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Strain-induced softening of glassy and crystalline polymers

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Abstract. The data on strain-induced softening of glassy and crystalline polymers accompanied by development of the capability of high reversible strains in the samples are analyzed. It is shown that in the first strain cycle, the test sample demonstrates properties typical of glassy or crystalline state, whereas repeated stretching induces transition into a rubber-like high-elasticity state in which the polymer is capable of high reversible strains. It is noted that this transition represents a physical basis of strain-induced softening of glassy and crystalline polymers. The bibliography includes 114 references.

I. Introduction

Strain-induced softening of solids under the force impact is observed if the strain of the solid is non-brittle. Indeed, if the yield strength of the solid is achieved, its current modulus of elasticity starts to decrease (softening occurs), and a maximum (sharp yield stress) may appear in the stress – strain curve. Softening of this type is characteristic not only of polymers. The strain-induced softening of filled rubbers is a representative example of strain-induced softening of polymers.[1, 2] Due to its practical importance, the softening of rubber was a subject of numerous studies. It was noticed that repeated deformation of filled rubber requires considerably less force than the first deformation. This effect is irreversible, and is attributed to specific features of the interaction of polymer chains with surfaces of the solid filler in the rubber bulk.

This review is devoted to analysis and generalization of available data concerning structural rearrangements in glassy and crystalline polymers under the action of mechanical stress. The major distinctive characteristic of such systems consists in that structural rearrangements result not only in abrupt changes in structural and mechanical behaviour of the starting polymer but also in the ability to exhibit anomalously high reversible strains in the temperature range below the glass transition temperature and/or melting point. It should be noted that at present there is no single point of view on the physical causes of high reversible strains of this kind, and there exist several different explanations to this phenomenon.

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II. Strain-induced softening of polymeric systems

1. Crystallizable rubber

The phenomenon of strain-induced softening has been known for quite a long time. The curves reflecting stretching and shortening (shrinkage) of gutta-percha are shown in Fig. 1.[3]

Gutta-percha is a geometric isomer of natural rubber. In contrast to natural rubber, gutta-percha is crystalline at room temperature.[4] The stress – strain curve for gutta-percha in the first cycle is typical of crystalline polymers (relatively high modulus of elasticity, yield stress, a plateau region). The elongation can be more than 500%. The stretched polymer spontaneously restores its size (see Fig. 1), *i.e.*, pronounced shrinkage typical of highly elastic polymers is observed. The mechanical behaviour of gutta-percha in the second cycle is also characteristic of a polymer in the high-elasticity state (low modulus of elasticity, absence of the yield stress and plateau region, very small residual strain).

This deformation behaviour is caused by melting of the continuous crystal framework in the first strain cycle under the mechanical tension,[5] resulting in that the highly elastic amorphous component of the polymer becomes the continuous phase. Naturally, the mechanical behaviour of gutta-percha during the second stretching is typical of rubber-like polymer.

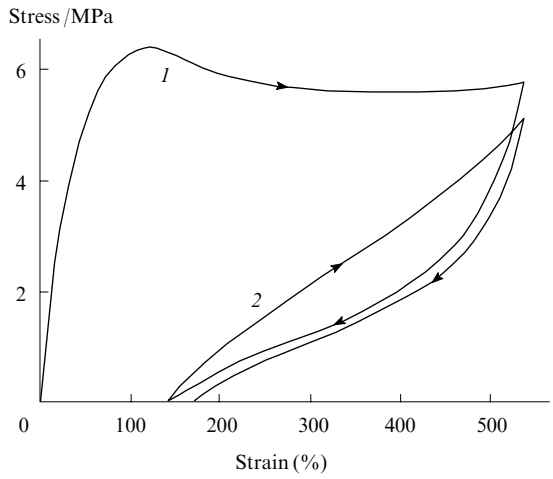


Figure 1. Stress–strain curve of gutta-percha at room temperature.[3]
Stretching: (*1*) primary and (*2*) secondary

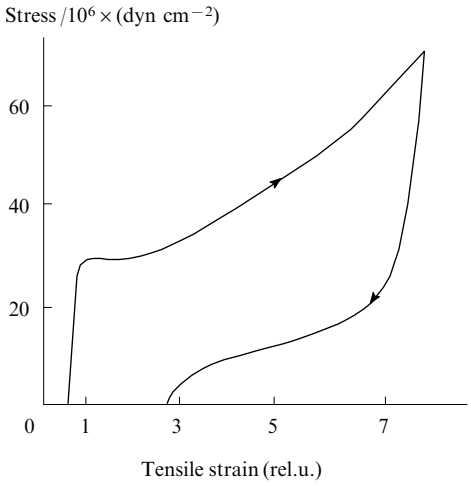


Figure 3. Stress–strain curve of a film of styrene–butadiene–styrene block copolymer.[6]

2. Block copolymers

Block copolymers are multiphase systems built of incompatible chain segments. The incompatibility results in phase separation in the block copolymer and emergence of clear-cut regular structures. There are systems with a continuous rigid phase, which occurs in the glassy state at room temperature, systems with a continuous rubbery phase, and also block copolymers with two continuous phases.[6,7] These features of block copolymers are determined, in particular, by block molecular masses, contents, the affinity to the employed solvent if they are isolated from solutions and by some other factors.[8]

Some insight into the structure of a polystyrene–polybutadiene–polystyrene (SBS) block copolymer can be obtained by staining technique: the rubbery (polybutadiene) phase gives dark streaks, whereas the polystyrene phase gives light ones.[6] The electron micrograph of an SBS film (Fig. 2) clearly indicates that it has a clear-cut lamellar structure formed by uniform-size alternating lamellae of polystyrene and polybutadiene. In this case, the rigid glassy phase of polystyrene is continuous in the bulk of block copolymer.

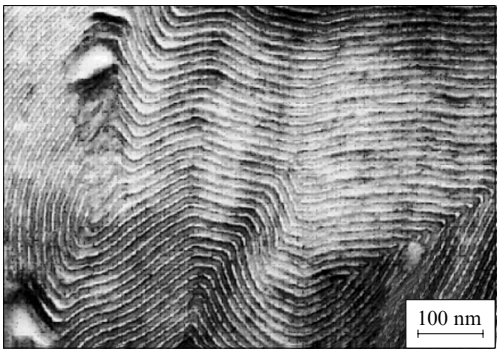


Figure 2. Electron micrograph of as-cast film of the styrene–butadiene–styrene terpolymer.[6]

The stress–strain curve for SBS is shown in Fig. 3. The effect of strain-induced softening is clearly seen here. As in the case of gutta-percha (*cf.* Fig. 1 and Fig. 3), mechanical behaviour typical of glassy polymers (a relatively high modulus of elasticity, yield stress and a plateau region) is exhibited by SBS in the first deformation cycle. However, during the first stretching cycle, some phase is formed, this phase having mechanical characteristics lower than the starting copolymer and being capable of high reversible strains.

Detailed analysis of morphological and mechanical behaviour of SBS showed the following:[6] if the block copolymer consists of continuous alternating layers of glassy and rubbery polymers, the material has high modulus, and the effect of strain-induced softening (the glass–rubber transition) takes place; if the block copolymer consists of glassy domains in the rubber matrix, its mechanical behaviour corresponds to filled rubber. The strain-induced softening of another type is possible in the latter case. The starting stress – strain curve is analogous to the curves of filled rubbers (low modulus of elasticity, absence of yield stress, high reversible strain), whereas the softening effect manifests itself in a shift of the curve to the region of low strains.[1,2] Therefore, strain-induced softening of block copolymers having continuous glassy phase consists in the destruction of this phase in the first cycle of deformation, which results in the rubbery phase becoming continuous, and this rubbery phase determines the reversibility of deformation in the second and subsequent cycles (see Fig. 3).

Thus, the mechanism of strain-induced softening in the above considered systems can be characterized as follows. These systems consist of two phases. In one case, they have continuous crystalline framework with rubbery filler, in the other case, they have continuous glassy framework also filled with a rubbery polymer. In both cases, the first cycle of deformation results in destruction of the rigid framework, and rubbery polymer becomes the continuous phase. It is not surprising that in subsequent cycles of deformation,

this component demonstrates a behaviour typical of a polymer in high-elasticity state (low modulus of elasticity, high reversible strain).

3. Strain-induced softening of glassy polymers

The strain-induced softening is typical not only of two-phase systems, but also of single-phase systems.

Crazing is one of the fundamental types of inelastic plastic deformation of glassy polymers.[9–11] The evolution of this plastic deformation is accompanied by formation and growth of special areas (crazes) containing oriented polymer. A transmission electron microscopy (TEM) image of a single craze in a strained thin film of polystyrene is shown in Fig. 4.

As can be seen, the craze is a certain disintegrity in the polymer. The important feature of the craze structure is that blocks of the starting non-strained material are joined by superfine bundles (fibrils) of oriented polymer, which are spaced apart. The diameter of such fibrils and the distances between them can range from a few to tens of nanometres. The most intensive crazing is observed when glassy polymers are stretched in adsorptionally active media (AAM).[9–11]

Crazing can arise not in all polymers but only in thermoplastic polymers capable of forced elastic deformation. One can say that materials that form a neck upon deformation are capable of deformation by the mechanism of crazing. Rigid-chain polymers (cellulose and its derivatives, aromatic polyamides and polyimides as well as highly cross-linked polymers) cannot be deformed by the mechanism of crazing.

The fact that polymers deformed in AAM according to the crazing mechanism exhibit mechanical properties unusual for the glassy state was discovered quite long ago. The reversibility of deformation of solvent-crazed polymer is a typical example. It is known that amorphous polymers deformed below glass transition temperature exhibit a phenomenon of so-called cold drawing, which manifests itself in the appearance and development of a neck. The neck material is completely stable at the temperature of deformation. To shrink the cold-drawn polymer, it is necessary to heat it up to the glass transition temperature.[12,13]

The fact that high reversible strains are characteristic of glassy polymers deformed in AAM according to the crazing mechanism was demonstrated for the first time by Volynskii *et al.*[14,15] After stretching, release from clamps of the tensile machine and removal of active liquid from the craze bulk, the polymer shrinks by nearly 100%. In other words, the strain-induced softening of a glassy polymer accompanied by occurrence of high reversible strains takes place when the polymer is deformed by crazing mechanism. Glassy polymers are single-phase systems; therefore, the mechanism of their stress-induced softening cannot be explained in such a way as was done for polymeric systems composed of rigid framework (crystalline or glassy) and rubbery filler (see above).

Let us consider the mechanical properties of a solvent-crazed polymers. The first systematic study of mechanical properties of dry (containing no low-molecular-weight liquid) crazes was performed by Kambour and Kopp,[16] who produced isolated crazes by deformation of glassy polycarbonate (PC) in ethanol. Using a special device, the authors measured the change in the distance between the edges of a single craze as a function of the force applied to the sample. The thus obtained stress–strain curves have a characteristic shape (Fig. 5). As can be seen, the yield stress of the craze material is several times lower than the yield stress of the initial non-deformed polymer.

