INVESTIGATION OF THE ENERGY EFFECTS ACCOMPANYING THE ELASTIC DEFORMATION OF UNIAXIALLY ORIENTED CRYSTALLINE POLYMERS


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The energy (thermal and mechanical) effects accompanying the elastic deformation of uni-axially oriented crystalline polymers have been investigated; it has been established that, when these polymers are stretched, heat is released. It is shown that the heat release in uniaxial tension is a consequence of localization of the elastic deformation in the poorly ordered regions of the polymer. The relation between the thermoelasticity of uniaxially oriented crystalline polymers and their supermolecular structure is examined.

According to modern ideas, based on extensive electron-microscope and x-ray diffraction data [1], the supermolecular structure of uniaxially oriented films and fibers has the form shown schematically in Fig. 1. The principal elements of the supermolecular organization of these polymers are fine (of the order of 100 Å thick), densely packed fibrils parallel to the orientation axis. The fibrils possess heterogeneous structure, and this heterogeneity (clearly revealed by small-angle x-ray diffraction as well as by electron microscopy) is associated with the alternation along their length of dense - crystalline - and less dense, poorly ordered regions, usually called amorphous. The direction of the axis of the macromolecules in both the crystalline and the amorphous regions is close to the direction of orientation of the polymer.

In view of the well-known ability of oriented polymers to undergo considerable reversible elongation, the problem of the relation between the elastic deformation of oriented polymers and their structure has recently attracted much attention. The use of small-angle and large-angle x-ray diffraction techniques to investigate the structural changes of elastically deformed, uniaxially oriented fibers and films of polycaprolactam (Kapron), polypropylene, polyethylene, polyethylene terephthalate (Lavsan), and polyvinyl alcohol has revealed that the elastic deformation of oriented crystalline polymers is concentrated in the amorphous regions of the fibrils [2]. The localization of the elastic deformation in the amorphous regions brings into the foreground the problem of investigating the structural characteristics of those regions, since their structure is responsible for the mechanical properties of oriented polymers. The problem of the structure and properties of the amorphous regions of the fibrils and the structural changes that take place during deformation is a rather complex one, since in this case direct x-ray structural methods are considerably less informative than when employed to describe crystallites.

Fig. 1. Diagram of the structure of a uniaxially oriented crystalline polymer, 1) Crystal- lite; 2) amorphous region; 0—0 orientation axis.
A very promising method of investigating the physicomechanical processes in polymers is that based on the investigation of the energy effects accompanying deformation phenomena. Theoretically, this method presupposes a thermodynamic rather than a purely mechanical approach to the deformation process. The classical theory of thermoelasticity leads, for example, to the conclusion that under isothermal conditions uniaxial elastic deformation must be accompanied by the absorption or release of heat [3]

\[ Q = \beta T \sigma, \]

where \( Q \) is the heat absorbed by unit volume of the investigated body; \( \beta \) is the coefficient of linear thermal expansion in the direction of the axis of extension; \( \sigma \) is stress; \( T \) is absolute temperature.

In the case of tension \((\sigma > 0)\) the sign of the right side of the equation is determined by the sign of the quantity \( \beta \). Most solids are known to have a positive coefficient of linear thermal expansion and, accordingly, in uniaxial isothermal tension they absorb heat. At the same time, it is well known [4] that the large reversible isothermal deformation of rubbery materials is accompanied by the release of heat, and the coefficient of linear thermal expansion of stretched rubbers is negative, which is fully consistent with Eq. (1). Rubber and, moreover, gaseous bodies exhibit this kind of behavior, because they possess entropy elasticity, as distinct from the energy elasticity characteristic of most solids.

It has been established [5, 6] that on a certain temperature interval a number of synthetic fibers shorten when heated, which, according to Eq. (1), should lead to the release of heat when the fiber is placed in elastic tension along the axis. Our recent determination [7] of the sign of the thermal effect in a series of elastically deformed uniaxially oriented polymers has shown that they indeed release heat in tension and absorb heat upon returning to the initial undeformed state. At the same time, the stretching of isotropic specimens of the same polymers is accompanied by the absorption of heat. Even formal consideration of this result leads to the qualitative conclusion that the type of elasticity changes on transition to the oriented state. It is quite obvious that the change in the sign of the thermal effect on transition to the uniaxially oriented state is associated with the structural transformations that take place in isotropic specimens when they are oriented. We also noted that changes in the structure of oriented polymers induced by varying the stretch ratio and the mode of heat treatment are quite strongly reflected in the thermal effect. Thus, we may assume that by investigating the energy characteristics of the elastic deformation of oriented polymers we shall be able to evaluate the structural changes that take place during deformation and establish a relation between the elastic deformation of oriented polymers and their structure.

Our object was to make a detailed investigation of the energy effects accompanying the elastic deformation of uniaxially oriented amorphous-crystalline polymers with the object of relating the reversible deformation with their structure.

The preliminary data have already been reported [7]. In our present research we selected for investigation uniaxially oriented films of high-pressure polyethylene (HPPE), low-pressure polyethylene (LPPE), polypropylene (PP), and polycaprolactam (Kapron). The LPPE was a polymer with molecular weight \(1.74 \cdot 10^5\) obtained on soluble catalysts.* From the starting product we molded isotropic films \((T_m = 170^\circ C, p = 100 \text{ atm})\), which were then subjected to uniaxial extension at \(T = 50^\circ C\) and a rate \(v = 0.012 \text{ mm/sec}\) to elongations of \(800\%\). The PP film was molded from granulated Moplen material \((\text{molecular weight } 4.47 \cdot 10^5)\) at \(T = 200^\circ C\) and a pressure of \(100 \text{ atm}\). The orientation parameters were the same as for LPPE film, orientation temperature \(20^\circ C\). The HPPE film was a commercial isotropic film, which was stretched by approximately \(600\%\) at \(20^\circ C\) and a rate of \(0.012 \text{ mm/sec}\). The Kapron film was also commercial and had been uniaxially oriented at the factory. Tests showed that it possessed a certain capacity for irreversible deformation and, accordingly, the specimens used in the experiments were obtained from the starting film by additional orientation to ensure reversible deformation. The elongation at break was measured and the following values were obtained: LPPE \(\epsilon_b = 15-20\%\); PP \(\epsilon_b = 15-20\%\); HPPE \(\epsilon_b = 30-35\%\); Kapron \(\epsilon_b = 30-35\%\). The dimensions of the investigated films were as follows: length 30-60 mm; width 2-4 mm; thickness 50-150 μm.

The microcalorimetric apparatus, the experimental procedure, and the methods of analyzing the most typical primary experimental data have previously been described in [8]. Accordingly, we will

*The material was obtained from the Institute of Chemical Physics, Academy of Sciences of the USSR.