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Abstract

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THE EFFECT OF LOADING ON THE SUPRAMOLECULAR STRUCTURE OF ORIENTED POLYMERS

Elucidating the structure of oriented polymers, data on which are based chiefly on X-ray structural and electron-microscopic studies, is important for understanding such properties of polymers as, for example, deformability and strength. At the same time, the details of the supramolecular structure of polymers (i.e., the mode of aggregation of chain molecules into formations from which the volume of the polymer is built), as well as the relation of this structure to physicomechanical properties, are still not fully known.

In the present work the effect of loading on the supramolecular structure of oriented crystallizing polymers was investigated. The main information on structural changes was obtained by the method of small-angle X-ray scattering.

The object chosen for study was a uniaxially oriented film of capron (polycaprolactam). The highly oriented state of the polymer object was achieved by stretching the film approximately 7-fold. Small-angle X-ray diffraction was measured from a film in the loaded state, which was produced by stretching the film along the orientation axis by amounts from 0 to 25–30% (further stretching caused rupture of the specimens).

Measurement of small-angle scattering was carried out on a slit-type apparatus with an angular divergence of the primary beam of about 5′. The design of the apparatus is described in papers (1, 2). Registration of the scattered radiation was performed with a scintillation counter. The measurements were made with CuKα radiation (wavelength λ 1.54 Å) in vacuum. The specimens were mounted with the orientation axis perpendicular to the slits and to the primary beam. The dependence of the scattering intensity I on the scattering angle φ was measured in a plane passing through the orientation axis of the specimen and the axis of the primary beam.

Fig. 1. X-ray scattering in a polycaprolactam film. Film thickness 70 μ. 1a—unloaded; 2—12% stretching; 3—24% stretching; 4—31% stretching; 1b—unloaded.

Figure 1 gives the results of measuring small-angle scattering in oriented capron

Figure 1. X-ray scattering in a polycaprolactam film. Film thickness 70 μ. 1a —unloaded; 2—12% stretching; 3—24% stretching; 4—31% stretching; 1b—unloaded.

Figure 1: Figure 1. X-ray scattering in a polycaprolactam film. Film thickness 70 μ. 1a—unloaded; 2—12% stretching; 3—24% stretching; 4—31% stretching; 1b —unloaded.

Fig. 2

Figure 2: Fig. 2

specimens in the unloaded state and under load at specimen elongations of 12, 24, and 31%. Stretching was carried out at room temperature. It is seen from the figure that the tensile load causes a systematic shift of the scattering maximum toward smaller angles (65′ for the unloaded state and 58′, 52′, and 48′ for the corresponding—

···stages of stretching) and a considerable increase in the scattering intensity at the maximum. This effect is reversible. After the load is removed, the position of the maximum and the intensity are practically completely restored. The original length of the specimen is also restored. Secondary stretching of the specimen repeats the effect.

Similar results for the effect of loading on small-angle scattering were obtained for the same film stretched at an elevated temperature (+70°), and also for capron fibers and polyethylene films.

Fig. 2

As is known ([3,4]), the presence of meridional small-angle scattering peaks is associated with the existence, along the orientation axis of crystallizing polymers, of so-called "large periods" —alternation of regions with different density. Using the values of the angles φ_m at which intensity maxima are observed, from the familiar relation for one-dimensional diffraction at small angles, $d = \lambda/\varphi_m$, it is possible to calculate the magnitude of the large period d and its change under load in the specimens studied. The period of identity proved to be equal to 82 Å before loading and to 92, 102, and 111 Å at the corresponding degrees of elastic stretching of the film specimens.

Consequently, as oriented capron is stretched, "stretching" of the large periods occurs; moreover, it should be noted that the relative increase in the periods practically coincides with the relative elongation of the specimens. The accuracy of the coincidence is shown in Fig. 2, where the values of the relative changes in the dimensions of the specimen and of the periods are compared with one another. Such coincidence of changes in the macroscopic dimensions of the specimen with changes in the parameters of the supramolecular structure of the polymer prompts a more detailed consideration of the observed phenomenon.

