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PHYSICAL CHEMISTRY

Specific Features of Plastic Flow of Biaxially Oriented Flexible-Chain Semicrystalline Polymers

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Plastic deformation of semicrystalline polymers is a focus of numerous studies, and various approaches are applied to describe it at different scale levels. When studying the strain–strength properties, extension beyond the yield point is usually performed. The yield point can manifest itself as a maximum (sharp yield point) on stress–strain (σ–ε) curves [1]. The sharp yield point corresponds to necking of a specimen. In some cases, double yield points [2–4] or self-oscillating neck propagation [5] are observed. The appearance of two maxima on the σ–ε curves has been observed only under certain loading conditions (temperature and strain rate) and is associated with structural rearrangement processes caused by homogeneous and heterogeneous deformation [1, 4]. It is believed that the first yield point is not a true plastic event since the corresponding strain is recoverable after unloading [3].

In this work, we have shown for the first time that formation of a biaxially oriented structure in flexible-chain semicrystalline polymers can be responsible for a two-peak tensile curve associated with the two-neck mechanism of plastic flow. Such a structural state of plastically strained polymers has been generated by equal-channel multiple angular extrusion (ECMAE). In ECMAE, a cylindrical billet is forced through a device consisting of several channels of the same diameter intersecting at specified angles [6]. As the deformation route, we used a route in which paired inclined deforming channels are in perpendicular planes rotating around a vertical axis at 90° intervals and are separated by vertical channels [7]. The choice of this deformation route is caused by that it enables the formation of a structure with crystallites preferably oriented parallel and perpendicular to the extrudate axis [7].

Studies were performed for Quadrant EPP Cestilene HD1000 high-density polyethylene (HDPE), Röchling Engineering Plastics Polystone isotactic polypropylene (PP), Quadrant EPP Ertalyte poly(ethylene terephthalate) (PETP), and Quadrant EPP Ertalon 6 SA polyamide-6 (PA-6). The initial specimens and billets for ECMAE were fabricated by machining of commercially available rods. The extrusion velocity was 0.6×10^{-3} m/s; the extrusion temperature was 383 K (HDPE), 413 K (PP, PETP), and 423 K (PA-6); the accumulated strain was $\varepsilon = 8.5$; the strain intensity was $\Delta\Gamma_1 = 0.83$, which corresponded to the optimal conditions of the process [7, 8].

Tensile tests were performed at room temperature in a universal test machine on dumbbell-shaped specimens (head size: diameter 10 mm, length 10 mm; handle size: diameter 5 mm, length 32 mm; State Standard GOST 11262-80). Specimens were cut along the extrusion direction. The crosshead speed was 10 mm min^{-1}. The extension process was video recorded.

Microhardness (H) was determined with a PMT-3 microhardness meter. The relative error in determination of H was no more than 5%. The microhardness anisotropy ΔH was found by the equation $\Delta H = 1 - \bar{H}^{\perp}/\bar{H}^{\parallel}$, where $\bar{H}^{\perp}$ and $\bar{H}^{\parallel}$ are the average microhardnesses in the cross and longitudinal sections of extrudates, respectively [9].

The change in the linear dimensions of the specimens was determined with a Netzsch DIL 402 PC/4 dilatometer on heating at a rate of 1 K min^{-1}.

Figure 1 shows the σ–ε curves for the pristine and deformed PA-6 and HDPE specimens. For the pristine polymers, the σ–ε curves (curves *1* and *2*) are typical of crystallizable polymers: they consist of a linear segment characterizing elastic deformation, a sharp yield point, and a forced elasticity plateau, and these features correspond to neck formation and propagation and strain-hardening stage. On stretching of the deformed polymers, two-peak σ–ε curves are observed (curves *3* and *4*) associated with the two-neck

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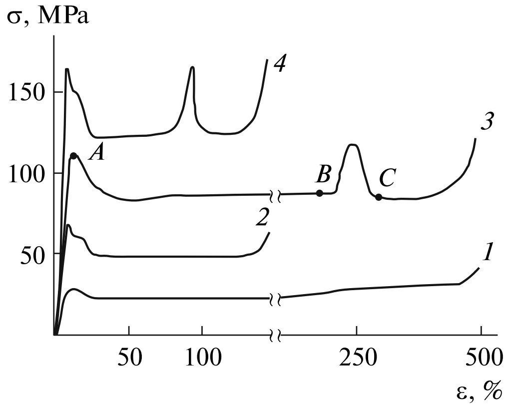

Fig. 1. Stress–strain (σ–ε) curves in tensile tests for (*1*, *3*) HDPE and (*2*, *4*) PA-6. (*1*, *2*) Initial specimens and (*3*, *4*) after ECMAE.