By conducting several consecutive stretching–relaxation cycles, it was established that the starting modulus of elasticity and yield stress decrease with craze widening. The modulus of elasticity is ~ 4 times lower than that of the starting non-deformed polymer. It was also shown[16] that dry crazes in PC deformed by 50%–60% are able to slowly and spontaneously restore their dimensions after unloading. It should be noted that this behaviour is untypical of a glassy polymer which has been oriented in the cold drawing mode. Thus, the mechanical properties of an isolated dry craze totally differ from the properties of the initial polymer.

A similar mechanical behaviour of solvent-crazed polymers was revealed by Volynskii *et al.*[15,17] It was found that the stress–strain curve for polyethylene terephthalate (PET) crazed in AAM has two yield stresses, the first one

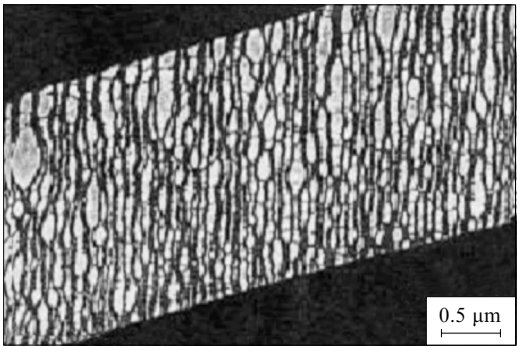


Figure 4. TEM image of a single craze in a strained thin film of polystyrene.[11]
The stretching axis is vertical.

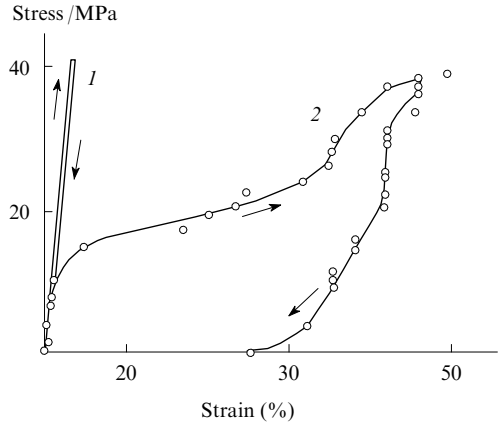


Figure 5. Constant-velocity stress–strain curves of PC (*1*) and a single craze in PC (*2*) up to the stress of 42 MPa.[16]

being significantly lower (~3 times) than the yield stress of the starting glassy polymer. It was also revealed in the same studies that the dimensions of solvent-crazed PET containing no liquid spontaneously decrease after stretching in air. The shrinkage is quite large in this case (up to 60%).

Unusual mechanical behaviour of solvent-crazed PET was demonstrated by Sinevich *et al.*,[18] who made an attempt to elucidate the role of capillary forces in the course of shrinkage during evaporation of the active liquid from porous craze structure. The capillary forces arising during evaportation of the AAM from crazes after polymer stretching can serve as the driving force of the reversible strain. To avoid appearance of capillary forces, the polymer was frozen just after its stretching in AAM, and the active liquid was then removed by freeze-drying. Therefore, the removal of the low-molecular-weight component was not accompanied by formation of concave menisci at the polymer–liquid–air interface, and, hence, no capillary forces promoting the collapse of crazes arose. Nevertheless, it turned out that the shrinkage of the dry solvent-crazed polymer at room temperatue reaches 30% after its release from clamps of a tensile machine. This mechanical behaviour of PET containing no liquid component seems unusual since its glass transition temperature (75 °C) is significantly above room temperature.

In the context of the subject matter under discussion, it is necessary to touch at least briefly upon the morphological and mechanical behaviour of polymeric glasses reinforced with rubber dispersions, a typical representative of which is high-impact polystyrene (HIPS). The methods for production of such materials are well known.[19] It should be noted that the presence of isolated rubber particles incorporated into the continuous glassy matrix is characteristic of the structure of HIPS and other plastics modified with rubbers (Fig. 6 *a*).[20–22] During deformation of such materials,

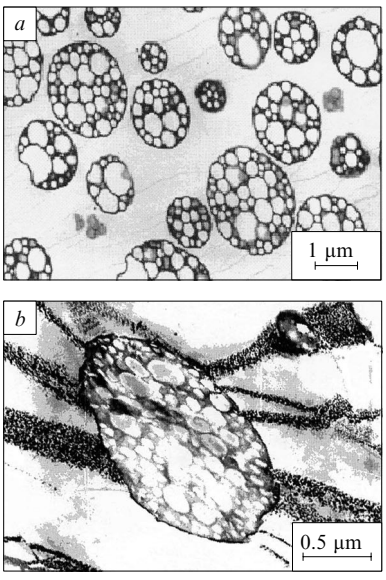


Figure 6. TEM images of HIPS samples before (*a*)[22] and after (*b*) deformation;[23]
(*a*): dark inclusions correspond to rubbery component (polybutadiene) dispersed in continuous glassy matrix (PS).

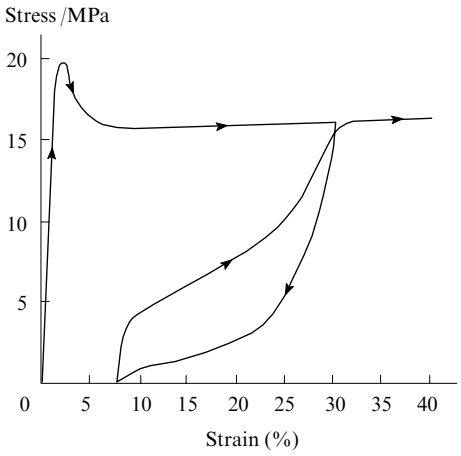


Figure 7. Stress–strain curve of high-impact polystyrene at 21 °C.[21]

crazes arise and grow between particles of the rubber phase in the glassy matrix (Fig. 6 *b*).[23] With formation of crazes, the material acquires properties unusual for glassy state.

The stress–strain curves of HIPS at room temperature are shown in Fig. 7. As can be seen, the mechanical behaviour of the material in the first cycle of deformation is typical of the glassy state (the initial straight-line portion, the yield stress, a plateau region). However the stress relief results in a large shrinkage of the polymer, and its subsequent deformation is indicative of strain-induced softening characteristic of solvent-crazed materials (*cf.* the curves in Figs 5 and 7). Note that softening of HIPS is related not to the existence of the rubber phase, but to the development of crazes since glassy component represents the continuous phase in high-impact plastics.

The material of crazes in polymers in the glassy state is not prone to fast healing of interfacial surfaces at temperatures below the glass transition temperature. Nevertheless, it was noted[16] that storage of a solvent-crazed polymer for a sufficiently long time results in fusion of walls of crazes and disappearance of their porous structure, the polymer becomes monolithic and transparent. This phenomenon was explored in some details taking PS as an example.[24] The authors initiated formation of crazes at different temperatures and measured the time of their appearance and the rates of their growth. After the removal of stress, the polymer was left for relaxation at different temperatures for different periods of time, then the stress was applied again and the initiation time and rate of growth were measured for the same crazes. With increasing relaxation time, the initiation time increased at a given temperature, whereas the rate of repeated growth decreased to zero, while new crazes sometimes appeared in the sample. The process of healing consisted, in particular, in that the craze chosen for observation disappeared during the healing cycle. The temperature–time diagram was constructed on the basis of these results, which makes it possible to determine the time necessary for complete healing at a given temperature. For instance, according to these data, the total healing time at 70 °C (the glass transition temperature for PS is 100 °C) exceeds 10^5 s, this value indicates high molecular mobility in

craze fibrils at temperatures below the glass transition temperature.

The possibility of large-scale molecular motion in crazes at temperatures below the glass transition temperature (T_g) of block PS was confirmed by Berger and Sauer.[25] The molecular mobility in crazed and block samples of PS and brominated PS was determined by measuring thermally induced depolarization currents. It was shown that electrical relaxation is significantly easier for highly crazed samples at temperatures that are almost 100° lower than the glass transition temperature. Low-temperature annealing (below T_g by 10–20°) substantially reduces the low-temperature relaxation, indicating healing of the fine material of crazes (coalescence of phase boundaries) and restoration of the block structure of the polymer. Clearly, this effect is caused by increased molecular mobility in crazes in the temperature region of the glassy state of block PS. The authors [25] explained the facilitation of mobility of molecules in crazes by their proximity to the free surface, although direct experimental investigations of specific features of molecular mobility in thin surface layers in polymers had not been carried out by that time.

In another study,[26] crazes were formed in thin films of PS, their dimensions were determined, and the distances between fibrils and fibril diameters were measured by electron diffraction directly in the video camera of a transmission electron microscope. It was demonstrated that the distance between fibrils increased from 25 to 350 nm over a period of 250 h at room temperature. Simultaneously the fibril diameters increased. These changes were accompanied by coalescence of fibrils, and after 750 h, no individual fibrils could be distinguished.

Atomic force microscopy is used to estimate mechanical characteristics of small (nanometre-sized) areas on the surfaces of polymers.[27–29] Direct measurements of the modulus of elasticity for a polystyrene film, including those for single crazes, were carried out by this method.[30] The modulus of elasticity of the craze material turned out to be very low, 3%–10% of the modulus of elasticity of the surrounding block polymer. In other words, the transformation of the polymer to the craze material is accompanied by significant changes in its physicomechanical characteristics and, particularly, in substantial decrease in its modulus of elasticity, *i.e.*, there is strongly pronounced effect of strain-induced softening.

Thus, numerous experimental studies of structure and properties of crazed polymers privide evidence for a special state of the polymer dispersed in the craze material. There is no doubt that the crazing process in a glassy polymer give rise to a 'phase' whose physicomechanical properties are untypical of the glassy state. This 'phase' has a low modulus of elasticity and is capable of high reversible strains. It is clear that this 'phase' is responsible for the strain-induced softening and the emergence of high reversible strains in the glassy polymer subjected to crazing.

4. The causes of strain-induced softening of glassy polymers during crazing

The mechanical behaviour of crazed polymers described above was so unusual for oriented glassy polymers that a new approach was required to explain its mechanism. Several mechanisms determining the morphological and mechanical behaviour have been suggested. It was suggested from the consideration of experimental data on the recovery of the size of crazes that the driving force of the shrinkage is entropic elasticity and, mainly, the excess of surface free energy owing to the large specific area of the material of crazes.[16] The entropic force was estimated from the kinetic theory of superelasticity. A calculation showed that, with the assumption that the modulus of elasticity of the craze material in PC is equal to its modulus at 160 °C (which is 15° higher than T_g), the strain causing the shrinkage is 3–4 MPa. The obtained value is significantly lower than the yield stress of polycarbonate at room temperature and, hence, such strains cannot result in shrinkage of the polymer. In addition, it was not explained how the entropic mechanism of reversibility of strains can operate at temperatures below T_g.

