Thermal viscosity of polymeric materials from the standpoint of quantum transfer theory

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Abstract. In the work a physical model of the amorphous part of microfibrillar was proposed. A determining equation of thermoviscoelasticity based on this model was obtained. The equation is suitable for modeling and forecasting of the stress-strain state of amorphous-crystalline materials.

1. Introduction

The study of the thermoviscoelastic behavior of polymeric materials is one of the most important tasks of materials science since during operation the materials and their products are subjected to various mechanical and thermal stresses. The properties of polymeric materials (fibers, threads, films, etc.) are determined by their initial structure at various levels. It is known that most fiber-forming polymers are characterized by the presence of two phases: ordered (crystalline) and disordered (amorphous). In this case, crystalline and amorphous regions don’t have clearly defined boundaries. The supramolecular structure of oriented polymers can be different, however the fibrillar structure most often occurs for synthetic filaments and fibers [1-4]. The fibrillar structure of oriented amorphous-crystalline polymers is characterized by longitudinal heterogeneity with alternating regions with high ordering (crystallites) and poorly ordered (amorphous layers) [5]. The mechanical properties of oriented polymer materials are primarily determined by the structure of the disordered phase.

The aim of this work is to develop a physical model of the amorphous layer and build on its basis a defining equation that allows to simulate and predict the behavior of amorphous-crystalline materials.

2. Modeling of thermal viscosity of polymeric materials

In order to explain the thermoviscoelastic behavior of polymer materials various mechanical and physical models are used [6, 8]. To describe the stress in state of polymeric materials a number of theories of linear [9–11] and nonlinear viscoelasticity [7, 11–17] based on the well-known principle of heredity of L. Boltzmann and differing in the form of relaxation and delay nuclei have been developed. As shown in [7, 8, 18, 19] and others the behavior of polymer materials in a stress state is determined by the number of transitions through potential barriers of different heights and widths. The theory of the quantization of deformation processes in polymer threads and fibers was developed in [20–24].
According to [20, 21, 24], the supramolecular structure of the amorphous layer will be represented as a set of groups of macromolecules (clusters) that can be in two different stable energy states depicted in figure 1.

![Figure 1](image)

**Figure 1.** Energy diagram of ACE (active conformational elements) versus cluster size.

Here $H$ is the height of the energy barrier; $U$ is the width of the energy gap; $\delta$ is the strain of a quantum corresponding to the transition of a macromolecule segment from state 1 to state 2. Note that for most polymeric materials the “straightened” state 2 has lower energy than state 1, i.e. the magnitude of the energy gap is negative <0. The latter circumstance explains the shrinkage of textile yarns observed for most polymeric textile materials.

During the transition of the cluster from state 1 to state 2 the strain quantum $\delta$ is freed and is absorbed in the opposite transition. An external force exerts an activating effect on the structural element lowering the potential barrier by the amount of elastic energy in the direction of the straight transition and vice versa, increasing the value of the barrier in the opposite direction (points $1'$ and $2'$ in figure 1).

If the polymer thread is considered as a set of such series-connected clusters then, as shown in [20-22, 24, 24], the polymer material obeys the following defining equation:

$$
\frac{d}{d\tau}(\varepsilon - x) + (\varepsilon - x)(e^{\gamma x^2} + Ae^{-\gamma x^2}) = q\text{sh}(\gamma x^2)
$$

In equation (1) the following notation is used: $\varepsilon$ – deformation; $x$ - the elastic part of the deformation; $\tau = \frac{t}{\tau_p}$ – dimensionless time; $\tau_p = \frac{1}{\nu}e^{H^*}$ – internal relaxation time, determined by the reduced height of the energy barrier $H^* = \frac{H}{O}$; $T$ – the thermodynamic temperature; $A = e^{U^*}$,

$$
q = \frac{2m_0\delta}{1 + A} = \frac{2m_0\delta}{1 + e^{-U^*}}
$$

- material constant depending on temperature; $m_0$ – the number of clusters per unit length.