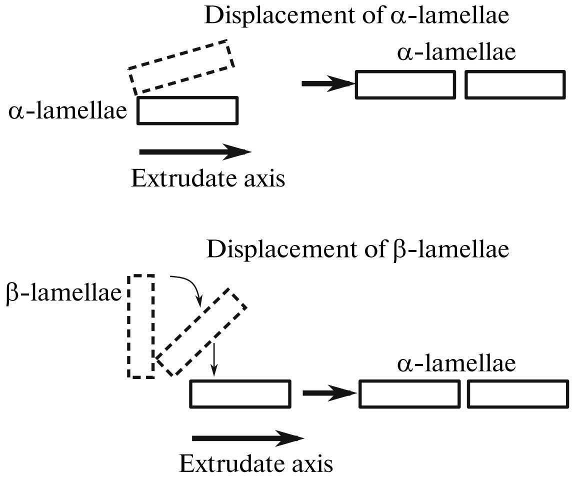

Fig. 2. Scheme of rearrangement of a biaxially oriented structure.

mechanism of plastic flow. The first yield point emerges when the first neck is formed in a specimen. Its movement along the specimen is accompanied by an insignificant increase in σ with an increase in ε, which points to the occurrence of the strain-hardening process. Once the propagation of the first neck has finished, further deformation first leads to the homogeneous elongation of the specimen and then to the formation of the second neck associated with the appearance of the second maximum on the σ–ε curve. Rupture happens after the second neck has propagated along the entire length of the specimen. Analogous σ–ε curves are observed for deformed PP and PETP.

On the basis of the available concepts [1, 10, 11], the structure rearrangement process upon stretching of a biaxially oriented semicrystalline polymer can be described in the following way. At the early stage (before necking), crystalline lamellae slide past each other upon deformation of amorphous interlayers (interlamellar shear, interlamellar separation as tie molecules become stretched or compressed, as well as rotation of bundles of lamellae). At the instant of formation of the first neck, crystalline lamellae oriented in directions close to the extrudate axis (α lamellae) start sliding so that they are aligned along the tensile strength direction (Fig. 2). At the same time, crystallites previously constituting unoriented lamellae are partially oriented. The corresponding stress level still does not suffice to draw into the deformation process lamellae oriented in the perpendicular direction (β lamellae). Further stretching results in the increase of stresses necessary for activation of reorientation of these lamellae, which is accompanied by the appearance of the second neck. As in the case of the initial polymer, stretching leads to the failure of a uniaxially oriented specimen.

The suggestion that two groups of oriented lamellae are successively involved in deformation is supported by the results of measuring microhardness anisotropy and dilatometry data. To obtain this information, tensile tests were interrupted before the first neck appeared, immediately after its propagation was finished, and before the completion of propagation of the second neck (Fig. 1, points *A, B*, and *C* in curve *3*), and corresponding specimens were cut out along the stretching direction. In the first case, the specimens were characterized by low microhardness anisotropy ($\Delta H = 0.04$) and a small change in linear strain ($\Delta l/l_0$) values on heating (Fig. 3, curve *1*), which is typical of a biaxially oriented structure [12, 13]. The specimens corresponding to point *B* (Fig. 1) had significantly higher microhardness anisotropy ($\Delta H = 0.28$), and the linear strain continuously decreased with increasing temperature (Fig. 3, curve *2*), which is evidence of the formation of predominantly uniaxially oriented structure [12]. The highest microhardness anisotropy ($\Delta H = 0.60$) and the largest decrease in linear strain with increasing temperature (Fig. 3, curve *3*) were observed for the specimens cut out from dumbbells after the formation of the second neck, which points to the creation of a high-oriented uniaxial structure.

The observed plastic flow character makes it possible to explain the behavior of flowing deformation and rupture strain of semicrystalline polymers subjected to ECMAE. It has been shown [7, 8] that, as distinct from common schemes of solid-phase extrusion, such as rolling, drawing, and hydrostatic extrusion, which are characterized by a monotonous decrease in plastic parameters with an increase in accumulated strain, in the case of ECMAE, these parameters first decrease and then increase up to the respective values of undeformed specimens. The origin of this difference is in that stretching of polymers subjected to ECMAE is accompanied by successive involvement of oriented crystalline lamellae of two types in plastic flow. The maximal plasticity margin is exhibited by polymers with the largest amount of lamellae uniformly distributed along and perpendicular to the stretching direction.

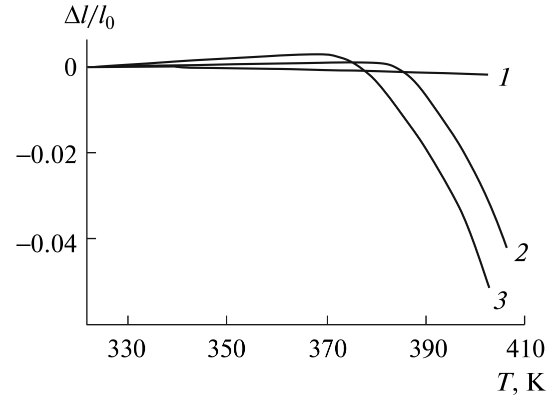

Fig. 3. Temperature dependences of linear strain ($\Delta l/l_0$) of HDPE specimens cut out from extrudates at different stages of tests: (*1*) before appearance of the first neck, (*2*) after completion of the first neck propagation, and (*3*) during propagation of the second neck.

Thus, the revealed two-neck mechanism of plastic flow of biaxially oriented semicrystalline polymers is associated with formation of two groups of crystalline lamellae oriented along the tensile strength direction and perpendicular to it, as well as with their successive involvement in plastic flow.

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