Therefore, an attempt was undertaken to calculate the shrinkage stress related to the changes in the surface free energy. It was assumed that polymer in crazes is dispersed in the form of long cylindrical threads with radius r and length H, the threads connecting the opposite walls of the craze. The authors believed that upon shrinkage, the threads become shorter and thicker. Essentially, this means a reduction of the interfacial surface area, which takes place in the liquid droplet by the action of surface forces. Obviously, for such a reduction of the surface area of cylindrical fibrils, the external forces (surface forces in this case) have to deform the glassy polymer, *i.e.*, they have to overcome the yield stress. Assuming that the thread volume is constant, the authors showed that the stress acting along the stretching (shrinkage) axis in the polymer is expressed as follows:

$$y = \frac{\gamma}{r}$$

where γ is the surface tension of the polymer. The restoring force calculated by this equation was about 4–9 MPa for polycarbonate.

Therefore, the overall shkinkage stress is 7–14 MPa, and this is also significantly lower than the yield point even for non-oriented polycarbonate at room temperature ($\sim$63 MPa). Therefore, surface forces cannot be the cause of deformation of polymeric fibrils that may result in shrinkage. Nevertheless, according to authors' opinion,[16] the calculated stress may be sufficient to collapse the crazes if one takes into account the following circumstances. First, the recovery rate in this case is much lower than the rate at which the yield point, which depends on the speed of testing, is usually measured. Second, the viscosity of the craze material may decrease during the test due to the large specific free surface area and high degree of dispersion of crazes.

When creating the theory of craze widening based on the phenomenon of meniscus instability, Kramer [31] postulated that the wall of a growing craze is coated with a thin layer of devitrified rubbery material. Note that the Kramer theory satisfactorily describes experimental data.

While considering the physicomechanical behaviour of crazed glassy polymers, one has to answer a principal question: what is the reason of high reversible strains in crazed polymers at temperatures below their T_g? The answer is given by recent studies.[32–38] It has been found and proven that T_g of thin films and surface layers of glassy polymers is sharply decreased. By now, the mechanism of this phenom-

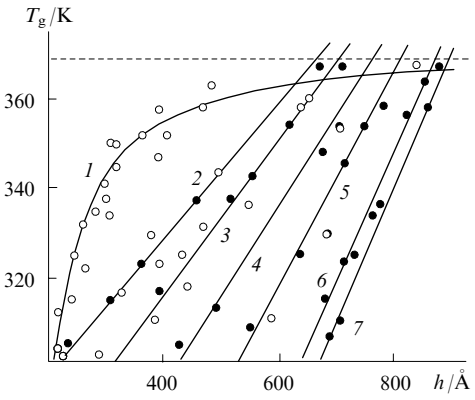


Figure 8. Dependences of glass transition temperatures of free-standing films of PS on their thickness obtained using ellipsometry (hollow circles) or Brillouin light scattering (dark circles).[32]
Molecular masses/$M \times 10^{-3}$: 116–347 (*1*), 541 (*2*), 691 (*3*), 1250 (*4*), 2077 (*5*), 6700 (*6*) and 9000 (*7*). The dashed line indicates the glass transition temperature of bulk PS.

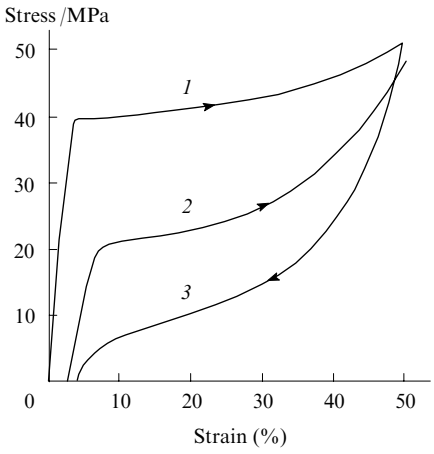


Figure 9. Typical stress–strain curve of lamellar (hard-elastic) PP at room temperature.[53]
The curves corresponds to the first stretching (*1*), second stretching (*2*) and shrinkage (*3*).

enon has not been completely studied and is still the subject of detailed investigations.[39–41]

The generalized dependence of glass transition temperature of PC on the thickness (h) of its films is presented in Fig. 8. As can be seen, the glass transition temperature rapidly decreases with decreasing h, starting from $\sim$80 nm. Depending on the molecular mass of the polymer, the decrease reaches many tens of degrees.

Essentially, crazing is the process of polymer dispersion to aggregates with the size of tens (hundreds) of Ångströms, therefore it is not surprising that the material of crazes has much lower glass transition temperature. Taking this idea into account, it is possible to explain easily and consistently the abnormal physicomechanical properties of crazed polymers which were discussed above: high reversible strain and low-temperature thermally induced shrinkage are related to the entropic elasticity of crazed polymers with depressed glass transition temperature.

Indeed, it was estimated that fibrils 10 nm in diameter contain not more than 10 chains. Therefore all the macromolecules in the craze fibrils are located in the surface layer, and their T_g is substantially lower than T_g of the surrounding block polymer. Macromolecules in fibrils are mutually oriented. The crazing results in the situation when the glassy block polymer is 'stuffed' with special zones (crazes) filled with oriented amorphous polymer with low (lower than the experimental value) glass transition temperature. Naturally, this rubbery material should undergo shrinkage (high reversible strain), and this is exactly what was observed experimentally (see Figs 5 and 7). Thus, the physical reason of the high reversible strains in crazed polymers in the temperature range of glassy state of block polymers is the depression in the glass transition temperature for amorphous polymers in thin films and surface nanometre-sized layers.

5. Strain-induced softening of crystalline polymers

a. Hard-elastic crystalline polymers

In the early 1970s, it was discovered that crystalline polymers like polypropylene (PP),[42] high-density polyethylene (HDPE),[43,44] polyvinylidene fluoride (PVF),[45,46] polyamide-6,6,[47] poly(4-methylpent-1-ene),[48] polyamide-11[49] and some other can exhibit absolutely unexpected properties.

It was shown[50–55] that crystalline polymers with rather high modulus of elasticity can be stretched by tens or even hundreds of percent. The most surprising fact is that such polymers demonstrate high reversible strain. After removal of the stress, they spontaneously and almost completely restore their size at the temperature of the experiment.

The stress–strain curve typical of such polymers is shown in Fig. 9. In the first cycle of deformation, the polymer exhibits a stress–strain curve characteristic of crystalline polymers (the initial linear segment, yield stress, a plateau region). When the stress is removed, the sample spontaneously shrinks practically to the starting size (high reversible strain) and exhibits a mechanical behaviour typical of rubbery polymers (low modulus, monotonically increasing strain) in the subsequent stretching cycles. This is indicative of strain-induced softening, which is analogous to the softening of amorphous polymers discussed above. Later on, the materials which exhibit properties of both rigid crystalline polymers and rubbery materials were termed hard-elastic crystalline polymers because their properties are in contrast with the well-known properties of highly oriented crystalline polymers with high modulus of elasticity (which are durable and little deformable).[56]

Such properties, unusual for oriented crystalline polymers, are determined by a specific structure. The structure can be represented as an ensemble of regularly arranged (parallel to each other) crystalline lamellae, in which the c axes of macromolecules are normal to the plane of the lamellae (Fig. 10).[7] The crystalline lamellae are separated by regularly arranged amorphous interlayers. This type of structure is formed either under the force action on the crystallizing polymer melts[43,57] or upon the thermally induced shrinkage of oriented crystalline polymers.[58] The effect of strain-induced softening (see Fig. 9) occurs if a hard-elastic material is stretched along the normal to the lamella plane.

Several reviews devoted to these materials have been published to date.[52–55] As noted above, an oriented crys-

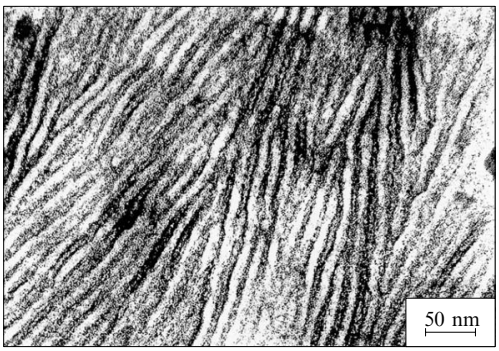


Figure 10. TEM image of a thin film of PP with lamellar structure obtained with the use of RuO_4 staining technique.[7]
Dark strips correspond to amorphous streaks, light strips represent crystalline lamellae.

talline (hard-elastic) polymer is able to be deformed by tens of percent (up to 100%) and shows a high reversible strain behaviour. X-Ray diffraction data[59] and the results obtained by atomic force microscopy[60] have demonstrated that high strains of such materials are accompanied by development of porosity and increase in the specific surface area. The porosity develops in the first stretching cycle in interlamellar zones of the polymer as the lamellae move apart from one another during stretching of the polymer in the direction normal to plane of crystalline lamellae. Such restructuring, at least in the early stages of the deformation, is schematically shown in Fig. 11.[7]

The results obtained in the study of the effect of the stretching temperature on the strain response of a hard-elastic polymer[61] are shown in Fig. 12. Clearly, the stress–strain curve of the starting polymer shifts to higher stresses with decreasing temperature as it could be expected. However the temperature has practically no impact on the effect of strain-induced softening. The deformed hard-elastic PP always demonstrated high reversible strain and rubbery

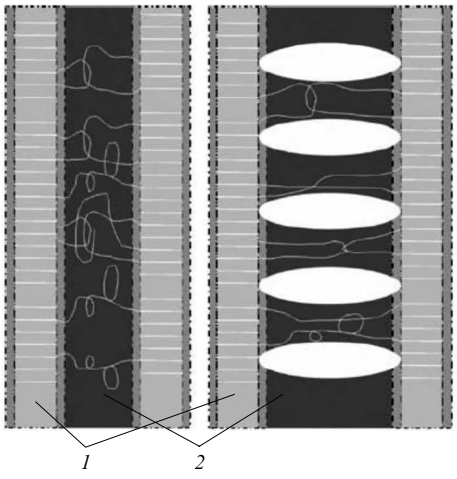


Figure 11. Scheme of formation of fibrillar-porous structure in interlamellar regions during stretching of a hard-elastic polymer.[7]
The crystalline (*1*) and amorphous (*2*) phases are indicated.