Equation (1) and its further modifications [26] are used quite successfully for modeling and predicting polymer textile materials.

However for the creep mode ($x = \text{const}$) a simple exponential solution of equation (1), well describes
and explains only the initial part of the creep curve which required complicating the model (introducing additional energy barriers, etc.).

Therefore we will present the following model of the amorphous part of the oriented polymer material: one set of parallel-connected elements obeying equation (1) some of which are not loaded. The model of the amorphous layer is presented schematically in figure 2.

Figure 2. The physical model of microfibrils.

Here \( d = a + b \) is a large period.

Neglecting the crystallite deformation we compose the balance of the number of forced conformational transitions from state \( 1' \) to \( 2' \) taking into account the fact that as loading in the amorphous interlayer, additional chains of macromolecules that were not loaded before will "turn on".

Let us consider a separate molecular chain of \( N_0 \) identical molecular chains bearing an average load \( f \) and containing \( m_0 \) per unit length of ACE. If the sample is in a state of thermodynamic equilibrium then the occupation numbers of the levels “1” and “2” obey the Boltzmann statistics, i.e.

\[
m_{1,2}^p = \frac{m_0}{1 + \exp[\pm U^*]},
\]

where \( U^* = \frac{U}{k_B T} \) is the reduced width of the energy gap.

Since an external force has an activating effect on the ACE lowering the barrier by the amount of elastic energy which is a quadratic form of the amount of elastic deformation in the direction of direct transition and vice versa, increases the barrier (this work must be additionally performed against external forces) in the opposite direction (points \( 1' \) and \( 2' \) on Figure 2). The energy value can be considered as some unstable intermediate short-lived state, an analog of which in chemistry is an activated complex or compound nucleus in nuclear physics.

We assume that at the initial instant of time, the occupation numbers of states 1 and 2 obey the Boltzmann statistics, i.e. relations (2) are satisfied and normalized to some fixed value \( m_0 \).

We use the technique proposed in [26].

Let \( \tilde{W}_{12} \) and \( \tilde{W}_{21} \) be the probabilities per unit time of transition from state \( 1' \) to state \( 2' \) and vice versa. It is determined by the reduced height of the potential barrier (\( \tilde{W}_{12} \) is the fraction of clusters that have passed from state 1 to state 2 per unit time). According to the statistics of L. Boltzmann
\[ \tilde{W}_{12} = v \cdot e^{-\tilde{H}_{12}} \]
\[ \tilde{W}_{21} = v \cdot e^{-\tilde{H}_{21}} \]

where \( v \) is the frequency of approach to the barrier. Note that the probability of finding a cluster in an unstable state with energy \( E = H \) is proportional to \( e^{-\tilde{H}} \).

In view of the foregoing, the cited barrier heights are equal to:
\[ \tilde{H}_{12}^* = \frac{\tilde{H}_{12}}{T} = \frac{1}{T} \left( H - \overline{\gamma}X^2 \right) = H^* - \gamma X^2 \]
\[ \tilde{H}_{21}^* = \frac{\tilde{H}_{21}}{T} = \frac{1}{T} \left( H - U + \overline{\gamma}X^2 \right) = H^* + \gamma X^2 - U^* \]

where \( \overline{\gamma} \) is the structurally sensitive coefficient which is determined by the elastic energy of the ACE; \( \gamma = \frac{\overline{\gamma}}{T} \) is reduced structurally sensitive coefficient.

Here it is taken into account that the true elastic modulus is proportional to the stiffness of the molecular chains, i.e. the change in the height of the energy barrier \( \Delta H \) is equal to:
\[ \Delta H = \frac{f^2}{2k} = \frac{F^2}{2kN_0^2} = \frac{s_0^2}{2kN_0^2} \sigma^2 = \frac{E_0^2 s_0^2}{2kN_0^2} X^2 \]
i.e. \( \overline{\gamma} = \frac{E_0^2 s_0^2}{2kN_0^2} \)

Here \( s_0 \) is microfibril cross-sectional, \( k \) is stiffness of the molecular chains of the amorphous layer, \( E_0 \) is true elastic modulus.

