (37)$$

with the boundaries

$$x_1 = \nu t \exp\left(\frac{|\tau|\Omega}{kT}\right)\exp\left(-\frac{U_0}{kT}\right) = q\exp\left(-\frac{U_0}{kT}\right) \quad (38)$$

and

$$x_2 = \nu t \exp\left(\frac{|\tau|\Omega}{kT}\right)\exp\left(-\frac{U_{\mathrm{m}}}{kT}\right) = q\exp\left(-\frac{U_{\mathrm{m}}}{kT}\right) \quad (39)$$

Eq. (37) can be written as

$$f(t) = -(kT)^2[f_2(t)\log(q) - f_3(t)] \quad (40)$$

with

$$f_2(t) = \int_{x_1}^{x_2} \exp(-x)\mathrm{d}[\log(x)] \quad (41)$$

and

$$f_3(t) = \int_{x_1}^{x_2} \exp(-x)\log(x)\mathrm{d}[\log(x)] \quad (42)$$

The integral $f_2(t)$ has been evaluated before, see Eqs. (21)–(24), applying the assumptions that for large t and finite U_0 the function $\exp(x_1)\ln(x_1) \rightarrow 0$ and for large U_{m} the function $\exp(-x_2) \rightarrow 1$. This yields

$$f_2(t) = \chi + \log(\nu t) + \frac{(|\tau|\Omega - U_{\mathrm{m}})}{kT} \quad (43)$$

where $\chi \approx 0.57722\ldots$ is Euler's constant. The integral $f_3(t)$ can be written as

$$2f_3(t) = \exp(-x_2)[\log(x_2)]^2 - \exp(-x_1)[\log(x_1)]^2 - \int_{x_2}^{x_1} \exp(-x)[\log(x)]^2\mathrm{d}x \quad (44)$$

Using the same assumptions for t, U_0 and U_{m} made above, the integral in Eq. (44) becomes

$$\int_0^{\infty} \exp(-x)[\log(x)]^2\mathrm{d}x = \frac{\pi^2}{6} + \chi^2 \quad (45)$$

Thus

$$2f_3(t) = \left[\log(\nu t) + \frac{(|\tau|\Omega - U_{\mathrm{m}})}{kT}\right]^2 - \frac{\pi^2}{6} - \chi^2 \quad (46)$$

After inserting Eqs. (43) and (46) in Eq. (40) the shear creep strain is found to be

$$|\epsilon_{13}(t)| = \frac{|\tau|}{2g} + \frac{I_0}{2}\left\{(kT)^2\left[\log(\nu t)\left(1/2\log(\nu t) + \frac{|\tau|\Omega}{kT} + \chi\right) + \frac{|\tau|\Omega}{kT}\left(\frac{|\tau|\Omega}{2kT} + \chi\right) + \frac{\pi^2}{12} + \frac{\chi^2}{2}\right] - \frac{U_0^2}{2}\right\} \quad (47)$$

For

$$\frac{|\tau|\Omega}{2kT} \gg \chi \text{ and } \frac{|\tau|\Omega}{kT} \gg 1/2\log(\nu t) \quad (48)$$

Eq. (47) becomes

$$|\epsilon_{13}(t)| \approx \frac{|\tau|}{2g} + \frac{I_0}{2}\left\{(kT)^2\left[\left(\frac{|\tau|\Omega}{kT}\right)\left(\log(\nu t) + \frac{|\tau|\Omega}{2kT}\right) + \frac{\pi^2}{12} + \frac{\chi^2}{2}\right] - \frac{U_0^2}{2}\right\} \quad (49)$$

So we find for the shear creep rate

$$\frac{\mathrm{d}|\epsilon_{13}(t)|}{\mathrm{d}[\log(t)]} = \frac{I_0}{2}kT\Omega|\tau| \quad (50)$$

The creep rate of the fibre is given by Eq. (28) so we derive

$$\frac{\mathrm{d}\epsilon_{\mathrm{f}}(t)}{\mathrm{d}[\log(t)]} = \frac{I_0}{2}\frac{kT\Omega|\tau|\sin\theta_0}{\cos\Theta} \quad (51)$$

Because $|\tau| = \sigma_{\mathrm{f}}\sin\theta_0\cos\theta_0$ Eq. (51) can be written as

$$\frac{\mathrm{d}\epsilon_{\mathrm{f}}(t)}{\mathrm{d}[\log(t)]} = \frac{I_0 kT\Omega}{2}\frac{\sigma_{\mathrm{f}}\sin^2\theta_0\cos\theta_0}{\cos\Theta} \quad (52)$$

Using the analytical approximation of θ_0 given by Eq. (29) and the approximation $\sin\theta_0 \approx \tan\theta_0$ for well-oriented fibres, we find for the fiber creep rate

$$\frac{\mathrm{d}\epsilon_{\mathrm{f}}(t)}{\mathrm{d}[\log(t)]} = \frac{I_0 kT\Omega}{2}\frac{\sigma_{\mathrm{f}}\sin^2\Theta}{\left(1 + \frac{\sigma_{\mathrm{f}}}{2g}\right)^2} \quad (53)$$

For $j_1 = I_0 kT\Omega$ this equation is similar but not identical to Eq. (30). This is caused by the fact that in the derivation of Eq. (30) presented in Ref. [6] the change $\Delta\theta = \theta(t) - \theta_0$ of the orientation angle during creep is calculated by considering the contribution of both the viscoelastic increase and the elastic decrease of the shear deformation. For the small creep strains which occur during creep of well-oriented fibres $\Delta\theta$ is very small, so the terms $\epsilon_{13}(t) = \tan(\theta(t) - \Theta) = \tan(\Delta\theta + (\theta_0 - \Theta))$ and $\tau(t) = \tau(\theta(t)) = \tau(\Delta\theta + \theta_0)$ can be developed up to a linear term in $\Delta\theta$. By inserting these approximations in Eq. (49) and using $j_1 = I_0 kT\Omega$ Eq. (30) is obtained.

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