

THE EFFECT OF LOW TEMPERATURES ON THE RHEOLOGICAL PROPERTIES OF AMORPHOUS AND AMORPHOUS-CRYSTALLINE POLYMERS

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1. Introduction

The comparative analysis of the results of low-temperature mechanical tests of the samples of amorphous and amorphous-crystalline polyimide of the kapton H type was carried out. In the experiments [1], tensile diagrams of such samples were recorded, namely, the dependences of the deforming stress σ on the strain ε at constant values of the strain rate and temperature: $T = 293$ K, 77 K, 4.2 K; $\dot{\varepsilon} = 7 \cdot 10^{-5} \text{ s}^{-1}$, $7 \cdot 10^{-4} \text{ s}^{-1}$, $6 \cdot 10^{-3} \text{ s}^{-1}$. The initial aim of these experiments was to study the effect of moderate (77 K) and deep (4.2 K) cooling on the structure and some mechanical characteristics of polyimide, important for its use in cryogenic and aerospace engineering. Later [2], there was a need and opportunity to supplement the experimental results with additional analysis in order to use them to test new aspects of the theory of low-temperature elastic-viscous deformation of polymers, in particular, the description of the effects of forced elasticity and their competition with brittle fracture processes.

2. Molecular model

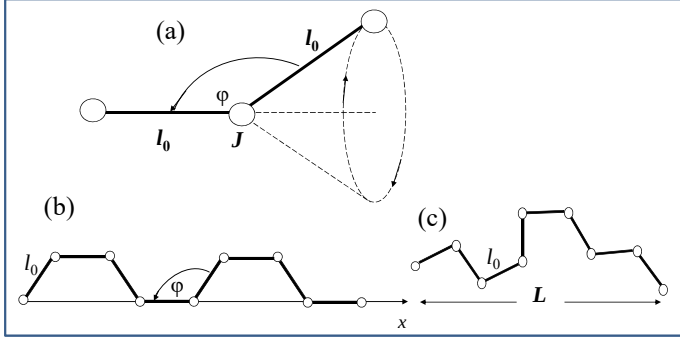


Fig. 1. Mechanical model (rods-joints) of the monomer structure of a molecular chain: limited rotation of adjacent monomer units (a); chain fragment straightened along the x axis (b); chaotic conformation of the chain fragment (c); l_0 is a monomer unit (rod), J is a simple covalent bond (joint), φ is a valence angle.

- **Amorphous polymer** is a macroscopic coil with a uniform average density, which is formed by a chaotic stacking of turns of a long molecular chain.
- The chain has a quasi-one-dimensional spatial structure: it consists of a sequence of identical atomic groups, i. e., **monomer units**, within which the atoms are united by rigid double and triple valence bonds.
- These units have longitudinal dimensions l_0 of the order of several nanometers and are interconnected by less rigid single valence bonds, which allow them to perform a rotational movement similar to the rotations of rigid rods connected by joints; the rotations are partially limited by the fixed values of the bond angle between the longitudinal axes of the adjacent units.
- The polymer deformation is a sequence of thermally activated excitation of **elastons**, i. e., straightening of short segments of molecular chains with nanometer scale sizes (**molecular segments**) between the points of self-intersection of the chain.

3. Rheological equation and its definition for active deformation process

$$\frac{d}{d\varepsilon} \sigma = M_e - (M_e - M_{he}) \beta \operatorname{sh} \left[\frac{\sigma - M_{he} \varepsilon}{(M_e - M_{he}) \varepsilon_T \sqrt{1 + \beta^2}} \right] \quad (1)$$

The equation parameters:

M_e, M_{he} are elastic characteristics of material;
 β, ε_T are kinetic coefficients.