In the steady state
\[ m_1^p \tilde{W}_{12} = m_2^p \tilde{W}_{21} \]
\[ m_1^p + m_2^p = m_0 \]

where \( m_0 = m_1^p + m_2^p = \text{const} \) is the total number of ACE per unit length of the sample. If at the initial moment of time the system is in an equilibrium unstressed state then
\[ m_1^p W_{12} = m_2^p e^{-\mu'} \]
\[ m_2^p W_{21} = m_2^p e^{-\mu' + u'} \]

where \( W_{12} \) and \( W_{21} \) are the probabilities of transition per unit time from state 1 to state 2 and vice versa without load.

From the AKE balance equation (7) follows the Boltzmann, i.e., relation (2).

To change the occupation numbers \( m_1 \) and \( m_2 \) during the time \( dt \) we can write an obvious kinetic equation, which is the ACE balance equation, namely:
\[ dm_2 = \left[ m_1^p \tilde{W}_{12} - m_2^p \tilde{W}_{21} \right] dt \]
Considering that the complete deformation of the amorphous interlayer can be represented as the sum of the elastic and conformational we have

\[ \frac{d}{dt}(\varepsilon - x) = \delta \frac{dm}{dt} = \delta \left[ m_0 \tilde{W}_{12} - m_2 \tilde{W}_{21} \right] = \delta \left[ m_0 \tilde{W}_{12} - (\tilde{W}_{12} + \tilde{W}_{21}) (m_2 - m_0^0 + m_2^p) \right] \]

or

\[ \frac{d}{dt}(\varepsilon - x) + (\varepsilon - x)(\tilde{W}_{12} + \tilde{W}_{21}) = \delta \left[ m_0 \tilde{W}_{12} - (\tilde{W}_{12} + \tilde{W}_{21}) m_0^0 \right]. \]

\[ \cdot \delta \left[ m_0 \tilde{W}_{12} - (\tilde{W}_{12} + \tilde{W}_{21}) m_2^p \right] + \delta (\tilde{W}_{12} + \tilde{W}_{21}) (m_2^p - m_2^0) \]

According to (6) we have

\[ m_0 \tilde{W}_{12} - (\tilde{W}_{12} + \tilde{W}_{21}) m_2^p = m_0 \tilde{W}_{12} - (\tilde{W}_{12} + \tilde{W}_{21}) m_0 \tilde{W}_{12} = \frac{2m_0 m_0 e^{-\gamma z}}{1 + e^{-\gamma z}} sh(\gamma X^2) \]

Thus, we again come to equation (1).

We take into account the effect of additional molecular chains involved as the amorphous fibril layer deforms.

Considering the deformations to be small, we take the number of additional chains is proportional to the level of deformation to a first approximation in terms of the degree of complete deformation of the material, i.e. according to the expression (5)

\[ \Delta H^* = \gamma \frac{X^2}{(1 + \alpha \varepsilon)^2}, \]

where \( \alpha \) is the coefficient of proportionality which describes the increase in the number of chains.

After all the same reasoning, it is possible to obtain a more accurate defining equation for amorphous-crystalline polymeric textile materials:

\[ \frac{d}{d\tau} [\varepsilon - z] + (\varepsilon - z)(e^{\gamma z} + A e^{-\gamma z}) = qsh(\gamma z^2) \]

\[ z = \frac{x}{(1 + \alpha \varepsilon)} \]

3. Conclusion

Equation (12) makes it possible to more accurately model the thermoviscoelastic properties of amorphous-crystalline textile materials. In particular, a numerical analysis of equation (12) for the creep process (\( x = const \)) allows us to expand the range of creep prediction by two decimal orders.

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