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Macro- and Microcreep of Oriented Poly(Amidobenzimidazole)

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Changes occurring during tensile deformation in highly oriented poly(amidobenzimidazole) (PABI) fibers have been investigated in time (creep) at room temperature. Macrodeformation was experimentally determined with stresses varying from 1.2 to 3.0 GPa. Microdeformation (tensile relative deformation of the PABI crystal lattice) was defined from the angular shift of meridional X-ray reflexes. It was shown that the creep of PABI fibers on both macro- and microlevels changed nonlinearly with stress. The measurements of the dynamic elastic modulus of PABI fibers allowed to establish that chain molecules in the PABI crystal lattice become more extended, i.e. *cis-trans* transitions occur. The transition kinetics determines the intensity of the lattice creep, or the creep of the whole fiber. The formula for the quantitative description of macro- and microcreep in PABI fibers is presented, which takes into account the nonlinearity of viscoelastic properties of PABI fibers and has a small number of parameters.

KEY WORDS Macrocreep, microcreep, PABI.

INTRODUCTION

The relation between the processes at the macro- and microlevels is of primary importance for the mechanics and physics of polymers. The establishment of this relation allows purposefully to improve the mechanical properties of polymers and solve the problems of durability prognostication.

A number of previous papers^{1,2} has reported that the creep of oriented flexible-chain polymers is stipulated by conformational changes of macromolecules in intercrystallite amorphous-like interlayers. As was shown experimentally on highly oriented fibers from rigid-chain polymers,³ their creep follows the same regularities as those for highly oriented fibers from flexible-chain polymers, like nylon-6, PET, and PAN.

The progress in deformation at the microlevel accounted for the *cis-trans* transitions in the amorphous regions of flexible chain polymers was considered by Zhurkov *et al.*⁴ The similar studies were made by Slutsker *et al.*⁵ for rigid-chain polymers. The authors testified that in oriented fibers from such polymers the deformation at microlevel is due to a great extent to the crystallite lattice deformation.

The aim of the present investigation was to establish the nature of the fiber creep for rigid-chain polymers.

MATERIALS

Highly oriented poly(amidobenzimidazole) fibers (PABI) with the Kevlar-like structure of macromolecules were used in this work. The experimental samples were threads composed of 140 monofilaments with the diameter of 12 μm . We studied the tensile deformation of highly oriented PABI fibers in a creep process at room temperature. Macrodeformation ε_M was experimentally determined with stresses (σ) varying from 1.2 to 3.0 GPa. Microdeformation ε_μ (the tensile relative deformation of the PABI crystal lattice) was measured from the angular shift of meridional X-ray reflexes at stress levels of 1.2 to 2.6 GPa.

RESULTS AND DISCUSSIONS

Figure 1a shows plots of the macrodeformation ε_M against time at different stress levels. The isochronous dependence of the deformation ε_t (t is the duration of deformation in min) on stress is shown in Figure 2. At some stress levels this dependence is seen to exhibit nonlinearity defined by the increase of the compliance $D = \varepsilon/\sigma$ with the stress increase. The creep behavior as a function of stress is initially characterized by the increase of the creep rate parameter $d\varepsilon/d(\lg t)$ and at high stresses by its decrease (see Figure 2). Hence, the dependence of the creep rate parameter $|d\varepsilon/d(\lg t)|_{t_1}$ at a fixed moment of time t_1 has the extremum. Such a dependence is similar to that for the flexible polymers and is caused by the decreasing with time of a portion of chain molecules which are capable of transitions.

Considering the microdeformation of fibers in the PABI lattice⁶ when loading the PABI sample at room temperature it was found that in the course of time the noticeable (though comparatively slow) growth of the tensile lattice deformation occurred. This phenomenon was called "lattice creep". As this deformation is reversible when the load is removed it is possible to speak about the singularity⁵ of the deformation behavior of the crystal lattice. Analyzing the structure of the PABI monomer unit Slutsker *et al.*⁶ assumed that the conformational *cis-trans* transitions for molecules in a crystal lattice are possible. These give the contribution to the full deformation at constant tensile loading.

In order to extend our understanding of the deformation mechanism, the lattice creep measurements in the present study were made at different tensile stress levels. The plots of the lattice deformation against $\lg t$ are shown in Figure 1b. The process of the lattice creep for all stress levels was found to have a damping character in a coordinate system ε, t . At the same time creep rate increases initially with stress and then decreases, i.e. coincidence between deformation behavior at micro- and macrolevel takes place. Figure 2 shows the plots of the isochronous deformation values and the creep rate parameter against stress for the crystal lattice. One should pay an attention to the similarity in the dependences of $\varepsilon(\sigma)$ and $d\varepsilon/d(\lg t)$ for macro- and microcreep, the absolute values of the deformations therewith are different ($\varepsilon_\mu = 0.7\varepsilon_M$).