$$\beta = \frac{M_e \sigma_T}{(M_e - M_{he}) \eta \dot{\varepsilon}}$$

$$\varepsilon_T = \frac{\sigma_T}{(M_e - M_{he}) \sqrt{1 + \beta^2}}$$

$$\sigma(\varepsilon; T, \dot{\varepsilon}) = (M_e - M_{he}) \varepsilon_T \sqrt{1 + \beta^2} \ln \left[\frac{\sqrt{1 + \beta^2} + \beta + 1 + (\sqrt{1 + \beta^2} - \beta - 1) \delta(\varepsilon)}{\sqrt{1 + \beta^2} + \beta - 1 + (\sqrt{1 + \beta^2} - \beta + 1) \delta(\varepsilon)} \right] + M_{he} \varepsilon, \quad \delta(\varepsilon) \equiv \delta(\varepsilon; T, \dot{\varepsilon}) = \exp\left(-\frac{\varepsilon}{\varepsilon_T}\right), \quad \varepsilon < \varepsilon_0. \quad (2)$$

3. Analytical approximation of the experimental tension diagrams

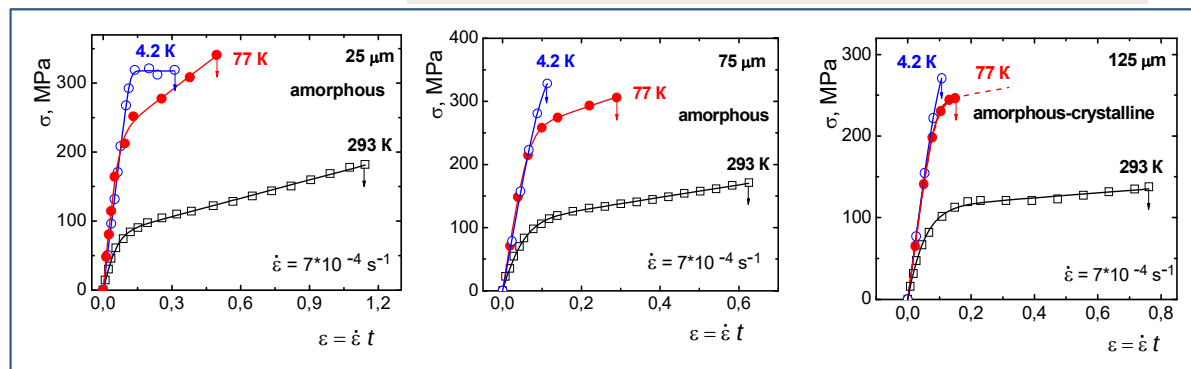


Fig. 2. The effect of moderate and deep cooling on the tensile diagrams of the polyimide films of different thicknesses: (○, ●, □) – experimental values of the deforming stress; (–) – analytical approximation by the formula (2).

A detailed comparison of the tensile diagrams of the polyimide samples with amorphous and amorphous-crystalline molecular structures showed that at $T = 293$ K both structures have clearly pronounced properties of the elastomers, namely, the rubber-like materials with high elasticity and the ability to reversible deformation. The amorphous samples retain these properties up to deep cooling ($T = 4.2$ K), and the amorphous-crystalline ones only to a state of moderate cooling: at $T < 77$ K they acquire the properties of glassy materials with brittle fracture at the initial stage of elastic deformation. The kinetics of highly elastic deformation of polyimide with molecular structures of both types is due to the thermomechanical activation of soliton-like elaston excitations on molecular chains in the amorphous component of the material and is described by a nonlinear rheological equation derived earlier for the molecular model of an amorphous polymer [3, 4]. By comparing the results of experiments and theory, an analytical description of the tension diagrams of polyimide samples with molecular structures of both types was obtained, as well as empirical estimates of their rheological characteristics and microscopic parameters of elaston excitations.

- [1]. V. A. Lototskaya, L. F. Yakovenko, E. N. Aleksenko, V. V. Abraimov, and W. Z. Shao, East Eur. J. Phys. 4, 144 (2020).
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- [3]. V. D. Natsik and H. V. Rusakova, Fiz. Nyzk. Temp. 48, 281 (2022) [LTP 48, 253 (2022)].
- [4]. V. D. Natsik and H. V. Rusakova, Fiz. Nyzk. Temp. 49, 246 (2023) [LTP 49, 228 (2023)].