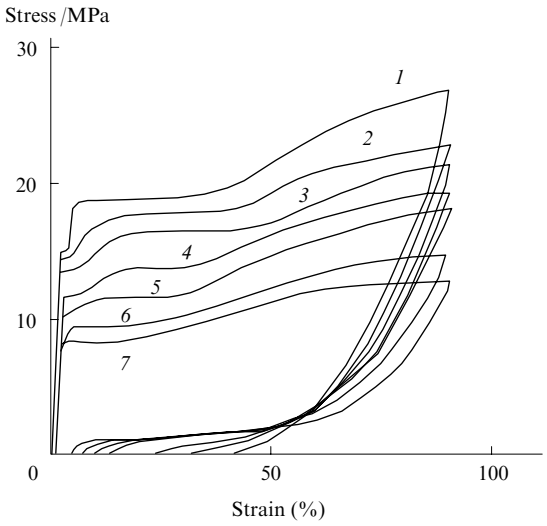


Figure 12. Stress–strain curves of hard-elastic PP obtained at −100 (*1*), −80 (*2*), −60 (*3*), −40 (*4*), −20 (*5*), 0 (*6*) and 20 °C (*7*).[61]

behaviour upon repeated stretching. Moreover, the higher the temperature of deformation of hard-elastic polymer, the larger its shrinkage. This fact indicates that the driving force of the reversibility is the entropy factor, whereas the reversible strain itself is related by some means to conformational reorganization in the polymer chains.

b. Crazing of crystalline polymers

The data considered in the previous Section indicate that the unusual properties of hard-elastic polymers, including their strain-induced softening, are, in particular, due to the development in them of nanometre-sized porosity and highly developed surface during the deformation process. At the same time, similarly to amorphous polymers, crystalline polymers are capable of deformation with the development of porosity according to crazing mechanism. The nanometre-sized porosity in this case is formed in the polymer even if no anisotropic lamellar structures typical of hard-elastic materials are present.

Important results were obtained in the study of the effect of gaseous media on the mechanical response of polymers. It is known that drawing of glassy and crystalline polymers in air results in the formation of a neck, and significant disintegrity of the material does not occur. In accordance with the Eyring–Lazurkin concept, mechanical characteristics of the polymer (yield stress, strength) usually increase on cooling. When the brittle point is reached, the neck is not formed, but destruction occurs at small deformations, as in the case of fragile low-molecular-weight solids.[62, 63]

However, if the experimental temperature approaches the dew point of the gas under which the deformation is carried out (N_2, Ar, O_2, CO_2 and so on), a high ductility of the polymer emerges unexpectedly. In the temperature range close to the dew point of each of the gases, the breaking elongation of the polymer sharply increases, while the yield stress decreases. Therefore, maxima appear in the temperature dependences of breaking elongation and yield stress. At the same time, the deformation of the same

polymers in vacuum or in helium does not result in the emergence of noticeable ductility.

The low-temperature ductility of a crystalline polymer (polypropylene) was revealed for the first time by Kargin and coworkers.[64–66] It was demonstrated that PP can exhibit very large strains (up to hundreds of percent) at low temperatures down to the temperature of liquid nitrogen. Moreover, these cryogenic strains were found to be reversible upon heating of the stretched polymer to room temperature.

The recovery of the original mechanical properties and structure in the process of annealing is typical of polymers deformed at low temperature. The stress–strain curves for PP at low (-50 °C) temperature, which is significantly lower than the glass transition temperature of this polymer, are shown in Fig. 13. As can be seen, a pronounced effect of strain-induced softening is already observed after the first cycle of stretching. The stretching curve shifts to lower stresses and the yield stress disappears. The curve resembles the stress – strain curve typical of rubbery polymers. Annealing of the stretched polymer at relatively low temperature (25 °C) leads to gradual recovery of the mechanical properties (and hence, structure) of the starting polymer, thus indicating high lability of the structure of the deformed polymer and tendence of the polymer to self-healing.

Later on, the low-temperature deformation of PP of this type was studied in detail.[67–69] After Andrianova and Kargin,[66] Olf and Peterlin[67,68] concluded that a polymer deformation leads primarily to an increase in its specific volume and the proportion of free volume. This effect is largely equivalent to the depression in the glass transition temperature of the polymer to a temperature below the experimental value. The specific volume and the proportion of free volume increase especially strongly in the accumulation sites of mechanical stress in the material. Because of large local concentration of stress, the polymer transforms into the rubbery state and becomes able to undergo large strains under stresses that are much lower than the yield stress of the material surrounding the stress acumulation site. In this connection, polymers undergo non-brittle destruction even at very low (up to 4 K)[70] temperatures. This is evidenced by the analysis of the surfaces of fracture of polymers, which indicates that a zone of plastic deformation always precedes the true fracture of destruction.

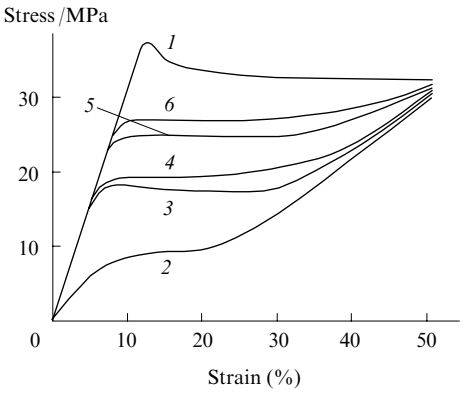


Figure 13. Stress–strain curves of PP at -50 °C.[67]
The curves correspond to (*1*) first stretching, (*2*) second stretching immediately after the first one, and (*3–6*) stretching after annealing of stretched samples at 25 °C for 15 min (*3*), 30 min (*4*), 4 h (*5*), 18 h (*6*).

The presence of a gas having high thermodynamic activity (in the vicinity of the dew point) greatly facilitates the development of plastic deformations and interfaces. It is due to sorption of the gas in the bulk and on the surfaces. The plasticizing effect of the gas in the bulk of the polymer is possible if it can migrate at a high speed into zones of active deformations.

However at cryogenic temperatures, the transport of gases is quite slow. For instance, the diffusion constant for nitrogen in PP at 77 K is 6×10^{-18} cm^2 s^{-1} (Ref. 71), *i.e.*, penetration of the gas into the polymer by 10 nm requires $\sim$300 s. This time is long, and such transport cannot ensure the experimentally observed facilitation of the cryogenic deformations of polymers.

The situation sharply changes if the stress concentrators in the polymer have the increased specific volume and proportion of the free volume in comparison with those of the surrounding material. In this case, due to larger mobility of the polymer chains, the velocity of the diffusion into the loosened zone sharply increases, the gas is adsorbed and dissolved in the local zones. This determines the ability of the material to high deformations.

It should be noted that the development of cryogenic deformations is not uniform in the polymer bulk, but first of all occurs in the stress accumulation sites. The zones of plastically deformed polymer with fibrillar-porous structure (crazes) are developed at these sites. The mechanical and thermomechanical properties of PP deformed by the crazing mechanism in liquid nitrogen at -196 °C, *i.e.*, far below the glass transition temperature of the polymer, were reported.[71] It was shown that crazes retain their size in liquid nitrogen at -196 °C after removal of the stress. However, they immediately collapse upon removal of nitrogen from their space, and this results in practically complete shrinkage. The stress–strain curve for the repeated deformation cycle of these polypropylene samples in liquid nitrogen is analogous to the curve of the 'dry' craze of an amorphous polymer (polycarbonate) obtained earlier.[16]

The initial modulus and the forced elastic limit in the repeated tests of PP after shrinkage are much lower than the corresponding values for the starting sample when it was deformed in liquid nitrogen. It is assumed that the stress causing the collapse of crazes upon removal of liquid nitrogen can be calculated by the formula

$$\sigma = \frac{2\gamma}{r}$$

where r is the radius of voids in the craze. The calculation results gives the value of $\sigma = 6$ MPa, which is significantly lower than the yield stress for PP at this temperature.

Thus, it is impossible to explain the reversibility of a high strain of crazed polymers merely by the action of surface forces, assuming that the craze material has mechanical properties of the initial glassy polymer.

The second important specific feature of crazing consists in that the porosity is localized in crazes that appear and develop in polymers under the influence of mechanical stress. This type of crazing called the classical solvent crazing (CSC) has been studied rather comprehensively,

being the subject of numerous publications, and many of them have been surveyed.[9, 31, 72 – 75]

It was shown in recent years that morphological and mechanical behaviour similar to that of hard-elastic materials may be exhibited by many crystallizable polymers (polyolefins, PET, polyamides, polyvinyl chloride, *etc.*) having no asymmetric crystal structure. This type of crazing called delocalized solvent crazing (DSC)[76 – 78] or intercrystallite solvent crazing[78] is observed upon deformation of crystalline polymers in active liquid media.

Consider the features of these types of crazing and conditions of their implementation. It is known that CSC has at least three well pronounced stages, those are initiation of crazes, their growth in the direction normal to the axis of the applied stress and craze widening (Fig. 14). The first stage is related to surface defects characteristic of all solids. The surface defects differ in the degree of risk of the development of zones of plastically deformed polymer (crazes).[79] That is why the number of crazes upon CSC can easily be controlled by changing the applied stress, the activity of the liquid medium or the method of mechanical surface treatment of samples.[80, 81]

The second stage, the craze growth, proceeds by spreading of the generated crazes in the direction normal to the axis of the applied stress until crossing the entire section of the polymer. And at last, the third stage, craze widening, is accompanied by moving apart of the walls of the craze in the direction of the applied stress. Obviously, the entire transition of the polymer into the oriented state occurs at this stage as a result of consumption of the starting non-oriented material in the course of its transformation into the highly dispersed state with formation of fibrils. Note that the proportion of the fibril material increases continuously during craze widening. This development of fibrillar-porous structure of crazes is called surface drawing of fibrils,[31] since the fibril diameter remains constant owing to continuous drawing out of the polymer from the craze walls.

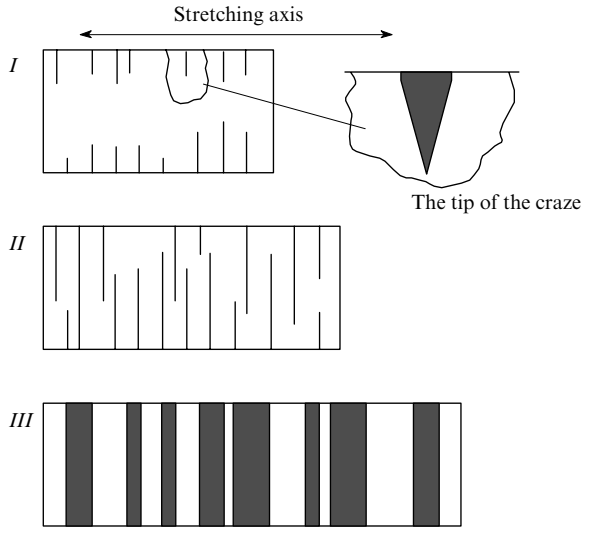


Figure 14. Schematic of the key stages of classical solvent crazing: craze origination (*I*), growth (*II*) and widening (*III*).[79]

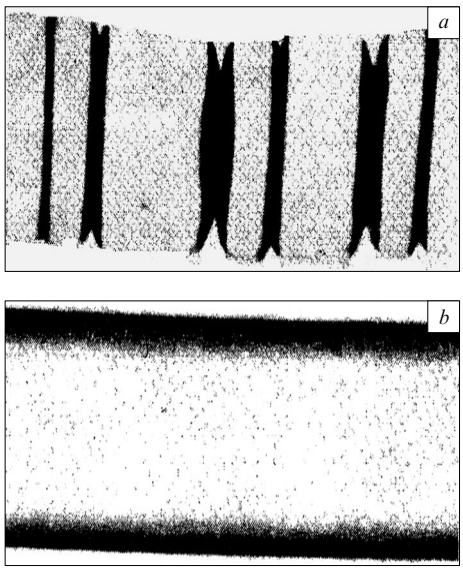


Figure 15. Micrographs of sections of PA-6 films subjected to the classical solvent crazing (*a*) and delocalized solvent crazing (*b*).[81]

The delocalized solvent crazing occurs by the simultaneous development of porosity in all amorphous streaks of crystalline polymer.[81, 82] Micrographs of sections of samples of a crystalline polymer (polyamide PA-6) deformed according to the CSC (*a*) and DSC (*b*) mechanisms are shown in Fig. 15. A dye was added to AAM in both cases, it efficiently marks the details of porosity development. As can be seen, the porosity develops in discrete crazes in the first case, whereas a continuous diffusion area is formed in the second case. The porosity development in polymers subjected to DSC is morphologically similar to that occurring during crazing in hard-elastic materials.