To elucidate the mechanism of the lattice creep of PABI lattice the dynamic moduli of the longitudinal elasticity have also been measured.

The velocity V of the ultrasound wave propagation (60 kHz) along the PABI fibers was experimentally determined. The dynamic modulus of elasticity E was determined by the well known formula $E = \rho V^2$, where ρ is a polymer density.

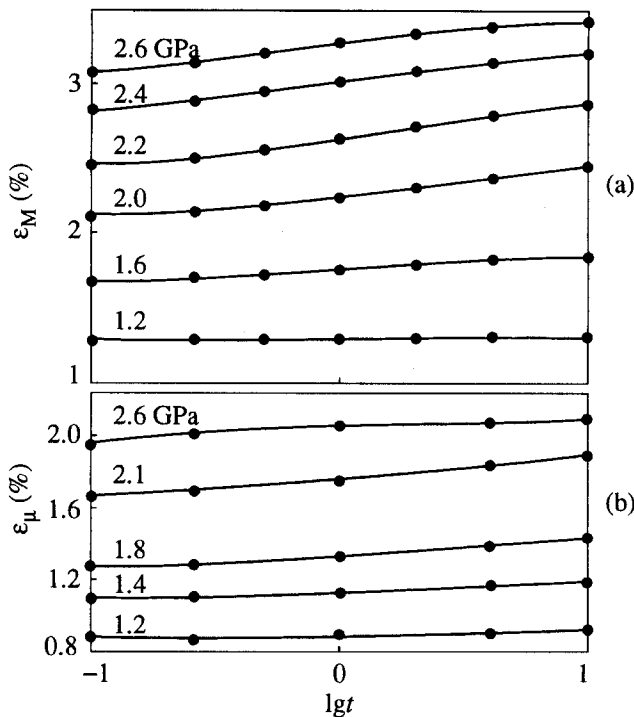


FIGURE 1 Creep curves for (a) PABI fiber and (b) PABI crystal lattice at different stress levels. t is measured in minutes.

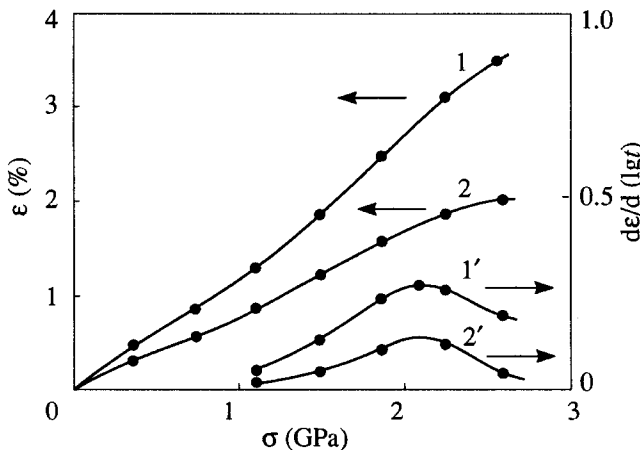


FIGURE 2 Dependences of isochronous values of PABI deformation and creep rate parameter $d\epsilon/d(\lg t)$, measured in 1 min after loading, on stress for ϵ_M (curves 1 and 1') and for ϵ_μ (curves 2 and 2').

Figure 3 shows E plotted against time at different stress levels. It is obvious that the character of these plots is very similar to those of ϵ_M and ϵ_μ (see Figure 1). It is noteworthy that at high stress and time levels the dynamic modulus reaches the value of about 200 GPa, i.e. it approaches the value of the theoretical modulus of elasticity of the

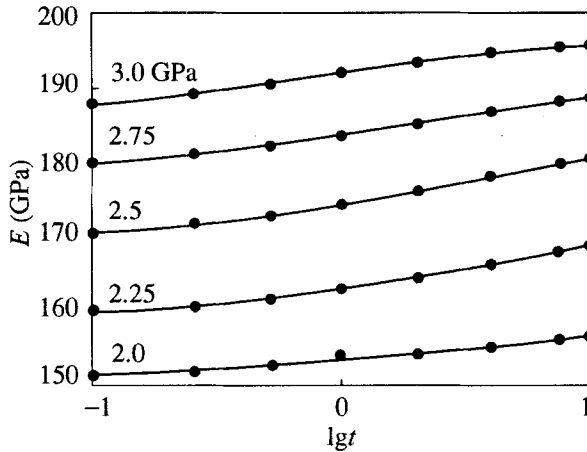


FIGURE 3 Acoustic modulus E against $\lg t$ plots for PABI fiber at different stress levels. t is measured in minutes.

fully extended organic chain macromolecule. This allows to conclude that under loading the macromolecules in a crystal lattice of PABI samples become increasingly extended with time. The completely extended macromolecule contains only *trans*-conformers. Thus a tensile loading results in *cis-trans* transitions. The kinetics of such transitions determines the intensity of the lattice creep, hence the creep of a whole fiber, intercrystallite and interfibrillar slippage makes less contribution to it.