Fig. 3

Figure 3: Fig. 3

According to current ideas, the presence of large periods is associated with the heterogeneity of the structure of the fibrils from which the volume of the oriented polymer is built. Fibrils, having transverse dimensions on the order of tens to hundreds of angstroms, are assumed to consist of alternating crystals and amorphous-like interlayers ([3,4]). A scheme of such a polymer structure is shown in Fig. 3.

Fig. 3. Scheme of the structure of an oriented crystallizing polymer.
1 —crystallite; 2 —amorphous-like interlayer; d —magnitude of the large period.

The question of the mode of packing of polymer chains in intercrystalline interlayers has not yet been definitively resolved, and there are only a number of hypotheses concerning their structure ([3–7]). Taking into account that one of the components of the large period is the crystallites, we undertook an additional X-ray study of the polymer crystallites under loading.

Data on the crystalline phase of the polymer—on the number and sizes of crystallites—were obtained on the basis of measurements of X-ray diffraction in the large-angle region.* Measurement of the intensity and angular sizes of the reflexes of crystalline reflections, carried out both in the equatorial and in the meridional regions (in the latter, the angular size of the reflex is associated with the size of the crystallites along the fibril), showed that the state of the crystalline phase during deformation of the specimen remains practically unchanged —

* Measurements were carried out on a URS-50I diffractometer.

one. In particular, the characteristic that is constant and of greatest interest to us is preserved—the size of the crystallites along the fibril axis, i.e., along the direction of the "axis" of the large periods.

This result makes it possible to ascribe the changes in the magnitude of the period observed under loading to only one of the two components making up the period, namely, to the amorphous interlayer between crystallites.

Upon stretching, the amorphous interlayer is rearranged in such a way that a "separation" of crystallites of constant size is permitted, as a result of which the periods increase. Such a rearrangement of the amorphous phase when the specimen is loaded may lead to a change in the average density of the substance in it. The observed sharp (almost by an order of magnitude) increase in the diffraction intensity (which is greater the more strongly the alternating regions differ from one another in density) apparently indicates that the difference between the densities of the crystalline and amorphous regions increases when the polymer is loaded*. Consequently, if the density of the crystalline phase is regarded as practically unchanged, one may conclude that, as the polymer is stretched,

Fig. 4. Schematic of the large period and the effect of loading on it. a—polymer not loaded, period d_a; b—polymer loaded, period d_b

Figure 4: Fig. 4. Schematic of the large period and the effect of loading on it. a—polymer not loaded, period d_a; b—polymer loaded, period d_b

the density of the amorphous interlayer decreases. This conclusion is consistent with the model of fibril structure proposed in works (4, 7). It is assumed that the fibril consists partly of polymer chains passing from crystallite to crystallite, and partly of folded chains forming crystallites (Fig. 4a). Such a model makes it possible to understand the decrease in the density of the amorphous interlayer when the specimen is stretched (Fig. 4b).

Fig. 4. Schematic of the large period and the effect of loading on it. a—polymer not loaded, period d_a; b—polymer loaded, period d_b.

Thus, on the basis of the results obtained, it appears possible to regard oriented crystallizing polymers as a particular construction of elastic elements—fibrils—in which elasticity is realized by means of the amorphous phase within them. It is evident that the deformability and strength of such a construction will be determined by the relative number of "through" molecules and by their packing.

In our opinion, further investigations by the method of small-angle X-ray scattering of changes in the supramolecular structure of polymers under loading will undoubtedly contribute to clarifying the question of the connection between structural features and the deformation and strength properties of polymeric substances.

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* A quantitative calculation of the change in the density difference requires taking into account the diffraction influence on the magnitude of the intensity maximum of the change in the crystalline fraction in the magnitude of the large period.

Note: Figure translations are in progress. See original paper for figures.