A necessary condition for implementation of DSC is the maximum structural heterogeneity of the polymer at the micro level. Microheterogeneity is typical of all crystalline polymers, which are two-phase systems composed of small crystallites ($\sim$100 Å) uniformly distributed in an amorphous matrix. Substantial difference in characteristics of the amorphous and crystalline phases is required for simultaneous deformation of all amorphous layers in the polymer (as it takes place in DSC) during its strain. Such a difference can be achieved if the amorphous component of the polymer is in the high-elasticity state. Evidently, at such deformation, there is only the stage of simultaneous widening of these layers throughout the whole bulk, and there are no stages of appearance and cross growth, which are typical of the classical solvent crazing. Since the amorphous component of a crystalline polymer is delocalized over the polymer bulk, the development of porosity is also delocalized throughout the whole strained polymer.

The difference in the mechanical behaviour of the amorphous layer and the crystalline phase can be varied by varying the plasticizer concentration in the amorphous zones or temperature and duration of annealing in the

case of PP. Thus, a gradual transition from one type of crazing to the other *via* a set of intermediate states is possible.[82]

The morphology of polymers subjected to DSC was unclear until recently and was considered based on a series of assumptions about the structure of the polymer deformed according to the DSC mechanism; the assumptions were derived from the data of powder diffraction and pressure-driven liquid permeability studies.[80, 82–85] According to these data, deformation of crystalline polymers in AAM occurs predominantly in amorphous areas between lamellae and is accompanied by transition of the polymer into the fibrillized state and formation of voids between fibrils.

Although this type of crazing was studied in detail,[80, 82–85] there were no direct data concerning the morphology of formed porosity. This is primarily due to the fact that removal of AAM from pores leads to the complete collapse (healing) of the porous structure. The results of scanning electron microscopy (SEM) studies of the structure of HDPE subjected to DSC are shown in Fig. 16 *a*. Extensive layers of oriented polymer are seen in the micrographs; however, separate structural units cannot be distinguished. One cannot even say with certainty that the material is porous. Thus, TEM studies of HDPE deformed in AAM and dried under isothermal conditions do not give information about the fine nanometre-sized porous structure or possibility to develop a structural model of a polymer deformed according to the DSC mechanism.

The native structure of strained HDPE in a liquid medium was established with the use of atomic force microscopy (AFM).[86] Using this method, one can explore objects directly in the liquid medium, thus preserving their structure. In the AFM image of HDPE deformed according to the DSC mechanism (see Fig. 16 *b*), the native structure and, in particular, lamellae, which are oriented mainly perpendicular to the strain axis, are clearly seen. The thickness of lamellae determined from cross-section profiles is ~50 nm. Fibrils oriented along the strain axis are located among the lamellae. The fibril length, or the distance between the neighbouring lamellae, is in the range of 50–150 nm. The voids between fibrils are also clearly seen in the AFM image.

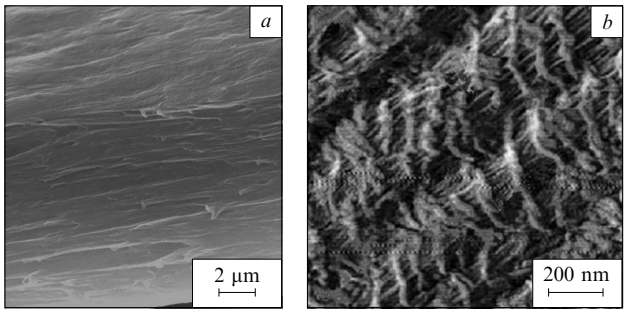


Figure 16. SEM image of a HDPE sample deformed in AAM and dried with fixed dimensions (*a*) and AFM image obtained directly in AAM for the same sample (*b*).[86]

As follows from the presented data, the structure of HDPE deformed by the DSC mechanism has certain resemblance to the structure of hard-elastic materials discussed above. So, crystalline polymers with lamellar structure can be deformed analogously to hard-elastic materials, exhibiting pronounced effect of strain-induced softening (see Fig. 9). The deformation of crystalline polymers according to the mechanisms of both classical and delocalized solvent crazing resembles the corresponding deformations of hard-elastic materials. All the deformations have the same common feature, *viz*., their development is accompanied by appearance and development of nanometre-sized porosity.

Therefore, it is not surprising that the mechanical behaviour of crystalline polymers strained in AAM has strong resemblance to the mechanical behaviour of hard-elastic polymers (see above). The stress–strain curves of isotactic PP deformed according to the DSC mechanism[84] are shown in Fig. 17 *a*, while analogous curves for HDPE are given in Fig. 17 *b*.[85]

All the features characteristic of strain-induced softening are apparent in both cases, *viz*., the initial curve demonstrates a linear part, yield stress and plateau region. High reversible strain is observed upon unloading, whereas

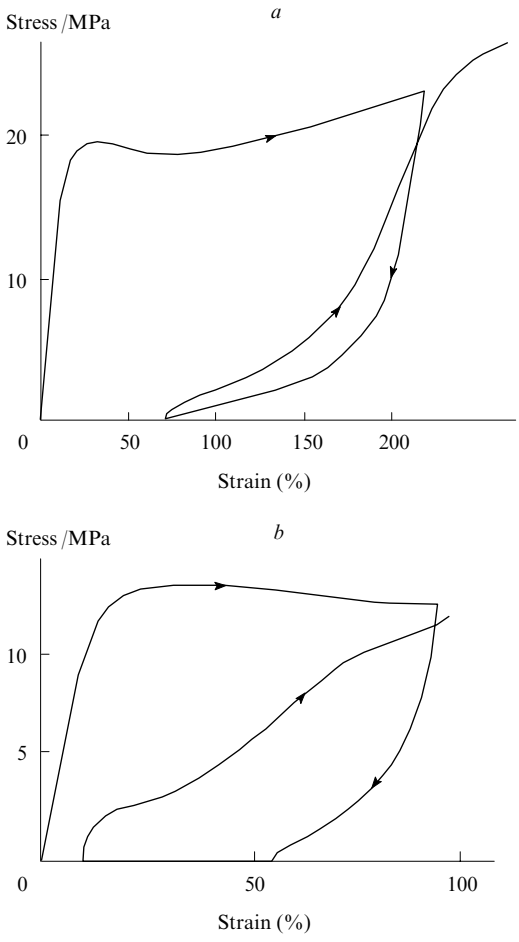


Figure 17. Stress–strain curves for stretching and shrinkage and repeated stretching of PP (*a*)[84] and HDPE (*b*) in heptane.[85]

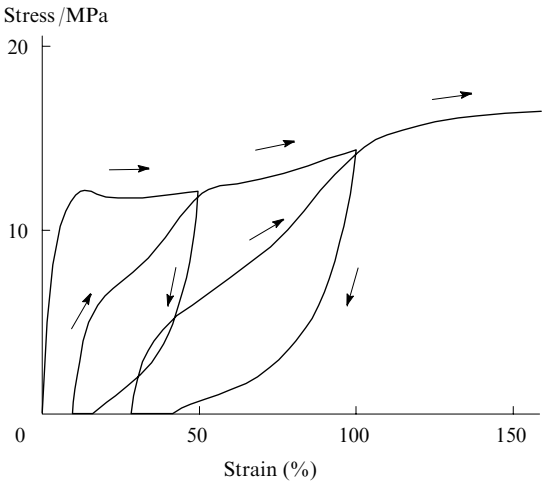


Figure 18. Stress–strain curves for stretching and shrinkage and repeated stretching in air of PP, which was preliminarily stretched in AAM (supercritical CO2) according to the delocalized solvent crazing mechanism by 100% and completely relaxed upon removal of AAM from its porous structure.[87]

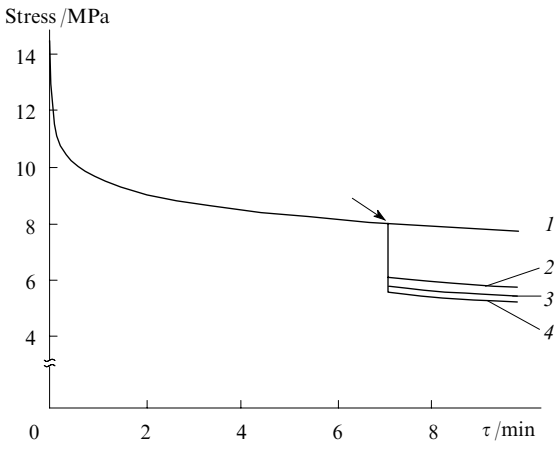


Figure 19. Time dependences of stress in hard-elastic PP stretched by 50%.[92]
At the point marked with arrow, the sample was brought in contact with ethanol (*2*), butanone (*3*) or hexane (*4*); curve (*1*) corresponds to relaxation of the polymer in air.

repeated application of stress to the sample results in its mechanical behaviour typical of rubbery polymers.

Moreover, if the polymer subjected to delocalized solvent crazing is released from the clamps of a tensile machine and removed from the liquid medium (the liquid should completely evaporate from pores of the polymer), the subsequent stretching of this sample in air exhibits a pronounced strain-induced softening. effect The stress–strain curves for PP that was prestreched by 100% in AAM by the DSC mechanism, then completely shrinked upon removal of AAM from its porous structure and then stretched again in air are shown in Fig. 18. Supercritical carbon dioxide was used as AAM;[87] it is a good crazing agent, which causes the same structural rearrangements in crystalline polymers (PP, HDPE) as other liquid media (hydrocarbons) usually used for DSC.