Comparative data are presented for the creep of the oriented rigid-chain polymer PABI and flexible-chain polymer PET. The comparison was made on the stress-time dependences of the acoustic elastic modulus. Figure 4 shows the plots of the acoustic modulus E_{ac} against time at different stress levels of the oriented PET at room temperature. The plots are seen to coincide with the analogous plots of PABI samples. This points out to general mechanism of the creep of both rigid- and flexible-chain polymers consisting in conformational transitions in molecules resulting in their gradual extension with time. It is clear from the present study that though the processes occurring in rigid- and flexible-chain polymers are similar considerable differences must be noted. In the rigid-chain polymers it is conformational transitions in the crystallite regions of polymer that contribute to their macrodeformation. In the flexible-chain polymers macrodeformation is mostly concentrated in the intercrystallite amorphous parts of polymer. In flexible-chain polymers crystallites exhibit insignificant deformation. It should be noted, however, that both the rigid- and flexible-chain polymers have identical molecular mechanism of creep.

The quantitative description of creep in PABI samples (both at macro- and microlevels) is the same as for the creep of oriented flexible-chain polymers. It is based on the similarity of stress and time dependences of the creep deformation of PABI and a series of fibers from flexible-chain polymers. To describe the creep of PABI samples stress dependences of isochronous values of deformation and creep rate parameter $d\varepsilon/d(\lg t)$ were used. Dependences of the creep process intensity $D' = \sigma^{-1}d\varepsilon/d(\lg t)$ versus the compliance level were also plotted (see Figure 5). The typical dome-shaped curves were used to define the parameters in the following formula for creep description

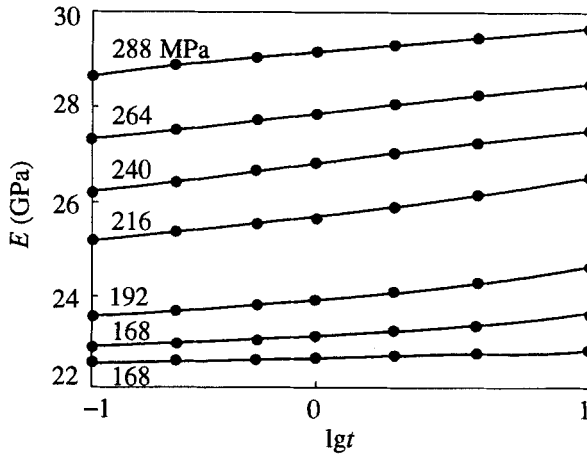


FIGURE 4 Acoustic modulus E against $\lg t$ plots for PET at different stress levels. t is measured in minutes.

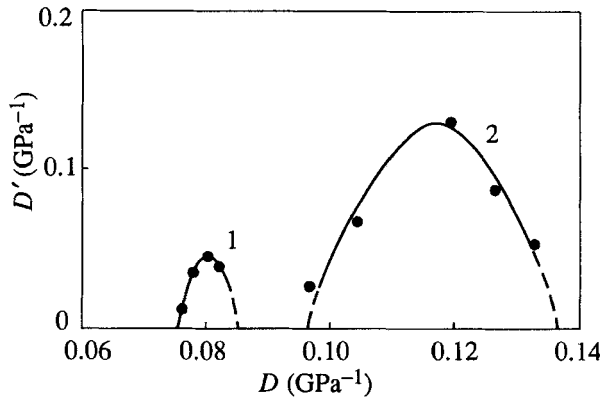


FIGURE 5 Creep intensity D' against compliance D plot for PABI crystal lattice (curve 1) and for PABI fiber (curve 2).

$$\varepsilon(\sigma, t) = D_0\sigma + (D_\infty - D_0) \int_0^t \sigma(\theta)r(t - \theta, \sigma)d\theta,$$

where D_0 and D_∞ are values of elastic and viscoelastic compliances; $r(t - \theta, \sigma)$ is a creep nucleus.

The given description takes into account the nonlinearity of viscoelastic properties of PABI fibers and has a small number of parameters. The values of parameters D_0 and D_∞ were found to be higher for the macrocreep compared with those for the microcreep. This is due to deformation of intercrystallite and interfibrillar regions in PABI which contribute to macrocreep.

CONCLUSION

In the rigid-chain as well as in the flexible-chain polymers the deformation develops in time owing to the conformational changes in macromolecules.

In contrast to flexible-chain polymers the conformational transitions in rigid-chain polymers occur not only in the intercrystallite amorphous regions (it dominates for the flexible-chain polymers) but also mostly in the crystal lattice that makes the main contribution to the sample creep.

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