After removal of the liquid from the porous structure of the polymer subjected to DSC, its further mechanical behaviour does not change, the effect of strain-induced softening manifests itself rather distinctly (*cf*. Figs 17 and 18).

Another important feature of hard-elastic and crazed polymers consists in spontaneous healing of nanoporous structure formed in the first stress–strain cycle (see below). Note that after shrinkage in the first stress–strain cycle, hard-elastic and solvent-crazed polymers gradually restore their initial structure. This process is spontaneous at temperatures significantly lower than the corresponding melting (crystallization) point.[88] The recovery accelerates sharply with temperature rise.[89] Direct microscopic observations [54] showed that the recovery of the initial structure of hard-elastic polymers is accompanied by not only closing of craze walls but also complete healing of nanoporous structure. The process of healing of the highly dispersed structure of both hard-elastic and solvent-crazed polymers is identical to this process for glassy polymers considered above.[16, 24, 90]

It should be noted that highly dispersed fibrillized material in the craze bulk has a highly developed surface; therefore, the contribution of surface forces to the unusual morphological and mechanical behaviour of hard-elastic and solvent-crazed polymers should be taken into account.[91] The effect of surface forces manifests itself in experiment, for example, in substantial change in the mechanical behaviour of loaded samples of these materials when they are brought in contact with active wetting liquid,[92] and in particular, in a significant decrease in stress, which depends on the type of liquid (Fig. 19). This change in the stress is reversible, the initial stress is recovered when the polymer is dried or the liquid medium is replaced.[93]

Brawn and Kramer [94] studied the kinetics of growth of stress that develops in PS containing crazes upon transfer of samples from one liquid medium to another and upon drying. The dimensions of the samples in these experiments were kept constant. For all of the used liquid media that cause no noticeable swelling of polystyrene (water–methanol mixtures), the stress was found to increase upon drying of the sample and to decrease upon wetting. The changes in the stress upon replacement of the surrounding liquid and drying are reversible and determined by the nature of the liquid, being independent of the order in which the sample is transferred from one liquid to another. Using estimates of the surface energy at the polymer/medium interface from the values of contact angles, it was concluded that the changes in the stress are predominantly related to the changes in the surface energy of the highly dispersed craze material. The value of the decrease in the stress in a medium ($\Delta\sigma$) corresponds to the equation

$$\Delta\sigma = \frac{2\Delta\gamma V_f}{D}$$

where $\Delta\gamma$ is the change in the polymer surface energy upon polymer transfer from one liquid medium to another, V_f is

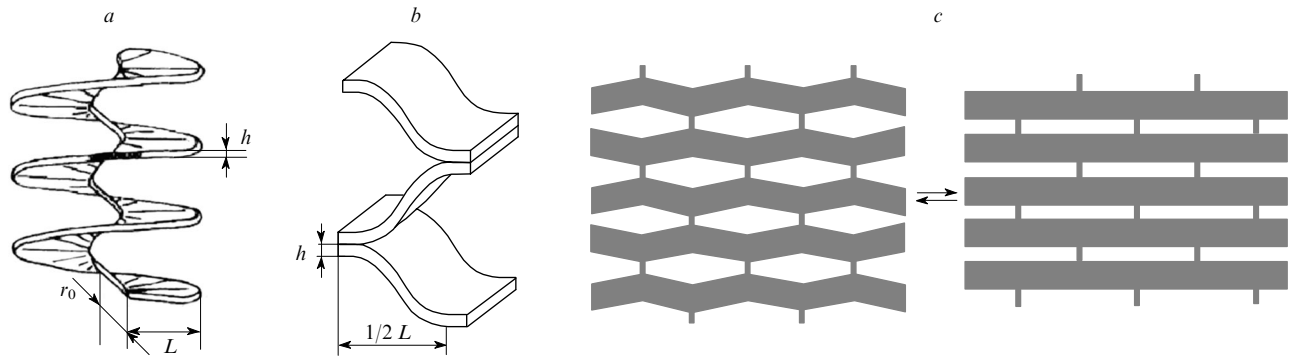


Figure 20. Schematic representation of structural models of hard-elastic materials: wire spring model (*a*), leaf spring model (*b*),[53] general scheme of reversibility of energy spring (*c*).[55]

the volume fraction of fibrils in crazes, D is the fibril diameter.

A proposed [94] method for estimation of the stress developing in fibrils under the influence of surface forces made it possible to estimate the contribution of this factor to the total stress, which is responsible for high reversible strain in hard-elastic polymers. As it has been shown,[95] this contribution does not exceed 40% of the necessary restoring force and, hence, it cannot be the only factor ensuring the high reversible strain.

Thus, the strain-induced softening, which gives rise to high reversible strains, is typical of deformable crystalline polymers. An important feature of such softening of crystalline (and glassy) polymers is the formation of highly dispersed nanoporous structure, which is, apparently, responsible for their very unusual mechanical behaviour.

The experimental data considered above demonstrate some features of morphological and mechanical behaviour of hard-elastic and crazed crystalline polymers, which do not fit into the conventional views about their structure and properties. One of the major tasks to be solved during the study of these features consists in getting explanation of the nature of reversibility of high strains of crystalline polymers in the temperature range below their melting points.

There are two types of reversible (elastic) strains of solids:

— strain which is determined by intermolecular interaction forces that operate at rather short distances, the reversible deformation due to these forces does not exceed 1% – 3%; this type of deformation develops almost instantly, and equally instantly the elastic solid takes its initial dimensions;[96]

— high reversible strain of a polymer being in high-elasticity state; this strain can reach hundreds and even thousands of percent and occurs due to transition of stretched chain molecules to the equilibrium folded conformations under the action of thermal motion (so-called entropic elasticity).[97]

The major difficulty is the need to interpret coexistence of properties inherent in crystalline polymers (high modulus, existence of yield stress and plateau region) and the properties typical of rubbery polymers (high reversible strain, low modulus, absence of yield stress) in the same material upon repeated strain. In other words, it is necessary to develop an adequate mechanism of strain-induced softening of crystalline polymers.

The authors of early studies [53, 55] devoted to elucidation of the nature of the reversibility of high strains tried to explain this phenomenon on the basis of some spring structural models since it was thought that entropic elasticity cannot appear in crystalline polymers. To account for hard-elastic behaviour of lamellar crystalline polymers, several models based on the assumption of energy character of reversibility of their deformations were suggested.[55] The typical examples of such models are shown in Fig. 20.

In all of these models considering the energy reversibility of the strains of hard-elastic polymers, the principal element of the structure is represented by a continuous rigid crystalline framework. It is natural as this deformation is reversible only in this case. Since the framework has points where the crystalline lamellae are linked, the stretching of such a model leads to formation of porosity due to their bending and shear (see Fig. 20).

However, these energy-based models of strain reversibility cannot explain, first, the effect of strain-induced softening of materials and, second, the process of healing of the deformed rigid-elastic materials, as well as a pronounced influence of temperature on these processes (see Fig. 12).

Moreover, it was demonstrated [54] that a strained hard-elastic polymer has no single crystalline framework (Fig. 21). The stretched hard-elastic polymer contains separated crystallites interconnected by fibrillar aggregates of macromolecules. It was also shown in the same study that upon relaxation of stretched hard-elastic polymer, the crystallites approach one another, and the fibrillar aggregates of macromolecules become indistinguishable.

Therefore, a new model of reversibility of hard-elastic materials was suggested;[54] this model combines both energy and entropy contributions. Nevertheless, it remained unclear how the entropic component can be realized in the framework of this model at temperatures below not only the melting point but also the glass transition temperature of its amorphous constituent.[98]

Thus, models of high strain reversibility in hard-elastic polymers upon deformation of their crystalline framework that are based on energy considerations alone are unworkable. To explain the high reversible strains in the hard-

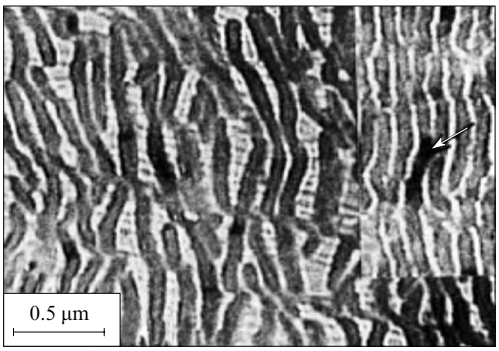


Figure 21. Electron micrograph of a thin film of hard-elastic HDPE stretched by 100% (the stretching axis is horizontal).[54]

elastic polymers, it is necessary to reveal the role and significance of the fibrillar aggregates of macromolecules, which interconnect separate crystalline lamellae to a single structure. This requires understanding of the nature of the fibrils and, first of all, of the phase state of the aggregates of oriented macromolecules.

The general picture of deformation of hard-elastic polymers and, apparently, also of polymers deformed by the delocalized solvent crazing was represented in the following way.[99] Predominantly amorphous streaks are stretched at the initial stages of deformation of a polymer with the lamellar structure (Fig. 22 *a*,*b*). It is evidenced, in particular, by linear relationship between the large spacing (the distance between neighbouring crystalline lamellae) and tensile strain of the polymer.[60,61] At quite high tensile strains (Fig. 22 *c*), cavitation is created in amorphous areas due to shortage of material necessary to compensate the Poisson contraction of deformed amorphous areas, and fibrillar aggregates of oriented macromolecules arise (this stage of deformation of a hard-elastic polymer is shown in Fig. 11).

According to this model,[99] the material of fibrils is broken out from crystallites, it is exactly what was postulated in earlier studies (see Ref. 92). However, earlier,[99] it was assumed that crystallization of oriented macromolecules in fibrils already occurs at early stages of deformation (Fig. 23 *a*). Afterwards, this orientational crystallization accompanied by skews and shears of starting crystalline lamellae actually results in the structure which is characteristic of a typical deformed crystalline polymer and includes the neck formation (Fig. 23 *b*,*c*).[56] In other words, the strained hard-elastic polymer is analogous to the crystalline cold-drawn polymer, whose structure is an aggregate of parallel packed crystalline fibrils with a clear-cut large spacing.

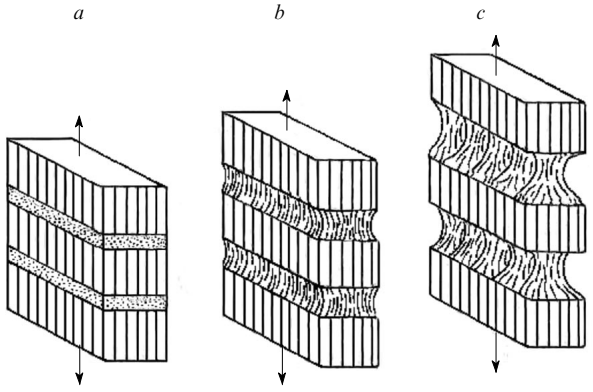


Figure 22. Schematic representation of structural reorganizations at initial stretching stages of a hard-elastic polymer.[101]
See the text for explanations of stages (*a* – *c*).

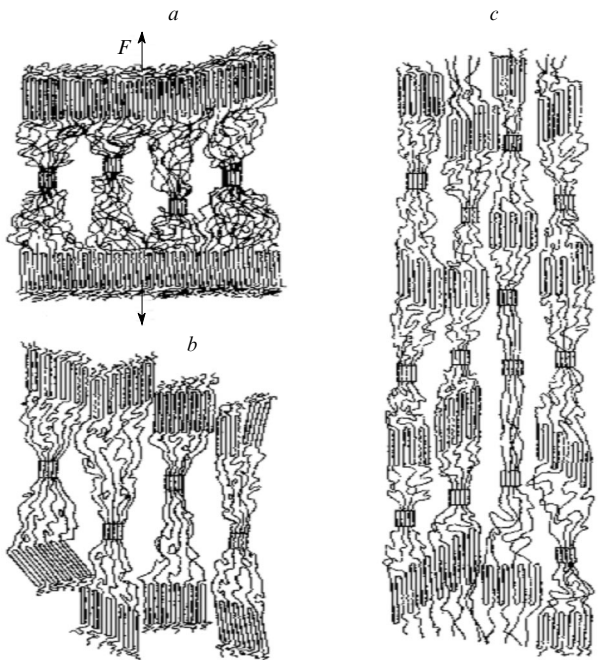


Figure 23. Schematic representation of structural reorganizations at different stages of stretching of a hard-elastic polymer.[99]
See the text for explanations of stages (*a* – *c*).

However, this model explains neither high reversible strains of the stretched hard-elastic and solvent-crazed crystalline polymers nor spontaneous healing of their porous structure, which is accompanied by restoring of the initial geometric dimensions. A necessary prerequisite for the implementation of both of these processes is high mobility of the polymer molecules, which is strongly restricted if the polymer is confined in the crystalline lattice.

At present, there is no doubt that physical properties of macromolecules in ultrathin films with a thickness comparable with the effective size of molecular coil can differ from their properties in the bulk since the contribution of the interphase component to the total free energy of the system increases.[100] Under the conditions of confined volume, the crystallization velocity and, what is especially important, the degree of crystallinity of the polymer decrease with decreasing thickness of the layer.[101 – 106] For example, it was shown [107] that the velocity of crystallization of polyethylene oxide in thin layers (13 nm – 2 μm) can decrease 40-fold in comparison with the velocity of crystallization in the bulk, starting from the

thickness of 150 nm. Simultaneously the morphology of crystals is changed.

The above-mentioned studies considered crystallization of polymers in thin films, while we surmise polymer crystallization in fibrils, which are one-dimensional structures. As noted above, such structures contain a few tens of oriented macromolecules in their cross-section. At the same time, the crystalline phase is the phase with long-range order of molecules that cannot be set up in such restricted volume. Naturally, the crystallization process is extremely difficult (if possible at all) within the volume of fibrils formed in the first stretching cycle in hard-elastic and solvent-crazed polymers. The analysis of the presented data leads to the conclusion that the fibrillar aggregates of macromolecules, which arise upon stretching of hard-elastic materials and solvent crazing of glassy and crystalline polymers, are in the amorphous state.

The dependences of specific surface area of films of hard-elastic PP and diameters of growing fibrillar aggregates of macromolecules on tensile strain are given in Fig. 24. As can be seen, the specific surface area of this material increases and reaches 100 $m^2\ g^{-1}$, this indicates the intensive development of internal interfacial areas. The porosity of the deformed polymer also increases, the pore size determined by mercury porosimetry is 0.2–0.015 μm.[51] However, the fibril diameter remains unchanged. This means that so-called surface drawing of fibrils takes place as it does in many other cases of crazing.[31] In other words, the fibrillar aggregates interconnecting neighbouring crystallites grow by consuming the material of these crystallites.[54, 109]

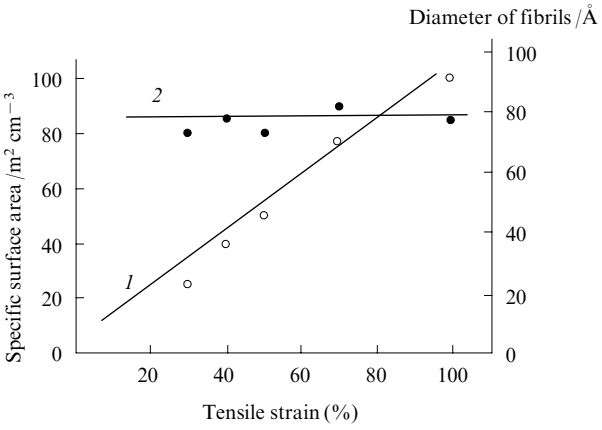


Figure 24. Specific surface area of hard-elastic PP (*1*) and the diameter of fibrils (*2*) *vs.* tensile strain.[108]

Here we will not analyze the processes of origination and growth of fibrils in the intercrystallite areas of lamellar crystalline polymers since these processes have already been discussed exhaustively.[109] It is more important here to trace the fate of these fibrils in the reverse process, *viz.*, in the course of shrinkage, which takes place in hard-elastic materials and is the initial cause of their strain-induced softening.

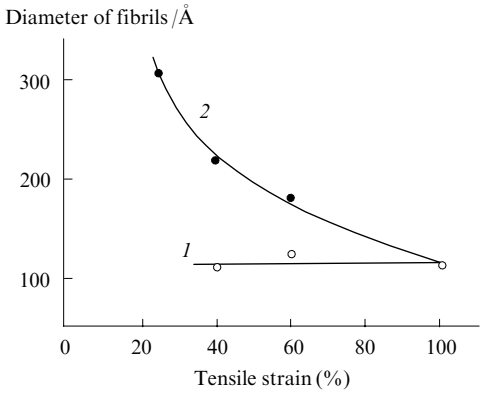


Figure 25. Diameters of fibrils which are formed during stretching of hard-elastic PP (*1*) and during subsequent shrinkage (*2*) *vs.* tesnsile strain.[108]

Thus, the fibrillar-porous structure in hard-elastic polymers is formed by surface drawing of fibrils with retention of their diameters. However, the question of what happens to the fibrils during shrinkage is topical. The dependences of the diameter of fibrils on relative elongation in the course of stretching of hard-elastic PP and during its relaxation are shown in Fig. 25. The diameter of fibrils strongly increases upon shrinkage, it completely corresponds to the behaviour of a rubbery polymer during reversible deformation. The specific surface area of a hard-elastic polymer decreases with increasing diameter of fibrils.[109] Since the volume of the rubber does not change upon deformation, the shrinkage of the oriented rubber (the reduction in its linear dimensions) should be accompanied by the increase in its cross-section. The available data clearly evidence that the fibrillized highly dispersed material exists in an amorphous and devitrified state characteristic of hard-elastic polymers.

It would seem that this result is in variance with the data of Sprague,[53] who found a negative elastic force coefficient upon heating of polyoxymethylene (Celcon) hard-elastic polymer. However, this polymer was obtained by annealing of a deformed hard-elastic product under special conditions. During such annealing, fibrillar aggregates which are formed upon stretching of a lamellar polymer become much larger, interfibrillar distances increase, and, naturally, an intensive crystallization of the polymer proceeds in large aggregates of macromolecules.[101, 110] Such a material is fully stable and suitable for its use as a separation membrane (Fig. 26).[111]

The entirely crystalline product has to exhibit a negative equilibrium force coefficient. Samples of PP subjected to crazing in AAM were studied.[110] The samples were stretched, their dimensions were measured, then the solvent was removed and the samples were subjected to annealing. If the samples were annealed in the free state, they demonstrated substantial shrinkage depending on the annealing temperature. Arising stresses were measured under the conditions of isothermal heating. The typical results of this study are shown in Fig. 27.

The increasing stress during annealing clearly indicates the filling of crazes in PP with an amorphous rubbery material. The analogous type of dependence of the force on temperature was previously observed in isothermal

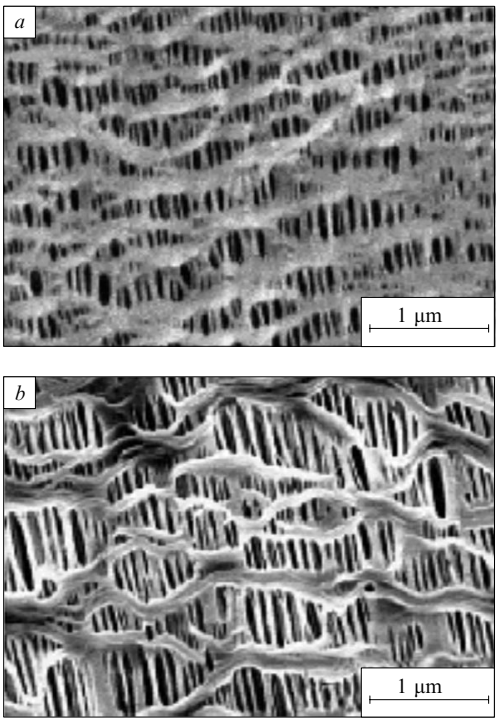


Figure 26. SEM images of commercially available membranes based on hard-elastic PP (*a*) and HDPE (*b*).[111]

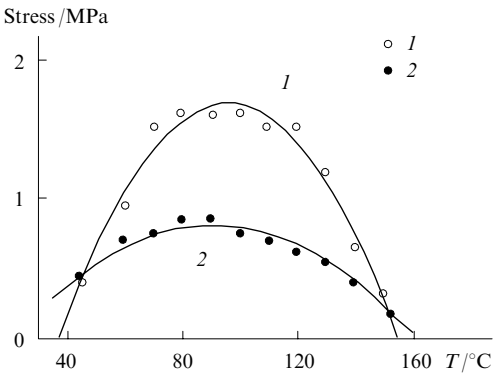


Figure 27. Curves of isothermal annealing of samples of PP strained in AAM according to mechanisms of delocalized (*1*) and classical (*2*) solvent crazing. Preliminary strain amounts to 100%.[110]

heating of low density polyethylene drawn in air to form a neck.[112]

The healing of crazes during the ageing process at room temperature (Fig. 28) and especially upon annealing also attests to the amorphous rubbery state of the material that fills the crazes. Indeed, the mechanism of healing of interfacial surfaces consists in mutual diffusion of chains or (and) their fragments through the interfaces. This process is possible only if macromolecules have large-scale mobility, *i.e.*, if they are in the high-elasticity state. If two identical polymers are brought into contact at a

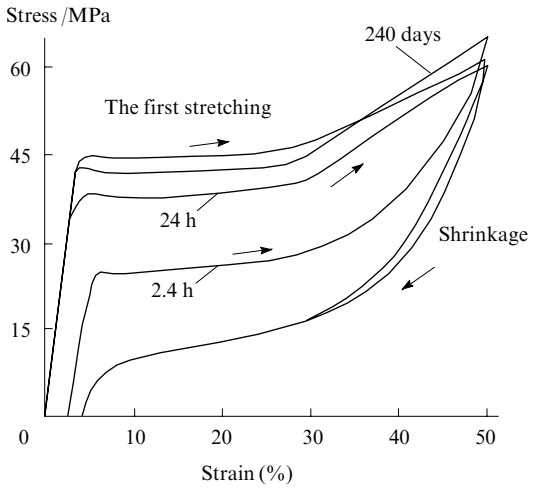


Figure 28. Stress – strain behaviour of hard-elastic PP in the course of its ageing at room temperature.[53]

temperature above their glass transition temperature, the interfacial surface between them usually gradually vanishes, and the material becomes monolithic. This phenomenon, described for the first time in a monograph,[113] was called autohesion and defined as follows: 'Autohesion, or autoadhesion, refers to the ability of the two surfaces of the same material brought into a contact to give a strong bond that prevents them from separating at the place of the contact'. This type of healing is related to the mutual diffusion of macromolecules or (and) their fragments through the interfacial boundary. In general form, the interfacial area of a polymer changes due to the diffusion of macromolecules through the sites of contact of identical polymer surfaces. The argument in favour of this assumption is the fact that all factors increasing thermal motion accelerate autohesion, whereas the factors decelerating diffusion weaken autohesion.[113] In essence, this process is similar to mixing of two volumes of the same liquid. The peculiarity of polymer systems is in the specific molecular motion of polymer chains.

This peculiarity were described most comprehensively and adequately in the so-called reptation model of molecular motion, which was advanced by de Gennes.[114] We will not dwell on proving this theory, but only note that the scaling law obtained by de Gennes was used to analyze a large body of experimental data obtained in studies of properties and behaviours of liquid polymers and solids, thus indicating that the reptation model[114] is quite efficient.

As noted above, the crazed and hard-elastic materials are prone to healing of their highly dispersed nanoporous structure. It is a spontaneous process leading to complete restoration of the initial polymer structure.[16] The example of such process in hard-elastic PP is shown in Fig. 28. As can be seen, the process of healing and restoration of properties of the starting polymer is very extended in time. There is no complete restoration even in 240 days, although the mechanical properties approach those of the initial polymer. It is not surprising, as diffusion is very slow, especially, in high-viscous media such as polymers.

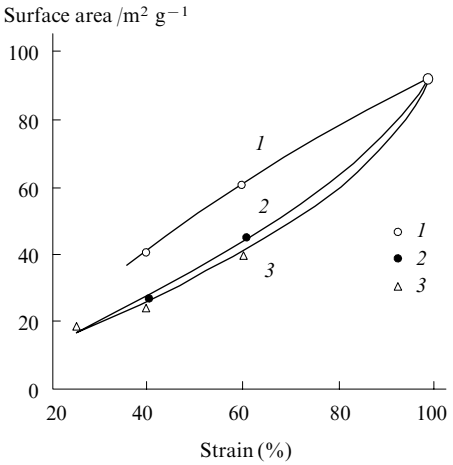


Figure 29. Surface area of hard-elastic PP *vs.* tensile strain developed in the first (*1*) and second (*3*) cycles of stretching; curve (*2*) corresponds to the same dependence in the course of shrinkage.[108]

The processes of development and healing of interfacial surfaces in polymers are not limited to the case considered above. The data shown in Fig. 28 demonstrate healing of the interfacial surface in a material that has undergone shrinkage. However, to understand the mechanism of strain-induced softening, it is very important to consider phenomena and, first of all, surface phenomena occurring in the course of reversible deformation. It is especially important since some researchers believe that the reversible deformation of this kind is an energy-controlled (surface) process. At the same time, any deformation of a solid, and in particular, of a polymer, which proceeds with changes in geometric dimensions, is accompanied by changes in its surface area, although the volume of the deformed polymer may remain unchanged.[97] In the case of solvent crazing of glassy and crystalline polymers, interfacial surfaces develop actively. Naturally, large interfacial surfaces have to affect the internal energy of the deformed polymer, and that was repeatedly noted in different studies.[93, 94, 99, 110]

As shown above, reversible strains of a hard-elastic polymers result in a strong increase in the diameters of fibrillar aggregates of macromolecules, indicating, first, their high-elasticity state and, second, changes of the surface area of fibrillar structures upon strain and shrinkage. Obviously, the geometry and the surface area of fibrillar aggregates of macromolecules may change only if there is mass transfer of the polymer from its surface to the bulk and back.

This is clearly evidenced by estimation of the surface area of the hard-elastic polymer during its deformation (Fig. 29). As can be seen, the interfacial surface of hard-elastic PP sharply increases upon the first stretching (up to 100 $m^2\ g^{-1}$ as noted above). Evidently, this increase occurs owing to appearance and growth of fibrillar aggregates of macromolecules of nanometre size in intercrystallite space. This process is entirely analogous to the process of development of interfacial surface during crazing of crystalline and amorphous polymers.[11, 79, 95] However, it has an important feature. It turns out (see curve *2*, Fig. 29) that the shrinkage of the hard-elastic polymer results in drastic reduction of the interfacial surface area, *i.e.*, its healing is observed. Note that the healing is very intensive, the surface area decreases at least $\sim$5-fold.

In essence, this healing process differs from the above-considered healing (see Fig. 9) of the interfacial surface of a hard-elastic polymer that has undergone shrinkage.[53] Such a strong reduction of the interfacial surface is virtually instantaneous. In other words, the diffusion of macromolecules from the bulk to the surface and back is governed neither by Fick's laws nor by de Gennes reptation, but is determined by some physical causes which strongly accelerate mass transfer.

It is of principal importance in this case that the development of interfacial surface during stretching of the polymer and its healing during shrinkage occur at rates incommensurable with those observed for spontaneous diffusion of chains or their fragments. It is well known from everyday experience that ordinary rubber can be stretched out by hands at any speed, with its surface area increasing severalfold. When released, it contracts almost instantly, hurting the fingers, and this contraction is accompanied by severalfold reduction (healing) of its surface area.

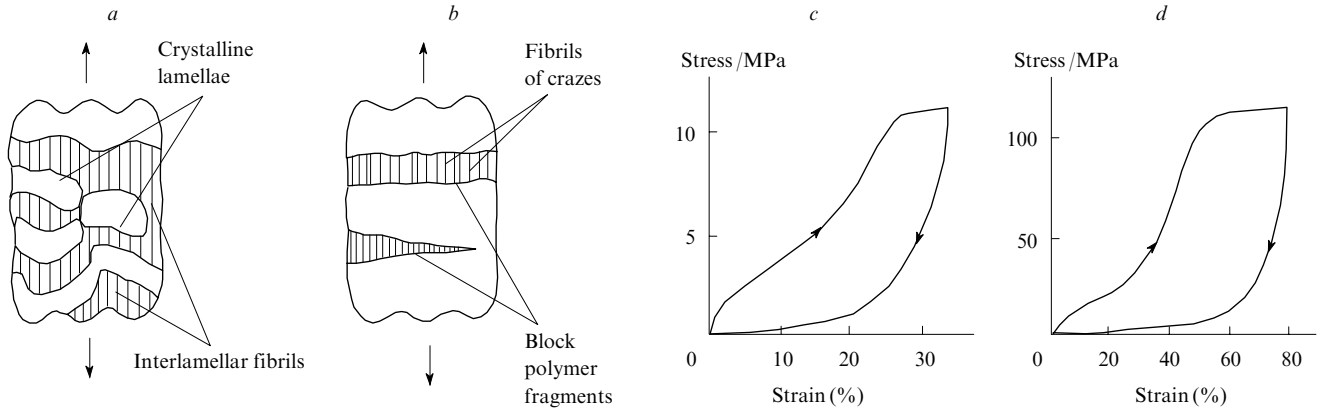


Figure 30. Schematic representation of structures of a strained hard-elastic polymer (*a*) and a solvent-crazed polymer (*b*),[108] and stress–strain curves of preliminary deformed high-impact PS (*c*) and fibres of hard-elastic HDPE (*d*).[54]

These simple observations lead to the conclusion that the major factor which determines the reduction in size of stretched polymers is entropic elasticity of chains, whereas healing accompanying reversible strain is rather an auxilliary process. Moreover, at present it is not clear how macromolecules in the rubber under deformation can diffuse from the surface into the bulk and back at such high velocities. In view of the above, one can conclude that the surface force cannot be the initial cause of reversible strains of crazed and hard-elastic polymers. The physical cause of the reversibility of the deformations is the entropic elasticity of polymer chains, while the surface forces just facilitate this.

Thus, the force softening of glassy and crystalline polymers has a general nature. The phenomenon consists in that the initial stretching curve is essentially a stretching curve of a glassy or crystalline polymer, whereas the subsequent stress – strain curves correspond to the high-elasticity state of the polymer that has been acquired under the influence of mechanical stresses in the first cycle of deformation. The physical sense of strain-induced softening of glassy and crystalline polymers consists just in the glass (crystal) – rubber transition.

III. Conclusion

From the above consideration, it is possible to conclude that the mechanisms of strain-induced softening of polymer systems, which is accompanied by development of highly dispersed nanoporous structure, have a general nature. The relevant systems include hard-elastic materials and solvent-crazed glassy and crystalline polymers.[108] The structures of a strained hard-elastic polymer and a solvent-crazed polymer are schematically shown in Fig. 30 *a*,*b*. The obvious morphological similarity of both materials is in line with their identical mechanical behaviour (Fig. 30 *c*,*d*). This similarity is not accidental. In the process of solvent crazing of glassy polymer, a highly dispersed oriented material is formed, which fills the crazes. The glass transition temperature of this polymer is lower than that of the surrounding bulk polymer by many tens of degrees. Naturally, in the second and subsequent cycles of deformation, the whole material demonstrates the mechanical behaviour typical of the rubbery state.

Solvent-crazed crystalline polymers and hard-elastic materials structurally similar with them also demonstrate the formation of highly dispersed fibrillar-porous material, which fills the intercrystallite space, in the first deformation cycle. Because crystallization of a polymer is strongly hampered in such thin aggregates as fibrils of nanometre size, the intercrystallite space is also filled with devitrified rubbery oriented material. This material, naturally, exhibits properties characteristic of rubber, and particularly, high reversible strain. Since the glass transition temperature for highly dispersed polymer is reduced by many tens or even hundreds of degrees, these materials show rubber-like behaviour even at very low temperatures. An additional proof of the entropic mechanism of high reversible strains in amorphous and crystalline polymers, which underlies the force-induced softening, consists in the ability of these materials to heal their nanoporous structure. The healing process occurs spontaneously in the temperature region much lower than the glass transition temperature and (or) melting temperature of deformed polymers in the bulk. The possibility of these processes is determined by high molecular mobility of macromolecules at phase boundaries due to a specific character of the polymer surfaces where macromolecules are in the high-elasticity state.

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